DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma.

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ABSTRACT

Biodegradable materials based on natural polysaccharides, particularly starch, can be used to fabricate starch based nano-composite film to reduce environmental problem. Starch can be produced at low cost and at large scale. Potato is an abundant and cheap agricultural source of starch. Starch is not a real thermoplastic material but, in the presence of a plasticizer, high temperatures and shearing, it melts and fluidizes like plastics. Plasticizing agents and nanofillers, like hectorite, montmorillonite, kaolinite clays, can improve mechanical properties of the films, resulting in materials with better flexibility and extensibility. The aim of the present work was to investigate the mechanical properties of thermoplastic starch reinforced with different types of plasticizers and clays at different concentration.

With the purpose of producing potato starch nano-composite films, four types of plasticizer such as glycerol, ethylene glycol, sorbitol, formamide and three types of clays such as hectorite, montmorillonite, kaolinite at various concentration (2, 5 and 10 wt%) were used. Nano-composite films were prepared using casting process at 70 °C. Tensile tests results infer that materials based on potato starch reinforced with nano clay particles can significantly improve the mechanical properties which can be used as an interesting biodegradable alternative for synthetic plastic materials, and after addition of three type of clays showed different mechanical behavior. The nano-composite film prepared using hectorite clay is better than montmorillonite clay and montmorillonite clay is better than kaolinite clay.

Dynamic Light Scattering measurements were performed at room temperature to determine particle size and zeta potential for starch and different type of clays. The degree of crystallinity of the starch-clay nano-composite was analyzed by X-ray Diffraction (XRD) which showed that starch-plasticizer crystalline structure was affected by clay integration. XRD analysis provided information of crystallite size of different types of clay. Crystallite size was found 6.5 nm, 26.1 nm, 25.9 nm for hectorite, montmorillonite, kaolinite clay respectively. When clay is used into starch matrix starch peaks turns to broad peak. In addition, both XRD and Fourier Transform Infrared Spectroscopy (FTIR) spectra showed a strong interaction between the clay and the starch molecules. The lower peak frequency of C–O group in starch represents the stronger the interaction between starch and plasticizers. The peak for pure starch powder appeared at 1170 cm⁻¹ but after addition of plasticizer the peak shifted at downward frequency (1150 cm⁻¹), which
indicates the presence of strong hydrogen bond. Scanning Electron Microscope (SEM) micrographs shows that clay particles were homogeneously dispersed in starch-clay nano-composite films at optimum clay concentration. Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) showed that Starch decomposed at 292 °C and charred with residue of 22%. Starch-glycerin film exhibits maximum decomposition temperature of 296 °C. Starch-glycerin-clay nano-composites film exhibit better thermal stability compared with starch-plasticizer film. Again, starch-glycerin- Hectorite nano-composite film displayed decomposition temperature at 316 °C whereas nano-composite films prepared using montmorillonite and kaolinite decompose at 306 °C and 311 °C, respectively. Starch film, where no plasticizer and clay is used, shows highest water uptake percentage and it decreases with addition of different plasticizer and further decreases with addition of different type of clays.
Abbreviation

MMT: Montmorillonite
SCN: Starch-clay nano-composite
SGH: Starch-glycerin- Hectorite
SMG: Starch-glycerin-montmorillonite
SKG: Starch-glycerin-kaolinite
DDS: Drug Delivery System
TPS: Thermoplastic starch
CHAPTER ONE

INTRODUCTION
1.1 INTRODUCTION

Humanity is facing increasingly difficult challenges in life despite the great advancements in science and technology over the last century. All the needs of modern society, e.g., food, fuel, energy, and materials, are highly dependent on diminishing fossil resources. The advancement in science and technology has enabled mankind to live longer and consume more of the world's resources. However, it is becoming increasingly clear that the resources required sustaining all the needs of the increasing human population and our modern lifestyle are depleting at a worrying rate. In addition, human activities have been altering the natural ecosystem by producing large quantities of wastes that are endangering the survival of all forms of life on earth [1].

Biodegradable polymeric materials have great potential in various practical applications [2]. The main reason for their interest is originated from their environmental friendly nature in contrast to the synthetic or non-biodegradable polymeric materials which are the major sources of waste disposal problem to the environment. As a consequence, there has been much activity over the past 30 years in the development of biodegradable plastic packaging materials. Various biopolymers, biosynthetic polymers, chemosynthetic polymers, their blends and composites have been investigated.

The ideal biopolymer is of renewable biological origin and biodegradable at the end of its life. Biopolymers include polysaccharides such as cellulose and starch; carbohydrate polymers produced by bacteria and fungi; [3] and animal protein-based biopolymers such as wool, silk, gelatin, and collagen. On the other hand, poly (vinyl alcohol) (PVA), poly (ε-caprolactone) (PCL), and poly (butylene succinate) (PBS) are examples of polymers that are synthesized artificially but are biodegradable. Natural starch, as one of the most abundant natural resources for polymer materials, is inexpensive and biodegradable. With necessary modification and processing, starch can be used as ideal “green” polymer material that comes from nature and readily goes to nature. Judicious chemical modifications can be made on starch because of its abundant hydroxyl groups. Starch is a semi crystalline polymer stored in granules as a reserve in most plants. It is composed of repeating 1, 4-α-D glucopyranosyl units: amylose and amylopectin [3, 4].
Recent interest in polymer matrix incorporated nano-composites has emerged with interesting observations involving exfoliated clay, carbon nanotubes, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals and a host of additional nano scale inorganic filler or fiber modifications. This research will involve polymer matrix based nano-composites with exfoliated clay being one of the key modifications. While the reinforcement aspects of nano-composites are the primary area of interest, a number of other properties and potential applications are important including barrier properties, flammability resistance, electrical/electronic properties, membrane properties, polymer blend compatibilization. An important consideration in this research work involves the comparison of properties of nano scale dimensions. Exfoliated clays could yield significant mechanical property advantages as a modification of polymeric systems [5–7].

Though starch-based materials are biodegradable, widely available and low cost, most of the starch based composites exhibit poor tensile strength, yield strength, stiffness and elongation at break, and poor moisture stability [8]. Incorporation of nano-clay in the starch matrix may be valued in terms of its superior mechanical performance for their applications as high competent biodegradable materials [9, 10]. Thus, in the work attempt will be made to fabricate starch-clay nano-composite [11-16] films by incorporating clay nano-particles in the starch polymer network at different conditions [17, 18] and their mechanical strength and biodegradability will be correlated with their network structure.

All natural starches have granular structure containing semi crystalline lamellae [19]. Both the glass transition temperature and the melting temperature of pure, dry starch are higher than its thermal decomposition temperature. Thus, the starch can only be processed as thermoplastic materials in the presence of plasticizers and under the action of heat and shear. Many low-molecular-weight materials have been used as plasticizers, such as water, glycerol, sorbitol, formamide, ethylene glycol etc. to produce thermoplastic starch (TPS). Water, among all the plasticizers, is the most effective.

Polymer-clay nano-composites represent a relatively new class of hybrid materials that has received widespread interest in the research community [20-29]. This interest is fueled by the promise of unprecedented performance, design flexibility and optimization. The mechanical property enhancement in polymer-clay nano-composites strongly depends on the dispersion of the clay nanoparticles in the polymer matrix and on the effective load transfer from the
polymer matrix to the nanoparticles. The dispersion of the clay nanoparticles can be classified as intercalation and exfoliation. Intercalated nano-composites are formed when the polymer chains are inserted into the layered silicate structure with fixed interlayer spacings. On the other hand, exfoliated nano-composites are formed when the individual silicate layers are individually dispersed in the polymer matrix by physical interaction.

The key to the successful development of polymer-clay nano-composites is to achieve complete exfoliation and uniform dispersion of the clay nanoparticles in the polymer matrix. For polymer nano-composites, strides have been made to incorporate large volume fractions of nano-fillers into various polymer matrices, thereby enhancing their physical, thermal and mechanical properties. However, despite consistent efforts by research groups world-wide, persistent challenges with poor miscibility and dispersion of nano particles especially at high volume fractions have prevented nano-composites from realizing their full potential. Notwithstanding a decent increase in properties at low volume fractions of clay nanoparticles, most reported nano-composites exhibit marginally increased or even decreased mechanical properties at high volume fractions [30]. In general, less than 5 v. % of clay nanoparticles can be dispersed uniformly into the polymer matrix [31], beyond which the properties usually begin degrading [32]. This problem is largely related to the difficulty of obtaining well-dispersed large volume fractions of clay nanoparticles and a lack of structural control over the internal organization of the nano-composites. This is largely due to strong tendency of clay nanoparticles to phase segregate and aggregate above certain concentrations, leading to formation of defects. Following are few of the many examples of nano-composites in which the mechanical properties tend to degrade at large volume fractions of clay nano particles.

In conclusion, the uniform dispersion of clay nano particles in the polymer matrix has a tremendous positive effect on the mechanical properties of nano-composites, yet it has proven difficult to disperse these nano particles consistently and uniformly. Hence, a “smart” nano-composite preparation method which enables the ability to disperse a wide range of volume fractions of nano clays within a polymer matrix while retaining consistent structural organization is crucial to optimally design nano-composites for their various applications. In this research, we approach the preparation of polymer-clay nano-composites using a slight modification of solution casting method. It is the simplest method used to prepare thin films from pre-cast film solution. The advantages of this technology include uniform thickness distribution, maximum optical purity and extremely low haze. The optical orientation is
virtually isotropic and the films have excellent flatness and dimensional stability. The cast film can be processed in-line with an optical coating design. The tremendous growth of new liquid crystal display applications has incited the development of new materials and improved processes for solvent casting and coating techniques. Main applications of films made by different polymer/solvent combinations are described [33]. The striking characteristic of the solution casting method is used to make flexible plastic components. It provides the capacity to combine macromolecules that are otherwise difficult or impossible to combine at the level of nanometer scale homogeneity.

1.2 OBJECTIVES

The main purpose of this work is to synthesize economically and environmentally feasible high strength starch-clay nano-composite films and probe their superior mechanical strength with the alteration of network structure. The objectives and possible outcome of this work may include:

1. Eliciting the physico-chemical characteristics of the synthesized nano-composite film.
2. The synthesized starch-clay nano-composite film will be completely bio-degradable and environmental friendly. The synthesized materials could significantly reduce the negative environmental impact in terms of energy consumption and greenhouse effect which is usual for traditional non-degradable polymeric materials. Establishing a route to avoid toxic or noxious components in the synthesis process and allow the method of composting into naturally occurring degradation products.
3. Establishing a facile route for the synthesis of mechanically strong starch based nano-composite films which is comparable to those of synthetic polymers, for example polyethylene, polypropylene, polystyrene, and polyethylene terephthalate and so on.
4. The synthesized nano-composite materials may potentially be used in a diverse range of fields where high mechanical strength and biodegradability are required such as the sectors of composting (bags and sacks), fast food tableware (cups, cutlery, plates, straws, etc.), packaging (soluble foams for industrial packaging, film wrapping, laminated paper, food containers), agriculture (mulch film, nursery pots, plant labels), hygiene (nappy back sheet, cotton swabs), slow release of active molecules in the agricultural and pharmaceutical area, smart sensors, fuel cell.
5. Establishing the correlation of superior mechanical strength and bio-degradability of the starch-clay nano-composite films with their morphological and structural changes.
CHAPTER TWO

LITERATURE REVIEW
2.1 BIOPOLYMER
Polymer science or macromolecular science is the subfield of materials science concerned with polymers, primarily synthetic polymers such as plastics. The field of polymer science includes researchers in multiple disciplines including chemistry, physics, and engineering. Polymer is a large molecule composing, hundreds of thousands of atoms formed by successive linking of one or two, occasionally more types of small molecules into chain or network structures. Biopolymers are a class of polymers produced by living organisms. Cellulose and starch, proteins and peptides, and DNA and RNA are all examples of biopolymers, in which the monomeric units, respectively, are sugars, amino acids, and nucleotides.

2.2 NATURAL BIODEGRADABLE POLYMERS
Biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred to as natural polymers. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes.

2.2.1 Cellulose
It is widely known that polysaccharides are produced by plants. These are a linear polymer with very long macromolecular chains of one repeating unit, cellobiose. Cellulose is crystalline, infusible and insoluble in all organic solvents [34]. Biodegradation of cellulose proceed by enzymatic oxidation, with peroxides secreted by fungi. Cellulose can also be degraded by bacteria. As for starch degradation products are non-toxic [35]. Cellulose is the most common biopolymer and the common organic compound on Earth and about 33 percent of all plant matter is cellulose. The total cellulose content in cotton is 90 percent and in wood it is 50 percent.

Cellulose esters represent a class of polymers that have the potential to participate in the carbon cycle via microbiologically catalyzed de-esterification and decomposition of the resulting cellulose and organic acids. Cellulose acetate is currently used in high volume applications ranging from fibers, to films, to injection moulding thermoplastics. It has the physical properties and relatively low material costs that have exerted to exclude other biodegradable polymers from being widely accepted in the marketplace.
2.2.2 Chitin and Chitosan

Chitin is the second most abundant natural biopolymer. It is a linear copolymer of N-acetyl glucosamine and N-glucosamine with β-1,4 linkage. These units are randomly or block distributed throughout the biopolymer chain depending on the processing method used to obtain the biopolymer. Chitin is usually found in the shells of crabs, shrimp, crawfish and insects. It could be considered as amino cellulose. Recent advances in fermentation technology suggest that the cultivation of fungi can provide an alternative source of chitin [36]. The study reports the exploitation of both sources to produce chitin. The protein content in chitin obtained from these two methods is different. It is less than 5% for the chitin extracted from shells and reaches 10 – 15% for the chitin produced by fungi. The molecular weights for all chitin samples were in the same range. A review of chitin and chitosan has been recently published [37]. The distribution of chitin and chitosan in nature and the biosynthesis of chitin and chitosan by applying microorganisms are discussed there. Chitinase, an enzyme, degrades chitin. As chitin has a poor solubility, it is often substituted for many applications [38].

Chitin is processed to chitosan by partial alkaline N-deacetylation. In chitosan glucosamine units are predominant. The ratio of glucosamine to acetyl glucosamine is reported as the degree of deacetylation. This degree may range from 30% to 100% depending on the preparation method and it affects the crystallinity, surface energy and degradation rate of
chitosan. Chitosan is insoluble in water and alkaline media. This is due to its rigid and compact crystalline structure and strong intra and intermolecular hydrogen bonding. Chitosan can only soluble in few dilute acid solutions. Then chitosan is dissolved in acidic solutions before its incorporation into biodegradable films [39]. Enzymes such as chitosanase or lysozymes are known to degrade chitosan. The applications of chitin and chitosan are limited because of their insolubility in most solvents. As chitosan has amino and hydroxyl reactive groups, chemical modifications can widely be employed. Modified chitosan have been prepared as N-carboxymethyl chitosan or N-carboxyethyl chitosan. They have been prepared for use in cosmetics and in wound treatment [40].

2.2.3 Lignin
Wood is composed of many chemical components, primarily extractives, carbohydrates, and lignin, which are distributed non-uniformly as the result of an atomical structure. Lignin is derived from the Latin term lignum, which means wood [41]. In 1838 Anselme Payen was the first to recognize the composite nature of wood and referred to a carbon rich substance as the “encrusting material” which embedded cellulose in the wood. In 1865 Schulze defined this encrusting material as lignin. Lignin has been described as a random, three-dimensional network polymer comprised of variously linked phenyl propane units [42]. Lignin is the second most abundant biological material on the planet, exceeded only by cellulose and hemicelluloses, and comprises 15-25% of the dry weight of woody plants. This macromolecule plays a vital role in providing mechanical support to bind plant fibers together. Lignin also decreases the permeation of water through the cell walls of the xylem, thereby, playing an intricate role in the transport of water and nutrients. Finally, lignin plays an important function in natural defense of a plant against degradation by impeding penetration of destructive enzymes through the cell wall. Although lignin is necessary to trees, it is undesirable in most chemical paper making fibers and is removed by pulping and bleaching processes.

2.2.4 Fiber
Since ancient Egypt natural fibers were already being used as reinforcement materials. These natural fibers are divided in three main categories: straw-fibers, non-wood fibers and wood fibers. The non-woods fibers won the interest of industry due to the mechanical and physical properties. Inside this category, another classification depending on the plant origin is made: as bast for kenaf, flax, jute and hemp; leaf for sisal, henequen and pineapple leaf fiber; and seed for cotton; fruit coconut.
Table 2.1: Classification of vegetable and cellulose fiber

<table>
<thead>
<tr>
<th>Bast</th>
<th>Leaf</th>
<th>Seed</th>
<th>Fruit</th>
<th>Stalk</th>
<th>Wood Fibers</th>
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</thead>
<tbody>
<tr>
<td>Flax</td>
<td>Sisal</td>
<td>Cotton</td>
<td>Coconut</td>
<td>Bamboo</td>
<td>Hardwood</td>
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<tr>
<td>Hemp</td>
<td>Manila</td>
<td>Kapok</td>
<td></td>
<td>Wheat</td>
<td>Softwood</td>
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<tr>
<td>Jute</td>
<td>Curaua</td>
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<td></td>
<td>Rice</td>
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<td>Kenaf</td>
<td>Banana</td>
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<td></td>
<td>Grass</td>
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<tr>
<td>Ramie</td>
<td>Palm</td>
<td></td>
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<td>Barley</td>
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<td>Banana</td>
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<td>Corn</td>
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<td>Rattan</td>
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The application of the natural fiber composites depends on the production cost and their functional properties. Generally natural fibers cannot provide the same mechanical properties as carbon fiber, but some of them can achieve the same behavior as fiberglass. In composite materials, before being used, natural fibers are subject to preparation for operations and modification of its surface. Following the latter, the fibers should have: good adhesion between fiber and matrix; suitable degree of polymerization and crystallization; resistance to humidity and homogenous physical properties; and nonetheless should be non-inflammable.

2.2.5 Protein

Proteins are thermoplastic hetero polymers. They are constituted by both different polar and non-polar α-amino acids. Amino acids are able to form a lot of intermolecular linkages resulting in different interactions. These offer a wide possibility of chemical functionalities and functional properties. Most of the proteins are neither soluble nor fusible, especially fibrous proteins as silk, wool and collagen. So they are used in their natural form. Casting of film-forming solutions allows the preparation of films. To process protein based bio-plastics, classical way is the thermoplastic processing, which consists of mixing proteins and plasticizers. Flexibility and extensibility of films are improved by the use of plasticizers [43, 44]. The biodegradation of proteins is achieved by enzymes, as protease, and is an amine hydrolysis reaction. Grafting of protein is a mean to control the rate of biodegradation.
2.2.6 Alginic acid

Many polysaccharides in solution form gels upon the introduction of counter ions. The degree of cross-linking is dependent on various factors such as pH, type of counter ion, and the functional charge density of these polymers. Alginates have been studied extensively for their ability to form gels in the presence of divalent cations.

Alginate is a binary linear hetero polymer containing 1, 4-linked α-L-guluronic acid and β-D-mannuronic acid. Alginic acid forms water-soluble salts with monovalent cations, low molecular weight amines, and quaternary ammonium compounds. It becomes water insoluble in the presence of polyvalent cations such as Ca$^{2+}$, Be$^{2+}$, Cu$^{2+}$, Al$^{3+}$ and Fe$^{3+}$. Alginate gels have been used widely in controlled release DDS. Alginates have been used to encapsulate various herbicides, microorganisms and cells. Some polysaccharides structures are depicted in Figure 2.2.

![Structures of some natural bio-degradable polymers.](image)

Figure 2.2: Structures of some natural bio-degradable polymers.
2.2.7 Starch
Starch, can be produced at low cost and at large scale. It is an abundant and cheap agricultural source of starch. Starch is not a real thermoplastic material but, in the presence of a plasticizer, high temperatures and shearing, it melts and fluidizes, like thermoplastic polymer. We, therefore, used starch in this work.

2.2.7.1 Introduction to Natural Starch
Starch is a carbohydrate material that can be hydrolyzed into small molecules by specific enzymes during animal metastasis, generating biological energy for animals. Many plants, in their fruits, seeds, tubers or rhizomes, grow with starch. Potato, corn, wheat and rice are major resources for production of starch worldwide.

2.2.7.2 Compositions of Natural Starch
Starch contains two major components: one is amylose, which is a linear polymer, and the other is amylopectin, which is a highly branched polymer. The repeat units in both amylose and amylopectin are identical (so-called α-D-glucosyl residues) but connected in different ways, as given in Figure 2.3. Most starch contain 20—30 wt % of amylose, although some waxy starches contain very little amylose. In amylose, α-D-glucosyl residues are linked by an α [1→4] bond. Typically, the molecular weights of extracted amylose are in the order of 105—106 g/mol [45]. Amylose generally is recognized as linear macromolecule. However, it has been reported that there is a slight degree of branching (9—20 branch points per molecule) in amylose from various botanical sources [46]. The length of side chains ranges from 4 to over 100 repeat units [47]. There is no effective way of separating the branched amylose from the linear amylose.

Side chains on branched amylose form small clusters rather than a random comb structure. Note that amylopectin also forms clusters by its branched side chains, which will be elaborated on later. Branched amyloses still have properties, such as iodine binding capability, which amylopectin does not have. In aqueous solutions, amylase molecules can form extended chains with a hydrodynamic radius of 7-22 nm. In natural starch, the amylose molecules tend to have a rather stiff left-handed single helical structure or form an even stiffer parallel double left-handed helix [48].

The helix consists of six $\alpha$-$D$-glucosyl residues per turn with a pitch of 0.8 nm. Figure 2.4 shows a single helix structure of amylose molecule. On each of the glucose residues, hydroxyl groups connecting with carbons on position 2 and 6 (C2 and C6) point outward of the helix, while the hydroxyl group connecting with carbon on position 3 (C3) points inward of the helix, which makes the inner surface of the helix more hydrophobic than the outer surface. Thus, amylose with a helix structure can hold the hydrocarbon portion of glycerides and fatty acid in its helix cavity to form a V-helix complex. The distinct capability of amylose to bind with iodine is also by holding iodine ions in its hydrophobic helix cavity. Amylopectin is a highly branched component of starch. The $\alpha$-$D$-glucosyl residues are mainly linked by $\alpha$ [1→4] bonds but with 5-6% of $\alpha$ [1→6] bonds at the branch points. Its molecular weight ranges 107-109 g/mol.
The amylopectin molecular chains can be classified into three categories by their ways of connecting with each other: the C chain carries the sole reducing end of the molecule; the A chain (unbranched) is only linked to the rest of the molecule through its potential reducing end; and the B chains carry one or more A chains and/or B chains. Figure 2.5 shows a schematic describing this classification.

In most experiments, the C chain is not distinguished from B chains. According to their positions in the cluster structure, B chains are further subdivided: $B_1$ is a short chain, being components of only one cluster while $B_2$, $B_3$, etc. are long chains that span over two, three, or
more clusters, thereby interconnecting them. The branching points on the amylopectin molecules are not randomly distributed but periodically clustered. The distance between two clusters on the same B chains is 2-2-α-D-glucosyl residues on average. Most short chains (the average degree of polymerization ranges from 14 to 18) are organized within clusters, while long chains (the average degree of polymerization is more than 55) usually span more than one cluster. The molar ratio of short to long chains, influenced by the source of starch, varies from 5 in potato starch amylopectin to 8—10 in cereal amylopectin. The distribution of chain length in amylopectin critically influences the inner assembly structure of starch granules and the interaction with the water or solvent.

2.2.7.3 Corn starch

The word „corn” is used in the United States as the common name for the cultivated member of the grass family (Gramineae) known to botanists as Zeamaysl. More specifically, „corn” means the seed produced by this plant. Outside of the United States, this crop is commonly known as maize. The mature corn kernel is composed of four principle parts: tip cap, 0.8%; pericarp, 5.3%; germ, 11.9%; and endosperm, 82%. The most important genetic change in corn for starch production was development of waxy maize (corn) hybrids. Starch from waxy maize, which contains 100% of the branched starch fraction, amylopectin, has become a major food starch. This corn must be grown in fields isolated from dent corn to prevent crosspollination, and generally will be grown under identity-preserved contracts to ensure delivery of uncontaminated shipments of maize to the wet-milling establishment and to provide adequate supply. The milling properties of waxy maize are similar to those of regular corn, except that the yield of soluble is a little higher, starch yield is lower and starch and gluten slurries filter and dry a little more slowly than those from normal dent corn. This characteristic has been shown to be caused by the presence of a small amount of a phytoglycogen. The addition of a small amount of an amylolytic enzyme to the slurries results in normal filtering and drying characteristics [49]. High-amylose corn having starch which contains 55 – 80% of the linear starch fraction, amylose, has also been developed [50] and must also be grown under contract. Production of amylomaize is even smaller than it is for waxy hybrids because of limited uses for the starch. Starch yields of high-amylose corn are lower than those of dent corn [51].
2.2.7.4 Wheat starch
Starch comprises 54-72% of the dry weight of wheat kernels [52, 53]. Starch content is positively associated with grain yield, but inversely related to protein content [54-56]. Normal wheat starch is comprised of 25% amylose and 75% amylopectin. Amylose is a mixture of linear and lightly branched (0.2 – 0.8% of linkages) molecules having a number average degree of polymerization of 1000 – 5000, whereas amylopectin is monodisperse and highly branched (4 –6% of linkages) with a DP of about 10 000 or more. The detailed structural features of amylose and amylopectin are dependent on the source of starch, even among wheats. Moreover, the proportions of amylose and amylopectin in starch may vary within a plant source, due to genetic mutation. Amylose and amylopectin are readily isolated and purified, but branched and linear amylose molecules from wheat starch have not been separated and isolated.

2.2.7.5 Tapioca starch
Tapioca starch is obtained from the roots of the cassava plant, which is found in equatorial regions between the Tropic of Cancer and the Tropic of Capricorn. Typically, cassava starch contains 17 – 20% amylose. Unlike corn (0 – 70% amylase content) and rice (0 – 40% amylose content), no significant variation of amylase content has been found in cassava starch. Similar to other starches, the amylase molecules of cassava starch are not completely unbranched as indicated by their beta-amylolysis limit, a value lower than that for corn, potato, rice and wheat starches. In addition, cassava amylose has a higher molecular weight than other starches. Each fraction can be classified in terms of its chain length (degree of polymerization, DP) and position in amylopectin molecules [57].

2.2.7.6 Potato starch
In some potato starch applications, as with applications of other native starches, the presence of amylose is undesirable. After gelatinization, it forms crystals which reduce paste clarity. Amylose retrogradation can be prevented by chemical modification; a new type of potato has been bred to solve this problem. This potato contains only amylpectin, it can be developed in two ways. One way consists of treating a mutation-sensitive potato with radiation or chemicals and selecting the desired variety. After successful selection the normal plant cross-fertilization method to produce starch potatoes is used. The second way involves genetic modification of the potato with an antisense technique to eliminate the formation of amylose. By this method, no materials are introduced into the potato which is not normally present,
and the amylopectin potato starch contains no genetically manipulated substances. This method avoids the time consuming (10 years) cross-fertilization program. Amylopectin starches, like waxy maize starch, are mostly used by the food industry. However, amylopectin potato starch has specific properties which are not available in current commercial starches.

Native potato starch, which is used in the food, paper and textile industries, is often not optimal for a particular application. Modifications are done to obtain the properties needed for specific uses. More than 500 modifications of potato starch are currently known. Potato starch and its derivatives have special properties, such as a low gelatinization temperature and a high paste consistency. Potato starch is preferred in the food industry, because its pastes have a good clarity (due to a small amount of lipid sand protein) and a neutral flavor. In the paper industry, there is also a preference for potato starch. The reason for this is the high molecular weight of its amylose and its good solubility. Cationic potato starches are preferred for internal sizing due to the concurrent presence of phosphate groups. Potato starch dextrins also have an advantage over other starches as an adhesive, because of the good remoisten ability [58] and a desirable rheology resulting in a perfect direct tack. Textiles are manufactured better with potato starch due to its film properties [59], paste penetration depth [60] and adhesive power [61].

2.3 SYNTHETIC BIODEGRADABLE POLYMERS

Biodegradable synthetic polymers such as poly (glycolic acid), poly (lactic acid) and their copolymers, poly (p-dioxanone), and copolymers of trimethylene carbonate and glycolide have been used in a number of clinical applications.

2.3.1 Polyesters

A vast majority of biodegradable polymers studied belong to the polyester family. Table 2.2 lists the key polymers in this family. Among these poly (α-hydroxy acids) such as poly (glycolic acid) (PGA), poly (lactic acid) (PLA), and a range of their copolymers have historically comprised the bulk of published material on biodegradable polyesters and have a long history of use as synthetic biodegradable materials [62-66] in a number of clinical applications. These polymers have been used as sutures [67] plates and fixtures for fracture fixation devices [68] and scaffolds for cell transplantation [69].
2.3.2 Poly (glycolic acid), poly (lactic acid) and their copolymers

Poly (glycolic acid) (PGA) is a rigid thermoplastic material with high crystallinity (46-50%). The glass transition and melting temperatures of PGA are 36°C and 225°C, respectively. Because of high crystallinity, PGA is not soluble in most organic solvents; except highly fluorinated organic solvents such as hexafluoro isopropanol.

The attractiveness of PGA as a biodegradable polymer in medical application is that its degradation product glycolic acid is a natural metabolite. Numerous studies [70-72] have established a simple degradation mechanism via homogeneous erosion. The degradation process occurs in two stages, the first involves the diffusion of water into the amorphous regions of the matrix and simple hydrolytic chain scission of the ester groups. The second
stage of degradation involves largely the crystalline areas of the polymer, which becomes predominant when the majority of the amorphous regions have been eroded.

Poly (lactic acid) is present in three isomeric forms d (-), l (+) and racimic (d, l) and the polymers are usually abbreviated to indicate the chirality. Poly (l) LA and poly (d) LA are semi-crystalline solids, with similar rates of hydrolytic degradation as PGA. PLA is more hydrophobic than PGA, and is more resistant to hydrolytic attack than PGA. For most applications the (l) isomer of lactic acid (LA) is chosen because it is preferentially metabolized in the body. Poly (lactic-glycolic acid) (PLGA) copolymers and PGA are among the few biodegradable polymers with Food and Drug Administration (FDA) approval for human clinical use.

2.3.3 Polylactones

Poly (caprolactone) (PCL) is the most widely studied in this family [73]. PCL is a semi crystalline polymer with a glass transition temperature of about –60ºC. The polymer has a low melting temperature (59 to 64ºC) and is compatible with a range of other polymers. PCL degrades at a much lower rate that PLA and is a useful base polymer for developing long-term, implantable drug delivery systems. Poly (caprolactone) is prepared by the ring-opening polymerization of the cyclic monomer ε-caprolactone. Catalysts such as stannous octet are used to catalyze the polymerization and low molecular weights alcohols can be used as initiator and to control the molecular weight of the polymer [74, 75].

2.4 THERMOPLASTIC STARCH (TPS)

The term “thermoplastic” indicates that these materials melt on heating and may be processed by a variety of moulding and extrusion techniques. The most common thermoplastics are polyethylene, polystyrene and polymer chloride together with a number of more specialized engineering polymers. If one of the reacting substances in a step polymerization possesses more than two functional groups, then the reaction will lead naturally to branched structures. As these intercome bines, random three-dimensional networks are developed. Ultimately the network extends throughout the mass of polymerized material, which therefore in effect constitutes a single giant molecule. Such structures are by their very nature incapable of melting or of truly dissolving. Important examples are the phenolic and amino resins. Similar thermo set network structures may be formed by cross linking linear chains in a second post polymerization or 'curing' reaction, which may be free radical initiated.
The production of TPS (also known as plasticized starch, PS) basically involves three essential components, namely: starch, plasticizer and thermo-mechanical energy. The thermo-plasticization of starch entails the collapse of starch crystallinity (which in general is about 15-45% of the granule molecular order) through the formation of hydrogen bonds between the plasticizer and starch in the presence of some energy, invariably severing the hydrogen bonds between the hydroxyl groups of the starch molecules to form TPS [76]. Therefore, the crystallinity observed in TPS is due to the hydrogen bonds formed between starch and the plasticizer molecules and according to [77], this degree of crystallinity is expected to be rather low. It is important to mention that there must be sufficient amount of plasticizer (30% wt for glycerol-PS) for the formation of a homogeneous (continuous) phase to occur, otherwise some starch granules will remain intact in the TPS, a condition that can make the TPS fracture under tension at very low strains. Plasticizers impart pliability by modifying the free volume of the matrix such that starch chains enjoy more mobility [78]. The use of starch alone is not encouraged because of its lack of melt-processability and humidity-resistance which in turn militates against its suitability for extrusion or injection molding [79].

The most common plasticizers used are water and glycerol, which often times are used together. The TPS thus produced exhibits two major drawbacks, namely, poor mechanical properties and water resistance. To this end, four areas of consideration are being explored; these include plasticizers, starch forms (in relation to chemical modification and amylose/amylopectin ratio), reinforcements (organic and inorganic), polymer orientation and blends with other synthetic polymers (discussed in the following sections). Accordingly, materials such as ethylene bisformamide, urea [80], formamide [81], sorbitol [82] and xylitol [83] have been investigated for their plasticizing abilities. Using corn starch [84], reported that extruded ethylene bisformamide-PS showed better water resistance than glycerol-PS but rather lower corresponding tensile strengths at plasticizer contents measured, with both decreasing in strength with increase in contents. The glass transition of the ethylene bisformamide-PS was found higher than that of glycerol-PS (63.3°C against 38.3°C) since ethylene bisformamide form stronger hydrogen bonds with starch than glycerol. Thunwall et. al. [85] reported that glycerol plasticized potato starch produced using hydroxypropylation/oxidation modified starch exhibited a modestly higher resistance than that of native starch. However, increase in glycerol content reduced the moisture resistance of the TPS regardless of the type of starch used. Modified native potato starch and high amylose starch offered reduced viscosity levels (measured at 140°C) for starch melts containing 30%
(dry mass) glycerol. In comparison with high polyethylene Thunwall. al. further noted that polyethylene melt at 180°C had lower viscosity than native potato PS and hydroxypropylation/oxidation-modified high amylose PS but higher than that of hydroxypropylation/oxidation modified native potato PS, all at 140°C. They also discovered that starch melt drawability, a crucial property in film production, generally increased with glycerol and chemical modification but decreased with temperature, but in comparison with PE melt, PS melt was very much lower in extensibility. It is important to mention that it is rather difficult to make thin blown films with granular starches as fillers in polymer composites due to their big particle size range (5-100 μm). Hence the preference for TPS [86] approached the issue slightly differently by blending cassava starch (74.70±1.76%) plasticized with water and glycerol, and another with water and Buriti oil, all in ratio 50:15:35 (mass/vol/vol) with polystyrene in different ratios by mass. It was observed that blends with TPS plasticized by buriti oil were apparently more thermally stable than those by glycerol. A reduction of up to 60% in the water uptake of TPS could be achieved by replacing glycerol with sugar/water mixture as plasticizer though with a concomitant reduction in the TPS crystallinity [87]. One property peculiar to TPSs plasticized with polyols (such as glycerol, sorbitol, glycol and sugars) is their retro gradation (recrystallization due to reformation of hydrogen bonds between starch molecules) propensities as they age, a condition that leads to embrittlement. This phenomenon could be inhibited using formamide as plasticizer (since it could form stronger or more stable hydrogen bonds with starch –OH groups) but with a reduction in tensile strength and modulus against a simultaneous increase in elongation at break and energy break vis-a-vis glycerol plasticized starch [88]. Amides generally form stronger hydrogen bonds with starch -OH groups than polyols in the following order: urea > formamide > acetamide > polyols [89]. Though with a compromise on tensile stress, similar result of inhibited retro gradation coupled with reduced shear viscosity (improved fluidity) of TPS, improved elongation, thermal stability and water resistance at high relative humidities was achieved by yu et. al. [90] when glycerol plasticized TPS was modified with citric acid in comparison with the unmodified glycerol TPS. Torres et. al. [91] explored some natural fibers reinforcing potentials for thermoplastic starch in their work published recently. Three material variables were considered, namely: starch (sweet potato, corn and potato starches), plasticizer (ethylene glycol, glycerol, chitosan, water and propylene glycol) and fiber (jute, sisal and cabuya with fiber lengths of 5±1 mm). All these factors coupled with process (compression molding) conditions such as time and temperature were found to affect the tensile strength of the TPS. Individual assessments (done keeping
other variables constant) shows that potato starch, sisal and ethylene glycol gave the highest tensile strength results whereas water and cabuya fiber gave the highest impact strength.

Besides discrete macro fibers as reinforcements for TPS, cellulotic nanofibers, such as cellulose microfibrils [92] and tunicin whiskers [93] have also been investigated. Two types of wood pulps (bleached Kraft pulp from Eucalyptusuro grand is and unbleached thermo mechanical pulp of Eucalyptus grandis) were evaluated by De Carvalho et. al. [94] in reinforcing TPS produced with corn starch (28%amylose) and glycerol. It was found that though increase in glycerol (above 30%) decreased both the tensile strength and modulus, increase in fiber (pulp) contents (from 5-15% of matrix mass) remarkably increased both the tensile strength and modulus in all cases. On the other hand, the tensile strains of the composites decreased with the addition of fiber or glycerol to the raw matrix. Interestingly, regardless of glycerol amounts, fiber breakage as against debonding was observed on all fracture surfaces, an indication of a strong fiber-matrix interfacial bonding.

In agreement with similar work, the equilibrium water absorption of the TPS matrix increased with glycerol and was found higher than those of TPS-fiber composites (thus, implying improved moisture resistance by fiber inclusion), which were similar irrespective of formulation. Besides organic materials like natural fibers, the potentials of inorganic minerals such as hydroxyapatite [95] as reinforcement materials for TPS have been reported. The reinforcing potentials of clay were examined by Hwan-Man [96] whereby TPS/clay nanocomposites produced from native potato starch and natural montmorillonite (clay) were found to possess higher tensile strength and thermal stability, and lower water vapor transmission rate than ordinary TPS. In addition their recent study of the effectiveness of fly ash in reinforcing corn PS prepared with glycerol and formamide-urea combination as plasticizers observed considerable increase in the tensile stress, Young’s modulus and water resistance, though with a corresponding decrease in ductility. Fly ash was also found to inhibit retrogradation.

Lastly, Yu, Let. al. [97] exploited polymer orientation technique in improving extruded corn TPS sheet. The orientation was achieved by drawing at different speeds TPS sheet extrudates from the die under positive tension by a three-roller system in front of the die after which the mechanical properties were measured along and across the extrusion direction. Unlike elongation, both tensile modulus and yield strength improved in both directions. However,
the effect of orientation was influenced by amylose/amylopectin ratio, such that differences in modulus and yield stress in the two directions widened with increase in amylase while differences in elongation became pronounced at higher amylopectin contents. These directional differences in tensile properties are much higher in conventional polymers and for instance, may be in the order of 10 times in polypropylene. On a broader view, amylose contents have actually been found to proportionately influence mechanical properties such as tensile modulus, tensile strength and elongation of TPS [98, 99].

2.5 GELATINIZATION OF STARCH

Gelatinization of starch is usually known as the disruption of the crystalline structure and ultimately the destruction of the starch granular structure when heat and water (or other effective solvents) are applied. In the presence of excessive water (usually > 90 wt %), starch granules start to swell because the amylose molecules are preferentially solubilised in the water. Below a characteristic temperature known as gelatinization temperature, the crystalline region, mainly composed of high molecular weight and branched amylopectin molecules, still maintains its integrity. Above the gelatinization temperature, the crystalline region starts to lose its order and swell irreversibly [100]. If approximately treating starch granules as a polymer network, the swelling of the starch before the occurrence of gelatinization can be considered as a reversible equilibrium. In this equilibrium, the affinity between the polymer network and the solvent generates osmotic pressure (favoring the swelling), which is equal to the restoring force (disfavoring the swelling), from the stiffness of polymer network. Obviously, enhancing the temperature or choosing the solvent that has a high affinity with starch will increase swelling. Swelling above the gelatinization temperature is profoundly irreversible.

2.6 POLYMER NANO-COMPOSITE

Polymer composites in which the size of the reinforcement is on the order of nanometers are called polymer nano-composites. These materials are generally lightweight, are often easy to process and provide property enhancements extending orders of magnitude beyond those realized with traditional polymer composites. Examples of commonly used reinforcements, often termed nano-fillers, include carbon nanotubes (CNTs) [101-103], layered silicate clay nanoparticles [104-106], cellulose nanocrystals [107], graphite nanoflakes [108-110] etc.
These nano-fillers have at least one characteristic dimension on the order of nanometer sand can range from isotropic elements to highly anisotropic needle-like or sheet-like elements. While CNTs and cellulose nanocrystals are generally cylindrical in shape, clay nanoparticles are disk-shaped with a high aspect ratio. The structures of some of these nano-fillers are shown in Figure 2.6.

Figure 2.6: Structures of commonly used nano-fillers

Over the last 2 decades, clay nanoparticles have attracted great interest in academia and industry because of the relatively easy processibility, low cost and fairly predictable stiffening behavior when introduced into polymers [111-118]. A clay nanoparticle is composed of stacked structures of 1 nm thick silicate layers with a variable basal distance.
Montmorillonite (MMT), shown in is an example of a clay nanoparticle generally used in polymer-clay nano-composites because it is readily available and has exceptional mechanical properties [119]. The in-plane modulus of elasticity has been estimated to be 270 GPa by Monte Carlo simulations [120]. MMT, a member of the smectite family, is 2:1 clay, meaning that its crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an octahedral sheet of aluminum. Each silicate layer, around 1 nm thick, is regarded as a rigid inorganic polymer consisting of mainly silicon and oxygen, and a small amount of aluminum, magnesium and other metal ions. An alkali metal cation (typically, Na+) holds the silicate layers together by an intermolecular force. In a polar solvent, such as water, this intermolecular force is broken and the basal distance of the silicate layers expands by solvation of the cation leading to exfoliation of silicate layers into individual sheets. The individual sheet of silicate layer contains a negative charge and has an aspect ratio of 100: 1 to 1000: 1.

The use of clay nanoparticles as precursors to nano-composite formation has been extended into various polymer systems including nylon 6 [121,122]; epoxys [123, 124]; polyamides [125, 126]; polystyrenes [127]; polyurethanes [128]; polyolefins such as polypropylene [129–133], polyethylene [134–135]; among others. Although the first clay-reinforced resin known as Bakelite was introduced in early 1900’s, the research on polymer-clay nano-composites was stimulated by the pioneering work at Toyota. Kojima et al. [136] showed a combined enhancement of modulus, strength and toughness in a Nylon 6-clay nano-composite. At a loading of 4:2 wt.% (>1:5 v.%) clay, the modulus doubled and the ultimate tensile strength increased more than 50%. These results sparked the research in the nano-composites area and since then the manufacture of polymer nano-composites has received much attention both by academics and industry [137].

2.7 PROPERTIES OF POLYMERIC MATERIALS

Types of polymer 'properties' can be broadly divided into several categories based upon scale. At the nano-micro scale, properties directly ascribe from the chain itself. These can be thought of as polymer structure. At an intermediate microscopic level, properties describe the morphology of the polymer matrix in network space. At the macroscopic level, properties describe the bulk behavior of the polymer. The bulk properties of a polymer are those most
often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

### 2.7.1 Crystallinity

The term crystallinity has a somewhat ambiguous use in polymer chemistry. A synthetic polymer may be described as crystalline if it contains regions of three-dimensional ordering on atomic rather than macromolecular length scales. It usually arises from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions. The degree of crystallinity can express in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline [138].

The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Increasing degree of crystallinity tends to make a polymer more rigid. It can also increase the brittleness of polymeric materials. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline/glassy regions.

### 2.7.2 Tensile strength

The maximum stress that a material can withstand while being stretched or pulled before failing or breaking is known as Tensile strength. Elongation at break, also known as fracture strain, is the ratio between changed length and initial length after breakage of the test specimen.

On the other hand, Stress is defined as force per unit area. It has the same units as pressure, and in fact pressure is one special variety of stress. However, stress is a much more complex quantity than pressure because it varies both with direction and with the surface it acts on.

Strain is defined as the amount of deformation an object experiences compared to its original size and shape. For example, if a block 10 cm on a side is deformed so that it becomes 9 cm long, the strain is (10-9)/10 or 0.1.
Stress-Strain diagram

The tensile strength of a material quantifies how much stress the material will endure before failing [139]. This is very important in applications that rely upon polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. Usually tensile strength increases with polymer chain length in the polymer matrix.

2.7.3 Young's Modulus of elasticity

Young's Modulus quantifies the elasticity of the polymeric materials. It is defined as the ratio of rate of change of stress to strain. Like tensile strength this is highly relevant in polymer applications involving the physical properties of polymers.

2.8 PROPERTIES OF CLAYS

Incorporation of nano clay such as Hectorite, Montmorillonie, kaolinite etc. in the polymer shows superior mechanical performance. These clay are describe below.

2.8.1 Properties of Hectorite clay

Hectorite is a soft, white clay mineral with a chemical formula of Na\(_{0.3}\)(Mg, Li)\(_3\)Si\(_4\)O\(_{10}\)(OH)\(_2\).
2.8.2 Properties of montmorillonite clay

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming clay. Chemical formula: \((\text{Na, Ca})_{0.33}(\text{Al, Mg})_2(\text{Si}_4\text{O}_{10})\).

2.8.3 Properties of Kaolinite clay

Kaolinite is a soft, earthy, usually white mineral. Chemical Formula: \(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\).
2.9 NON-BIODEGRADABLE POLYMERS AND THEIR IMPACTS ON ENVIRONMENTAL POLLUTION IN BANGLADESH

In all stages of a synthetic polymer life, from manufacturing to disposal, negative social and environmental impacts are evident. The planet’s environment, including its soil, water, and air, is affected directly in numerous ways, beginning with the extraction and use of fossil fuels during the manufacturing process of plastic bags. Emissions resulting from this process are also very harmful to both humans and the physical environments, and the transportation of plastic bags from their origin to their place of use also contributes significantly to the environmental pollution. Further negative impacts are found during the use and immediate disposal of synthetic polymer products especially plastic bags, particularly in non-industrial nations where waste management services are not well-developed. In these regions, plastic bags are found everywhere, from remote tourist destinations to city streets where they can risk the society in various ways.

Polyethylene materials are not biodegradable. Whenever a polyethylene bag is thrown away, it does not decompose through natural processes. It contributes to the accumulation of non-destructive waste of permanent nature. If anybody looks at any garbage dumping site, he will observe this fact that although other garbage matter get decomposed and merged into the soil but polyethylene bags remain intact with their different colors. Polyethylene remains intact in the soil and disturbs the flow of nutrients to the soil and hinders entering sunlight. It destroys the beneficial bacteria of soil and losses soil fertility. It hinders the way of soil compaction, which in the long run effects the construction of foundation of the different structure. Using Polyethylene is not environment friendly. Medical reports find it as an agent of cancer, skin...
diseases and other health problems. The users are more exposed to these types of health hazards when polyethylene is used to pack bread, biscuits, potato chips or other food items. In the developed countries, food is wrapped in food-graded plastic or polyethylene, but in Bangladesh this was not strictly followed and sometimes colorants are used, some of which may be carcinogenic.

Polyethylene industries for shopping bag production emerged in Bangladesh in early 80's and within a decade the industry reached in such a level that the jute bag production forced to be almost closed. The use of polyethylene shopping bags had been so enormous that one could find the polyethylene bags everywhere i.e in the street, dumpsites, drains, ditches, open-fields, roof tops, hanging from trees and overhead cables, floating on ponds, canals, rivers. Survey report showed that near about 10 million polyethylene bags were used every day and every year about 3000 million bags were dumped in Dhaka City alone. The steadily growing use of polyethylene bags posed an ominous environmental problem in the city as well as in rural areas. This enormous use of polyethylene bags led to severe environmental impacts like soil degradation, loss of soil fertility, blocking up of drainage and sewerage systems, causing water logging and the spread of harmful microbes and bacteria. The worst example of adverse effect caused due to polyethylene bags was the delaying process of recession of flood water in Dhaka city during 1998. The question of plastic bags ultimately comes down to the issue of use. If people are willing and able to use environmentally-friendly alternatives, such as reusable cloth or plastic bags, the decreasing use of plastic bags will reduce their overall footprint. However, without educating the public concerning the impacts of plastic grocery bags or constructing barriers to their use, business will continue as usual. Many governments have chosen the route of taxes or levies on plastic bags, to great success. Perhaps in a culture where convenience often comes before environmental concern, speaking to consumers” pocketbooks may be the only way to effectively deal with this ever-increasing problem.

2.9.1 Anti-polythene Campaign

Environment and Social Development Organization (ESDO), an environmental NGO for the first time started campaign against polythene shopping bags in Bangladesh in 1992. It drew attention of the press as well as of the Government. A number of non-government organizations and public leader came forward to support the campaign. Some organizations demanded banning of production and use of polythene shopping bags. Based on the popular demand, in 1993, Ministry of Environment and Forest took an initiative to ban the production
and trade of polythene bags outside Export Processing Zone (EPZ) with the approval of the cabinet, but it was not materialized. However, anti-polyethylene campaign was picking up steadily and spreading from the capital city to other cities and towns.

The campaign reached to its peak in the aftermath of 1998 flood, when two third areas of the country including a large part of the Dhaka City was under knee deep water for nearly two months. Clogging of city drains by polyethylene bags was the reason for delaying process of recession of flood water of Dhaka City. The people realized that indiscriminate use of polythene has been the root cause of their suffering. In 1999, Ministry of Environment again started campaign against polyethylene through its Sustainable Environment Management Program, which led to the formation of a task force by the government under the ministry to work towards framing a strategy for phasing out of polythene shopping bags. The task force recommended for undertaking a detailed study on the production, marketing and use of polythene shopping bags and its socio-economic impacts before making the final decision.

2.10 IMPORTANCE OF BIODEGRADABLE POLYMER IN BANGLADESH

Advancement of science and technology promote us to produce materials that can withstand extreme temperatures, and durable and easy to use. But what we forget is that these advanced products do not break down naturally. When we dispose them in a garbage pile, the air, moisture, climate, or soil cannot break them down naturally to be dissolved with the surrounding. They are not biodegradable. However natural waste and products made from nature break down easily when they are disposed as waste. But as more and more non-biodegradable materials pile up, there is increased threat to the environment. To understand the seriousness of the problem caused by non-biodegradable waste, we can check about what's happening to particular places where plastic and other materials are used for almost everything.

One of the most common household wastes in Bangladesh is polythene- mostly used as polythene bags for shopping and carrying light things. Since they are cheap, they are used by almost everyone from the local vegetable seller to the supermarket. The hazard that polythene causes to the environment is very serious. Keeping in mind the potential hazard of biodegradable waste, it is important for us to know in what way we can help to make sure that less non-biodegradable material is left on the planet. Become an environment friendly consumer by following the everyday tips at on how we can contribute to less non-biodegradable materials.
CHAPTER THREE

EXPERIMENTAL
3.1 MATERIALS

Montmorillonite Clay (Aldrich, Japan); Hectorite Clay (Wako, Japan); Kaolinite Clay (Fluka, Japan); Glycerin (Merck, Germany); Sorbitol (Merck, Germany); Formamide (Merck, Germany); Ethylene Glycol (S.D. Fine chem. Ltd., India) were purchased and used as received. Deionized water was used throughout the experiment unless otherwise noted.

3.2 EXTRACTION OF STARCH FROM POTATO

500 g potato were weighted and cut into very tiny size using commercially available fine vegetable slicer. 1L distilled water was mixed with the paste and stirred properly using glass rod until water color changes to purple. Then, liquid portion of the potato juice was separated with fine mesh and poured into Petri dish for 3 to 4 hours at room temperature. Starch particles were settled down in the petri dish. The settled starch particle was washed several times with distilled water and dried at 105°C in the oven to remove any available water. The percent of yield of the extracted potato starch is 10 wt%. Schematic diagram of extraction of starch from potato are below.

Figure 3.1: Extraction of starch from potato.
3.3 PREPARATION OF STARCH-PLASTICIZER COMPOSITE FILM

3.3.1 Preparation of starch- glycerin film

800 mg extracted starch powder was dissolved in 13 mL distill water in a vial. 30 wt % glycerin was mixed with water in another vial and was added slowly into the starch solution, while stirring. The mixed solution was heated slowly in a oil bath at 70°C temperature, allowing the gradual evaporation of the solvent. Then the suspension was poured in polyethylene sheet and put into a vacuum oven at 40°C until no weight changes were observed. By maintaining the amount of suspension on the polyethylene sheet, the thickness of the starch/ glycerin film can precisely be controlled.

![Diagram of Preparation of Starch-plasticizer composite films](image)

Figure 3.2: Preparation of Starch-plasticizer composite films

3.3.2. Preparation of starch-ethylene glycol film

Starch-ethylene glycol film was prepared following the same method used for starch-glycerin film.

3.3.3. Preparation of starch-sorbitol film

Starch-sorbitol film was prepared following the same method used for starch-glycerin film.
3.3.4. Preparation of starch-formamide film

Starch-formamide film was prepared following the same method used for starch-glycerin film.

3.4 PREPARATION OF STARCH-CLAY COMPOSITE FILM

3.4.1 Preparation of starch- Hectorite composite film

800 mg starch was dissolved in 14 mL of water upon heating. In another container, (2-10) wt % hectorite nanoclay was dispersed in a single solvent or co-solvent by using ultrasonic bath for 30 minutes and was added slowly into the starch solution with continuous stirring. The mixture of starch and hectorite nanoclay were stirred constantly for several hour at 70°C, allowing the evaporation of the solvent. Then the suspension was poured into polyethylene sheet and put into a vacuum oven at 40°C until no weight changes were observed.

Figure 3.3: Preparation of starch-hectorite composite film

3.4.2 Preparation of starch-montmorillonite composite film

Starch-montmorillonite composite film was prepared following the same method used for Starch-hectorite composite film.
3.4.3 Preparation of starch-kaolinite composite film

Starch-kaolinite composite film was prepared following the same method used for Starch-hectorite composite film.

3.5 PREPARATION OF STARCH-PLASTICIZER-CLAY NANOCOMPOSITE FILM

3.5.1. Preparation of starch-plasticizer-hectorite nano-composite film

800 mg starch was dissolved in 14 mL of water upon heating. Different types of plasticizers including glycerin, sorbitol, ethylene glycol and formamide with varying amount was used to improve the compatibility between hydrophilic starch granules and nanoclay particles. In presence of plasticizers, the intermolecular and intramolecular hydrogen bonds in starch become weak and starch molecule become flexible. In another container, (2-10) wt% hectorite nanoclay was dispersed in a single solvent or co-solvent by using ultrasonic bath for 30 minutes and was added slowly into the starch solution with continuous stirring. The mixture of starch and hectorite nano clay were stirred constantly for several hour at 70°C, allowing the evaporation of the solvent. Then the suspension was poured into polyethylene sheet and put into a vacuum oven at 40°C until no weight changes were observed.
3.5.2. Preparation of starch-plasticizer-montmorillonite nano-composite film

Starch-plasticizer-montmorillonite nano-composite film was prepared following the same method used for Starch-plasticizer-hectorite nano-composite film.

3.5.3 Preparation of starch-plasticizer-kaolinite nano-composite film

Starch-plasticizer-kaolinite nano-composite film was prepared following the same method used for Starch-plasticizer-hectorite nano-composite film.

Table 3.1 to 3.8 represents the prepared sample at a glance.

Table 3.1: Preparation of starch composite with and without different plasticizers

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Native starch (mg)</th>
<th>Water (ml)</th>
<th>Plasticizer (%)</th>
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<tbody>
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<td>20</td>
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<tr>
<td>05</td>
<td>800</td>
<td>20</td>
<td>Formamide 30%</td>
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Table 3.2: Preparation of starch- hectorite clay composite with different plasticizers

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<th>Sample no</th>
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<th>Water (ml)</th>
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Table 3.3: Preparation of starch-glycerine-hectorite nano-composite films with varying percentage of hectorite clay

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<th>Sample no</th>
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<th>Water (ml)</th>
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<th>Clay (%)</th>
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Table 3.4: Preparation of starch-montmorillonite clay composite with different plasticizers

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Table 3.5: Preparation of starch-glycerine-montmorillonite nano-composite films with varying percentage of montmorillonite clay

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Table 3.6: Preparation of starch-kaolinite clay composite with different plasticizers

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<td>Formamide 30%</td>
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Table 3.7: Preparation of starch-glycerine-kaolinite nano-composite films with varying percentage of kaolinite clay

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<td>20</td>
<td>Glycerin 30%</td>
<td>kaolinite 5%</td>
</tr>
</tbody>
</table>

Table 3.8: Preparation of starch-clay composite with different types of clay

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Native starch (mg)</th>
<th>Water (ml)</th>
<th>Clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>800</td>
<td>20</td>
<td>Hectorite 10%</td>
</tr>
<tr>
<td>02</td>
<td>800</td>
<td>20</td>
<td>Montmorillonite 10%</td>
</tr>
<tr>
<td>03</td>
<td>800</td>
<td>20</td>
<td>Kaolinite 10%</td>
</tr>
</tbody>
</table>
3.6 CHARACTERIZATION

3.6.1 A. Dynamic Light Scattering

Dynamic Light scattering measurements were performed at 25 °C with Zetasizer Nano ZS from Malvern Instruments. The DLS measures Brownian motion of the particles and relate this to their size in a sample through a correlation function. The aqueous solution or suspension of the sample was illuminated with a laser light of 532 nm wavelength. About 1 wt % aqueous suspension of starch, hectorite clay, monmorillonite clay and kaolinite clay were prepared and stirred vigorously before measurements. The dispersed sample was then sonicated at a frequency of 40 KHz for 30 minutes using a VWR ultrasonic cleaner. The intensity fluctuation in the scattered light was analyzed to determine the particle size. The particle measurement in a DLS instrument is the diameter of the sphere that diffuses at the same speed as the particle being measured.

3.6.1 B. Zeta Potential

When a charged particle is suspended in liquid, ions of an opposite charge will be attracted to the surface of the suspended particle. A negatively charged sample attracts positive ions from the liquid and conversely a positive charged sample attracts negative ions from the liquid. Ions close to the surface of the particle, will be strongly bound while ions that are further away will be loosely bound forming what is called a diffuse layer. Within the diffuse layer there is a notional boundary and any ions within this boundary will move with the particle when it moves in the liquid; but any ions outside the boundary will stay where they are – this boundary is called the Slipping plane. A potential exists between the particle surface and the dispersing liquid which varies according to the distance from the particle surface – this potential at the slipping plane is called the zeta potential. To measure the zeta potential of the samples a universal dip cell was used in Figure 3.2. The Universal „Dip“ cell is used to provide a method to measure the zeta potential of both aqueous and non-aqueous samples. For aqueous samples the dip cell can be used in conjunction with the disposable polystyrene. For non-aqueous samples use the reusable Glass - square aperture.

Figure 3.5: Universal dip cell
3.6.2 A. Scanning Electron Micrograph

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques.

SEM were carried out by Field Emission scanning Electron Microscope, model JEOL JSM-1600F, Japan. The magnification range is from 20X to approximately 30,000X and spatial resolution of 50 to 100 nm. All sample were coated with platinum by auto fine coater, Model JEOL JFC-1600 before measurement.

3.6.2 B. Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum.

3.6.3 A. Fourier Transform Infrared analysis (FTIR)

Fourier Transform Infra Red (FTIR) is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger prints of the sample. This makes infrared spectroscopy useful for several types of analysis like identifying unknown materials, determining the quality or consistency of a sample, and determining the amount of components in a mixture. Materials can be identified from their functional groups, chemical bonds etc. which can be detected through their characteristic infrared absorption frequencies or wave lengths. FTIR studies were conducted using (Perkin Elmer, USA, and Model: Frontier FT-NIR/MIR). Sample with KBr with a 1:100 “samples-to-KBr” ratio was maintained to prepare disk. The sample disks were then scanned in the wave
number range of 4000 to 400 cm\(^{-1}\) with an average of 30 scans per measurement. The resolution of the spectrometer was 4 cm\(^{-1}\).

### 3.6.3 B. Attenuated total reflectance (ATR)

The infrared spectra were obtained using a FT-IR spectrometer (Perkin Elmer, USA, Model: Frontier FT-NIR/MIR), equipped with a horizontal attenuated total reflectance (HATR) cell. The sample films were cut into rectangular shape with dimensions 70 mm × 20 mm and the thickness of these films were 0.1 mm. Samples were placed in Zn-Se plate before measurement. The spectra were recorded in absorbance units and the wave number ranged from 4000 to 650 cm\(^{-1}\). Each sample was scanned 30 times for spectrum integration, and the scanning resolution was 4 cm\(^{-1}\).

![Figure 3.6: Attenuated total reflectance (ATR)](image)

### 3.6.4 Tensile Strength

The tensile test of the nano-composite films were performed by a Universal testing machine (Instron, Model 3369, USA). The load cell used for the tensile test was an Instron static load cell with a 50 kN capacity. Gauze length was 20 mm. The samples were cut into rectangular shape with dimensions 70 mm × 20 mm for the tensile test. The thickness of the films was 0.1 mm. A cross-head speed of 2 mm/min was used for the test. Tensile test was performed to determine the stress-strain behavior of the films. The upper yield stress on the stress-strain curve was considered as the tensile strength. For all the results reported in this dissertation, at least 3 replicates of specimens were tested, and an average value of the measured values was used. Tensile strength and elongation at break (Eb) of the films were calculated from the result. Identical moisture content (50% relative humidity) was maintained during analysis.

\[
\text{Tensile strength, } Ts \text{ (M Pa)} = \frac{\text{Load}}{\text{Thickness (mm) } \times \text{Width (mm)}}
\]
Elongation Break, Eb (%) = \frac{\text{Displacemental break}}{\text{Gauze length}} \times 100

3.6.5 X-ray Diffraction (XRD)
X-ray diffraction has played a pivotal role to identify and characterize solid samples. The nature of bonding and the working criteria for distinguishing between short-range and long-range order of crystalline arrangements from the amorphous substances are largely derived from X-ray diffraction and thus it remains as a useful tool to obtain structural information. X-ray diffraction pattern of amorphous polymer will not show any sharp and high intensity peaks whereas the nano-composites of amorphous polymer show sharp and high intensity peaks. This is due to the development of crystallinity in the amorphous polymer.

XRD analysis was carried out by BRUKER, D 8 ADVANCE; Germany. All specimens for XRD were prepared by solution casting method. The sample film was cut into rectangular shape with dimensions 30mm × 10mm × 0.1mm (Length × Width × Thickness). The detail configuration of the instrument is as follows: Tube: Cu, Target: Cu K alpha (1.5406 Å), Monochromator: Graphite, Voltage: 40kV, Current: 40 mA, Scan Step: 0.02 degree, Speed: 2.0 degree/min. XRD peaks were analyzed using Diffract Plus EVA 16.0 Software.

3.6.6 Thermogravimetry and Differential thermal analysis (TG-DTA)
The basic instrumental requirement for thermogravimetry (TG) is a precision balance with a furnace programmed for a linear rise of temperature with time. The results may be presented as a curve, in which the weight change is recorded as a function of temperature or time; or as a derivative thermogravimetric (DTG) curve, where the first derivative of TG curve is plotted with respect to either temperature or time. The thermogravometric analysis was performed by (DT/TGA 7200, HITACHI, Japan). All TGA data was obtained under a nitrogen atmosphere at a heating rate of 10°C/min, and the thermal degradation temperature was determined at the specific point of the original weight. Samples with weights ranging from 5 to 10 mg were heated from room temperature to a final temperature of 900°C. Air was purged at a flow rate of 20 mL/min. Sample weight was recorded as a function of temperature.
3.6.7 Water Absorption Test
Water absorption tests of the starch-clay nano-composites were conducted respect to cumulative time. The 0.1 mm thin film samples were cut into a circle shape with 12 mm diameter. The samples were dried in an oven at 105 °C for about 2 hrs, cooled in a desiccator and immediately weighed to the variation of 0.0001 g using Denver Instron balance. The dried and weighed samples were immersed in distill water for about 1 day. Excess water on the surface of the samples was soaked by dry tissue and the weights of the samples were taken. Three specimens of each composition were tested and reported the average result. The percentage increase in weight after immersion in water was calculated as follows:

\[
\text{Increase in weight, } \% = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100
\]

3.6.8 Biodegradability Test
Biodegradability test of the starch-clay nano-composite films were carried by soil burry test. The test is conducted with respect to time. After one month, weight loss occurred in the experimental sample which is determined by using the following equation.

\[
\text{% of Biodegradability} = \frac{W_2 - W_1}{W_1} \times 100
\]

Where, \( W_1 \) = Initial weight of specimen before degradation.
\( W_2 \) = Final weight of specimen before degradation.
CHAPTER FOUR

RESULT AND DISCUSSION
4.1. DYNAMIC LIGHT SCATTERING (DLS)
Dynamic light scattering measurements were performed to analyze the size distribution and stability of the particles.

4.1.1 Dynamic light scattering (DLS) analysis for Starch
A starch samples suspended in water was used for DLS analysis. Due to presence of strong inter and intra molecular hydrogen bonding in starch molecules, they cannot be approached by water molecules; thereby, form a relative “hydrophobic core”. On the particle / water interface, there is interaction (hydrogen bonding) between the starch (unbounded –OH group) and water which acts like a surfactant, to keep particles apart. However, the interaction between starch and water will be finally replaced by interaction between the starch molecules. This will cause agglomeration and precipitation. Hydrodynamic radius of extracted starch was found as 302 nm in Figure 4.1.1.

![Dynamic light scattering for extracted potato starch powder.](image)

Zeta potential value is directly correlated with the stability of colloidal dispersions. It indicates the degree of repulsion between adjacent, similarly charged particles in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. The average zeta potential value for starch granules is –18 mV, which indicates the relative instability of starch particles in solvent.
4.1.2 Dynamic light scattering (DLS) analysis for Hectorite clay

Hectorite clay disperses much more easily in water to give colorless, transparent, and highly thixotropic gels. Thixotropy is observed as a fluid like behavior of the gel when subjected to a shear force above threshold strength. The average hydrodynamic radius of hectorite clay is 155 nm (Figure 4.1.2). Its zeta potential value is -32.3 mV indicating the moderate stability of hectorite particle in solvent.

![Figure 4.1.2: Dynamic light scattering for hectorite clay particles.](image)

It also gives a broad peak in the high hydrodynamic radius size region. The broad peak suggests the prominent aggregation of particles in Figure 4.1.3.

![Figure 4.1.3: Dynamic light scattering for hectorite clay for aggregated particle.](image)
4.1.3 Dynamic light scattering (DLS) analysis for Montmorillonite (MMT) clay

After MMT powder and water had been mixed, some particles had a tendency to settle rather than disperse. Sonication helps to keep the particles suspended, but it could result in an undesired reduction of the platelet size. MMT particles in the “as-dispersed” and sonicated suspensions have the same effective hydrodynamic radius. Sonication apparently does not break down the platelets, nor does it seem to promote exfoliation. Nonetheless, we routinely sonicate MMT suspensions to help promote good mixing and dispersion. The average hydrodynamic radius of MMT particle is 300 nm (Figure 4.1.4). From this analysis for MMT clay gives zeta potential value is -20.9 mV, indicating the poor stability of MMT particle in solvent.

Figure 4.1.4: Dynamic light scattering for montmorillonite clay particles.
4.1.4 Dynamic light scattering (DLS) analysis for Kaolinite clay

Kaolinite fine particle are dispersed in water by sonication. Sonication helps to keep the particles suspended, but it could result in an undesired reduction of the platelet size. Even though due to high aggregation factor, it showed around about average 250 nm hydrodynamic radius. From dynamic light scattering analysis shows Zeta potential value of -28.9 for kaolinite clay. This value indicates that the moderate stability of particle size in solvent. Figure 4.1.5 represents the hydrodynamic radius for kaolinite clay.

Figure 4.1.5: Dynamic light scattering for kaolinite clay particles.
4.2 SCANNING ELECTRON MICROSCOPE (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS) ANALYSIS

4.2.1 SEM and EDS Image of starch

The surface morphology of starch granules at the microscopic level was examined by SEM. SEM images of native potato starch granules are shown in Figure 4.21. Potato starch granules are round or oval in shape with smooth surfaces and wide distribution of sizes. Figure 2.1 shows different particle size distribution of starch granules ranging from several hundred nanometers to few micrometers.

Figure 4.2.1: SEM images of extracted potato starch.
EDS provides rapid qualitative and quantitative analysis of elemental composition. Only carbon and oxygen peaks are appeared in the EDS spectrum where carbon atom contains 88.90 % and Oxygen atom11.10 % for starch in Figure 4.2.2. Starch particles successfully extracted from potato because only C and O exist there.

Figure 4.2.2: EDS of starch granules.
4.2.2 SEM and EDS image of hectorite clay

Typical SEM images of hectorite nano-clay are shown in Figure 4.2.3. Hectorite forms agglomerations in water. The hectorite nanoclay granules usually exists as sheet in the suitable dispersion medium but in its dried forms granules appeared as spherical particles ranging from several hundred nm to few µm due to strong aggregation factor. Further magnification of these aggregated spherical particles (Figure 4.2.3 C) shows the real nanometer range nano-clay particles.

Figure 4.2.3: SEM images of hectorite nano-clay.
EDS provides the information regarding elemental percentage present in hectorite clay (Figure 4.2.4). Hectorite clay contains oxygen, sodium, magnesium and silicon with 38.17 %, 2.91 %, 22.64% and 36.27 % respectively which coincides with its original structure.

![EDS of Hectorite clay](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>(k)eV</th>
<th>Mass%</th>
<th>Sigma</th>
<th>Atom%</th>
<th>Co</th>
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<td>38.17</td>
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</tr>
<tr>
<td>Na K</td>
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<td>0.10</td>
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<tr>
<td>Mg K</td>
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<tr>
<td>Si K</td>
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<td>45.34</td>
<td>0.38</td>
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<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Figure 4.2.4: EDS of Hectorite clay.
4.2.3 SEM image of starch-glycerin film

The micrographs of starch-glycerin composite film are shown in Figure 4.2.5. The surface morphology of the film (Figure 4.2.5) showed a relatively smooth and continuous layer by layer morphology which confirmed a dense and homogeneous structure. Figure 4.2.5 B and C showed a patchy and rough cross-section which may occur because of the flexibility of starch polymer in the network of starch-glycerin films.

Figure 4.2.5: SEM images of starch-glycerin film A, B surface view, C. Cross-sectional view.
4.2.4: SEM and EDS image of starch-glycerin-hectorite nano-composite film

Figure 4.2.6 shows the SEM image of the starch-glycerin-hectorite nano-composite containing 10 wt% clay platelets. The small dot circles in the images come from the hectorite present in the network. The clay exists mostly as either single platelets (exfoliation) or as stacks of several platelets (intercalation). Nevertheless, it is clear that a nano-composite provides a higher modulus. SEM image of the fracture surface of a starch-glycerin–hectorite nano-composite film is shown in Figure 4.2.6 A compared to starch-glycerin film showed in figure 4.2.5 B. Starch-glycerin–hectorite composites showed rough and corallike view and displayed porous network structure.

Figure 4.2.6: Scanning electron microscope (SEM) image of starch-glycerin-hectorite nano-composite film.
EDS provides some elements with percentage of atom for starch-glycerin-hectorite clay in figure 4.2.7. Carbon, oxygen, sodium, magnesium and silicon atom with 80.29%, 19.64%, 0.01%, 0.03% and 0.02% respectively confirmed that hectorite was homogeneously incorporated in the starch-glycerin-hectoritenano-composite film.

Figure 4.2.7: EDS image of starch-glycerin-hectorite nano-composite film.
4.2.5: SEM and EDS Image of montmorillonite clay

SEM image of montmorillonite in Figure 4.2.8 indicate nearly spherical montmorillonite clusters, approximately 1 µm in diameter due to the large montmorillonite aggregation. At a higher magnification, a single micro cluster can be seen resting on a base of flat montmorillonite flakes. The outer shell of the cluster appears to be composed of several montmorillonite flakes enveloping a central core.

Figure 4.2.8: SEM image of montmorillonite clay.
EDS provides some elements with percentage of atom for montmorillonite clay in Figure 4.2.9. MMT clay contains oxygen, magnesium, aluminum, silicon and calcium with atom percent 54.41%, 0.81%, 4.21%, 40.23% and 0.33% respectively which coincides with its original structure.

Figure 4.2.9: EDS image of Montmorillonite clay.
4.2.6: SEM and EDS image of starch-glycerin-montmorillonite nano-composite film

Figure 4.2.10 represents the surface morphology of the starch-glycerin-MMT nano-composite film. In this film, nano-clay particles were homogeneously dispersed in the network of nanocomposite film. Better dispersion of clay that means exfoliation of clay could be obtained in the case of nano-composite film.

Figure 4.2.10: SEM images of starch-glycerin-MMT nano-composite film.
EDS provides some elements with percentage of atom for starch-glycerin-MMT nano-composite film in Figure 4.2.11. The film contains carbon, oxygen, sodium, aluminum, silicon, potassium and calcium with percentage of atom 78.76, 19.13, 0.25, 0.57, 1.53, 0.26 and 0.21 respectively while MMT clay contains oxygen, magnesium, aluminum, silicon and calcium with atom percent 54.41%, 0.81%, 4.21%, 40.23% and 0.33% respectively. These elemental peaks suggest us the successful incorporation of MMT in the film.

Figure 4.2.11: EDS image of starch-glycerin-MMT nano-composite film.
4.2.7 SEM and EDS image of kaolinite clay

The SEM images of kaolinite clay are displayed in the figure 4.2.12 at different magnification ratio. Kaolinite are crystalline, rolled and rough edged.

Figure 4.2.12: SEM image of kaolinite clay.
EDS provides some elements with percentage of atom for kaolinite clay in figure 4.2.13. Kaolinite clay contains oxygen, aluminum, silicon and iron with atom percent 68.37%, 13.35%, 18.11% and 0.17% respectively which coincides with its original structure.

Figure 4.2.13: EDS image of kaolinite clay.
4.2.8 SEM and EDS Image of starch-glycerin-kaolinite nano-composite film

The SEM images of starch-glycerin-kaolinite nano-composites are shown in Figure 4.2.14. The bright spots on the image represent size and particle distribution of clay stacks in figure 4.2.14 A. It is apparent that clay particles are uniformly distributed in the starch-glycerin film. The results suggest that the use of glycerin promoted the clay disaggregation as well as its better homogenous dispersion in starch matrix owing to the hydrophilic nature of glycerin and compatible with starch and clay through hydrogen bonding interaction. Consequently, the kaolinite accumulations during blending at the gelatinization temperature under mechanical stirring were easily dissociated into small particles, which occurred due to better dispersion of the clay.

![SEM image of starch-glycerin-kaolinite nano-composite film](image)

Figure 4.2.14: SEM image of starch-glycerin-kaolinite nano-composite film.
EDS provides elemental percentage of atom for starch-glycerin-kaolinite nano-composite film. It contain carbon 80.59%, oxygen 19.19%, aluminum 0.19% and silicon 0.09%. Kaolinite contains oxygen, aluminum, silicon and iron with atom percent 68.37, 13.35, 18.11 and 0.17 respectively. So, it can be said that kaolinite was successfully utilized to have starch-glycerin-kaolinite nano-composite film in Figure 4.2.15.

Figure 4.2.15: EDS image of starch-glycerin-kaolinite nano-composite film.
4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS
AND ATTENUATED TOTAL REFLECTANCE (ATR)

4.3.1: FTIR spectra of starch-glycerin film

Native starch extracted from potato contains two different molecular structures: the linear
(1,4)-linked-α-D-glucan amylose and highly (1,6)-branched α-D-glucan amyllopectin. The
process of using thermal and mechanical energies to modify native starch granules into TPS
was well known. [139] The thermomechanical process with water and plasticizer broke starch
granules, the hydrogen bonding, and crystal structure of native starch. Strong interactions
between starch and plasticizers formed due to homogeneous distribution of starch and
different plasticizer. FT-IR spectra for native starch and starch film with different plasticizers
are shown in Figure 4.3.1 to Figure 4.3.3. Native starch presents several characteristic
absorbance bands and peaks (Figure 4.3.1 a). The region at 2,935 cm\(^{-1}\) and 3,450 cm\(^{-1}\)
corresponds to hydroxyl groups. The presence of CH\(_2\) groups determines the existence of the
peaks at 2,924 cm\(^{-1}\), 1,465 cm\(^{-1}\). In the fingerprint region starch-glycerin film three
characteristic peaks appeared between 1200 cm\(^{-1}\) and 900 cm\(^{-1}\), attributed to C–O bond
stretching of starch. The characteristic peak at 1150 cm\(^{-1}\) in Figure 4.1.1a is ascribed to C–O
bond stretching of C–O–H group in starch while two peaks at 1080 cm\(^{-1}\) and 1040 cm\(^{-1}\) are
attributed to C–O bond stretching of C–O–C group in the anhydroglucose ring.

Starch-plasticizer films exhibits different absorption peaks at the different wave numbers,
because glycerol, ethylene glycol, sorbitol, and formamide had different hydrogen bond-
forming abilities with both O of C–O–H groups and O of O–C anhydroglucose ring groups
in starch. The lower the peak frequency of C–O group in starch represents the stronger the
interaction between starch and plasticizers. Pure starch powder peak appeared at 1170 cm\(^{-1}\)
but after addition of plasticizer the peak shifted at downward frequency (1150 cm\(^{-1}\)), which
indicates the presence of strong hydrogen bond.
Figure 4.3.1: FTIR spectra of a) native starch, b) starch-glycerin film, c) starch-ethylene glycol film, d) starch-sorbitol film, and e) starch-formamide film.

Formamide gives two peaks for stretch in primary amides (-NH₂) near 3350 and 3180 cm⁻¹, which invisible in starch-formamide film and it becomes clear in third derivative of starch-formamide film IR spectra as shown in Figure 4.3.2.
Figure 4.3.2: Third derivative of starch-formamide film IR spectra.

Again, Figure 4.3.3 represents the FTIR spectra of starch, starch-glycerin film, starch-ethylene glycol film, starch-sorbitol film, starch-formamide film for –OH group at 3700-3000 cm\(^{-1}\) wave numbers. Starch gives peak at 3450 cm\(^{-1}\) due to –OH group, which shifted towards lower wavenumber upon addition of glycerin.

Figure 4.3.3: FTIR spectra of a) native starch, b) starch-glycerin film, c) starch-ethylene glycol film, d) starch-sorbitol film, and e) starch-formamide film in the 3700-3000 cm\(^{-1}\) region.
Figure 4.3.4 represents the C-O stretching peaks for starch in fingerprint region. Starch shows peak at 1170 cm\(^{-1}\) wave number but after addition of glycerin the peak shifted at downward frequency (1153 cm\(^{-1}\)), which indicate that stronger the hydrogen bond. Starch-sorbitol gives peaks at lower intensity than glycerin in Figure 4.3.3.

Figure 4.3.4: FTIR spectra of a) native starch, b) starch-glycerin film, c) starch-ethylene glycol film, d) starch-sorbitol film, and e) starch-formamide film in the 1200-900 cm\(^{-1}\) region.
4.3.2: FTIR spectra of starch-glycerin-hectorite nano-composite film

Native starch presents several characteristic absorbance bands and peaks (Figure 4.3.5a). The regions at 2,935 cm\(^{-1}\) and 3,450 cm\(^{-1}\) correspond to hydroxyl groups. In the fingerprint region three characteristic peaks appeared for starch-glycerin film between 1200 cm\(^{-1}\) and 900 cm\(^{-1}\), attributed to C–O bond stretching of starch.

Figure 4.3.5: FTIR spectra of a) starch, b) hectorite, c) starch-glycerin film, d) starch-glycerin-hectorite 2 wt % nano-composite film.
The stretching frequencies of the structural hydroxyl groups in hectorite gives weak sharp bands at 3666 cm\(^{-1}\). Hectorite, too, has an additional weaker but broader band at 3620 cm\(^{-1}\), which was detectable only after removing most of the interlayer water in figure 4.3.6. The possible presence of Li and Mg carbonates in non-silicate phases was checked by examining the IR spectrum of untreated hectorite, which revealed a band at approximately 1430 cm\(^{-1}\). (Si–O) peak observed near 1000 cm\(^{-1}\), (Mg–O) peak observed at around 460 cm\(^{-1}\) in figure 4.3.5.

![Hectorite 2nd derivative](image)

Figure 4.3.6: Second derivative of hectorite IR spectra.
Figure 4.3.7 represents the FTIR spectra of starch-glycerin film and addition of hectorite clay with varying percentage of hectorite clay. (Si–O) peak was observed near 1000 cm\(^{-1}\) which becomes clearer with increasing percentage of hectorite clay as shown in Figure 4.3.8.
Figure 4.3.8: FTIR spectra of a) starch-glycerin film, c) starch-glycerin-hectorite 2%, c)5%, and d) 10% nano-composite film in the 1200 - 900 cm$^{-1}$ region.
4.3.3: FTIR spectra of starch-glycerin-montmorillonite nano-composite film

The FT-IR spectra of starch, montmorillonite powder and its nano-composites are shown in Figure 4.3.9. The FT-IR spectrum of montmorillonite clay (Figure 4.3.10) showed the characteristic absorption bands of the clay at 1100 cm\(^{-1}\) (Si–O), 522 cm\(^{-1}\) (Al–O) and 463 cm\(^{-1}\) (Mg–O). The absorption peaks at 3630 cm\(^{-1}\) and about 3,400 cm\(^{-1}\) contributed to OH groups of montmorillonite powder. Also the main characteristic peak of starch in its spectrum (Figure 4.3.9 a) are the stretching and bending vibration of hydrogen bonding OH group of starch 3,450 cm\(^{-1}\) and 2935 cm\(^{-1}\). The stretching vibration of C–O bonding in C–O–H and C–O–C group in the anhydrous glucose ring appeared at 1,150 cm\(^{-1}\), 1,080 cm\(^{-1}\) and 1040 cm\(^{-1}\). The characteristic peak of C–O–C ring vibration in starch located at 760 cm\(^{-1}\) in Figure 4.3.10.

Figure 4.3.9: FTIR spectra of a) starch, b) montmorillonite, c) starch-glycerin film, d) starch-glycerin-montmorillonite 2 wt% nano-composite film.
Figure 4.3.10: FTIR spectra of a) starch, b) montmorillonite, c) starch-glycerin film, d) starch-glycerin-montmorillonite 2 wt % nano-composite film.

FT-IR spectra of the products obtained in the presence of different loading clay percent (Figure 4.3.11 b–d) showed a combination of clay and potato starch characteristics and all these film products exhibited the clay characteristic peaks: C–H stretching of aromatic ring (1,601 cm\(^{-1}\), 1,490 cm\(^{-1}\), 760 cm\(^{-1}\) and 700 cm\(^{-1}\)) and C =C in aromatic ring (1,700–2,000 cm\(^{-1}\)). The main bands for distinctive functional groups were identical in potato starch and pure clay, which makes observation of any modification in these bands difficult. However they obtained results showed that the peaks corresponding to clay become sharper and their intensity increases with increasing the loading clay percent. Also after cast, the peak corresponding to -OH group of MMT disappears in the spectrum related to the starch-glycerin-clay nano-composites film in comparison to that of MMT.
Figure 4.3.11: FTIR spectra of a) starch-glycerin, b) starch-glycerin-monmorillonite 2 wt %, c) starch-glycerin-monmorillonite 5 wt %, and d) starch-glycerin-monmorillonite 10 wt % nano-composite film.

Figure 4.3.12: FTIR spectra of a) starch-glycerin film, c) starch-glycerin-MMT 2% c) 5% and d) 10% nano-composite film at 1200-900 cm$^{-1}$ region.
4.3.4: FTIR spectra of starch-glycerin-kaolinite nano-composite film

Native starch presents several characteristic absorbance bands and peaks (Figure 4.3.13 a). The regions at 2,935 cm$^{-1}$ and 3,450 cm$^{-1}$ corresponds to hydroxyl groups. The presence of CH$_2$ groups determines the existence of the peaks at 2,924 cm$^{-1}$, 1,465 cm$^{-1}$. In the fingerprint region starch-glycerin film shows three characteristic peaks between 1200 cm$^{-1}$ and 900 cm$^{-1}$, attributed to C–O bond stretching of starch. The characteristic peak at 1150 cm$^{-1}$ is ascribed to C–O bond stretching of C–O–H group in starch while two peaks at 1080 cm$^{-1}$ and 1040 cm$^{-1}$ are attributed to C–O bond stretching of C–O–C group in the anhydroglucose ring.

A typical spectrum of kaolinite show four bands, at 3697, 3669, 3645 and 3620 cm$^{-1}$, and these characteristic bands are observed in the studied kaolinite samples from Figure 4.3.13 b. The band observed at around 3620 cm$^{-1}$ has been ascribed to the inner hydroxyls, and the bands observed at around the other three characteristic bands are generally ascribed to vibrations of the external hydroxyls. The studied kaolin sample exhibits the bands near the three characteristic bands at 3669, 3645 and 3620 cm$^{-1}$. The H-O-H bending of water is observed at 1620-1642 cm$^{-1}$. The absorption bands observed at 1620-2642 cm$^{-1}$ could be assigned to the OH vibrational mode of the hydroxyl molecule, which is observed in almost all the natural hydrous silicates. The bands between 3450 and 3670 cm$^{-1}$ are attributed to the -OH stretching mode. The H-O-H bending of water is observed at around 1633 cm$^{-1}$.

Figure 4.3.13: FTIR spectra of a) starch, b) kaolinite, c) starch-glycerin film, d) starch-glycerin-kaolinite 2% nano-composite films.
Figure 4.3.14: FTIR spectra of a) starch, b) kaolinite, c) starch-glycerin film, d) starch-glycerin-kaolinite 2% nano-composite films at 4000-3000 cm$^{-1}$ region.

In the 1000 cm$^{-1}$ and 500 cm$^{-1}$ region (Figure 4.3.15), main functional groups peaks Si-O and Al-OH are present. The Al-OH absorption peak was identified at 910 cm$^{-1}$ for the studied sample. The band at 914-936 cm$^{-1}$ corresponds to Al-OH bending vibrations of kaolinite.

Figure 4.3.15: FTIR spectra of a) starch, b) kaolinite, c) starch-glycerin film, d) starch-glycerin-kaolinite 2% nano-composite film at 1200-900 cm$^{-1}$ region.
Figure 4.3.16 - 4.3.18 represents the starch-glycerin-kaolinite 2 wt%, 5 wt% and 10 wt % nano-composite films. In addition of kaolinite clay into starch matrix with glycerin, the film gives its absorption peak clearly with increasing of kaolinite clay percentage.

Figure 4.3.16: FTIR spectra of a) starch-glycerin film, b) starch-glycerin-kaolinite 2%, c) 5%, and d) 10% nano-composite films.

Figure 4.3.17: FTIR spectra of a) starch-glycerin film, b) starch-glycerin-kaolinite 2%, c) 5%, and d) 10% nano-composite films at 4000-3000 cm\(^{-1}\) region.
Figure 4.3.18: FTIR spectra of a) starch/glycerin film, b) starch/glycerin/Kaolinite 2%, c)5%, and d) 10% nano-composite film at 1200-900 cm\(^{-1}\) region.
4.4 TENSILE STRENGTH TEST
The plasticizer interacts with starch polymer and lowers the intra/ intermolecular hydrogen bonding to increase the polymer mobility. As water is a plasticizer, the increase in relative humidity during storage has the same effect as for the rise of glycerol content. Commonly used plasticizers for plasticized starch include water, glycerol, formamide, ethylene glycol. These chemicals are small in molecular size and are hydrophilic. Water and glycerol have traditionally been considered as the most effective plasticizers. Formamide, which contains -CO-NH- functional group, has recently been proved as a good plasticizer. This is believed to suppress retrogradation and improve mechanical properties of TPS. Glycerin gave highest tensile strength compare to other plasticizer such as ethylene glycol, formamide and sorbitol.

Figures 4.4.1 to 4.4.8 give the tensile properties (tensile strength and elongation at break) of the nano-composites films based on a starch and plasticizer, and hectorite, or MMT or kaolinite nano-clays. The content and type of clay interfered strongly the mechanical properties of the materials. The use of clay in nano-composites has the purpose of improving mechanical properties. Starch or starch-plasticizers films generally show poor mechanical properties and provide a minimal barrier to moisture. The presence of plasticizer and nano-clays leads to overcome the brittleness of these films, and improve these properties.

4.4.1 Effect of plasticizers
Figure 4.4.1 gives the extension properties of starch-plasticizer film. The addition of a plasticizer to a film produces a film which is less likely to break and is more flexible and stronger. Starch-glycerin film is soft and flexible. Starch-sorbitol film is very hard and rigid. Starch-formamide and starch-ethylene glycol are also hard and rough.
Figure 4.4.1: Load vs displacement curve for starch-ethylene glycol, starch-formamide, starch-sorbitol, starch-glycerin films.

4.4.2 Effect of hectorite clay

Figure 4.4.2 shows that, tensile strength increased with addition of hectorite clay content at certain concentration. For that reason when 2 wt % hectorite clay was added, tensile strength decreases than starch-glycerin film. Low percent of clay intercalated the starch-glycerin film. But starch-glycerin-hectorite 10% film exhibits higher tensile strength than starch-glycerin film. Again starch-glycerin-hectorite 10% film, it shows higher mechanical strength compared to 5 % of clay film with starch and plasticizer due to homogeneous exfoliated network. SEM images of the films also testify the phenomenon.
4.4.3 Effect of montmorillonite clay

Incorporation of MMT nanoclays improved the mechanical strength of the films. The structure and properties of the resulting material is dependent on the state of the nano clay in the nano-composite, that is, whether starch polymer is exfoliated or intercalated state in the network. Intercalation is the state in which polymer chains are present between the clay layers, resulting in a multilayered structure. Exfoliation is a state in which the clays are completely separated and dispersed in a polymer matrix. Natural MMT is hydrophilic and is miscible with hydrophilic polymers, such as starch. In addition, starch–glycerin-MMT nano-composites have received prominence due to the mechanical reinforcement achieved, even at low concentrations.
Figure 4.4.3 also shows that mechanical strength decreases initially with addition of low percentage of clay and increases at optimum percentage of MMT clay. Low percentage of MMT increases the hardness and rigidity of the film, because the clay does not well disperse due to low amount. When 10 wt% clay is added, it became homogeneous dispersion.

Figure 4.4.3: Load vs displacement curve for starch-glycerin film, starch-glycerin-MMT 10 wt %, 5 wt and 2 wt % nano-composite films.
4.4.3 Effect of kaolinite clay

The effect of kaolinite clay depended on the used plasticizer. Combination of kaolinite clay with glycerin improved the tensile strength; High percentage of kaolinite clay gives high tensile strength. Figure 4.4.4 shows starch-plasticizer-kaolinite 10% nano-composite film shows good tensile strength compared to other films.

Figure 4.4.4: Load vs displacement curve for starch-glycerin film, starch-glycerin-kaolinite 10 wt, 5 wt % and 2 wt% nano-composite films.

4.4.4 Effect of different clays

Different types of clay such as hectorite clay, montmorillonite clay and kaolinite clay displayed different mechanical properties. Hectorite clay showed good tensile properties than MMT and kaolinite as shown in figure 4.4.5. All types of clay gives superior mechanical performance but starch-glycerin-hectorite nano-composite film is very soft and flexible compared to nano-composite film prepared by using MMT and kaolinite.
Figure 4.4.5: Load vs displacement curve for starch-glycerin-hectorite, starch-glycerin-
montmorillonite and starch-glycerin-kaolinite nano-composite films.

4.4.5 ELONGATION AT BREAK

Figures 4.4.6 to 4.4.8 show the elongation at break of the starch-clay nano-composite films. Elongation at break (%E) has been evaluated from the experimental stress-strain curves obtained for all prepared nano-composite films. Variability of TS and %E data exist due to several reasons: mixing procedure, the dispersion of nanoparticles, film casting, and also testing instrument.

Figure 4.4.6 to 4.4.8 shows the effects of clay content on tensile properties. It was obvious that addition of natural clay helped to improve the elongation at break of the films. This is suggested that good dispersion of clay platelets in the polymer reduced tensile ductility and impact strength compared to neat polymer.

Theoretically, the complete dispersion of clay layers in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. The coupling between the tremendous surface area of the clay and the polymer matrix facilitates stress transfer to the reinforcement film, allowing for such tensile and toughening improvements.
Regarding nanoclay particles, elongation at break increased with increase of hectorite content. The content of glycerol strongly influenced all studied properties for all studied formulations. Elongation at break is 350 % for starch-glycerin film. It was decreases with addition of 2 wt % hectorite clay at 375% and increases at around 580% and 664% for 5 wt % and 10 wt% hectorite clay, respectively.

![Figure 4.4.6: Elongation at break with different percentage hectorite of clay.](image)

Elongation at break increased with increase of MMT content. Elongation at break was 350 % for starch-glycerin film. It decreased with addition of 2 wt % MMT clay at 325% and further decreased at around 260% for 5 wt % and increased for 10 wt % MMT clay at 655%.
Elongation at break increased with increase in kaolinite content. Elongation at break was 350% for starch-glycerin film. It decreased with addition of 2 wt % kaolinite clay at 246%, further decreased at around 92% for 5 wt % and increased for 10 wt % kaolinite clay at 521%.

Figure 4.4.7 Elongation at break with different percentage MMT of clay

Figure 4.4.8 Elongation at break with different percentage kaolinite of clay
4.5 X-RAY DIFFRACTION (XRD) ANALYSIS

The clay dispersion within starch has been characterized by XRD, which are the most frequently used methods to study the structure of nano-composites. Depending on the relative distribution/dispersion of the stacks of clay platelets, three types of Starch-Clay nano-composite (SCN) can be described: intercalated SCNs, where clay particles get into the starch resulting in a well ordered multilayer morphology built up with alternating polymer and inorganic layers; flocculated SCNs, where intercalated stacked clay particle are sometimes flocculated due to the hydroxylated edge interactions, and exfoliated/delaminated SCNs, where the clay particles are completely homogenously dispersed in the polymer matrix. Because of the hydrophilic nature of starch in aqueous media, this biopolymer has good miscibility with different types of clay such as hectorite, MMT, kaolinite and can easily intercalate into the inter layers.

The XRD pattern of potato starch showed the characteristic crystalline peak at about 17.05° and showed few amorphous peaks at 19.48°, 22.14° and 24°. These peaks are broad and featureless that indicate the semi crystalline structure of starch granules.

Figure 4.5.1: XRD pattern of extracted potato starch completely coincides with standard Maize strach.
The XRD pattern of hectorite showed the characteristic broad peak at about 19.48° and showed another peak at about 34.94°. These peaks are semi-crystalline and amorphous. The average crystallite size of starch granules determined using Scherer’s formula

\[ t = \frac{k\lambda}{\beta \cos \theta} \]  

where \( t \) is the crystallite size, \( \beta \) is the full width at half maximum of the peak, and \( k \) is an instrumental constant. The average crystallite size was found 6.5 nm.

Figure 4.5.2: XRD pattern of hectorite granule completely coincides with standard hectorite pattern.
The XRD pattern of MMT showed the characteristic crystalline peak at about 26.6 ° and showed several amorphous peaks. It showed semi crystalline structure of MMT granule. The average crystallite size was found 26.1 nm.

Figure 4.5.3: XRD pattern of montmorillonite granule completely coincides with standard montmorillonite pattern.
The XRD pattern of kaolinite showed the characteristic crystalline peak at about 12.52° and 24.8° and showed several amorphous peak. Kaolinite is crystalline in nature. The average crystallite size was found 25.9 nm.

Figure 4.5.4: XRD pattern of kaolinite granule completely coincides with standard kaolinite pattern.
4.5.1 XRD analysis for starch-glycerin-hectorite nano-composite film

Figure 5.5 shows that, Hectorite clay gives amorphous peak. Starch-glycerin film displayed amorphous peaks. In corporation of glycerin and hectorite clay into starch granule, starch peak turns to broader. With variation of clay percentage, starch-glycerin-hectorite nano-composite film peaks increses width with incresing clay percentage. Starch-clay-hectorite 10 wt % nano-composite film showed highly amorphous peaks. The peaks indicate that the film is soft and turns to biodegrability. The average crystallite size was found for starch-clay- hectorite 2 wt% nano-composite film is 1.7 nm.

![XRD pattern of starch-glycerin-hectorite nano-composite film.](image)

Figure 4.5.5: XRD pattern of starch-glycerin-hectorite nano-composite film.
4.5.2 XRD analysis for starch-glycerin-MMT nano-composite film

Figure 4.5.6 shows that, montmorillonite clay gives crystalline peak. Starch-glycerin film displayed amorphous peaks. Incorporation of glycerin and MMT clay into starch granule, starch peak correspondings to turns to broader. With variation of clay percentage, starch-glycerin-MMT nano-composite film peak intensity decreases with incresing clay percentage. Starch-clay-MMT 10 wt% nano-composite film showed amorphous peaks although starch-glycerin-MMT 2 wt% nano-composite film showed crystalline peaks. The peaks indicate that the film is soft and turns to biodegrability. The average crystallite size was found for starch-clay-MMT 2 wt% nano-composite film is 4.3 nm and starch-clay-MMT 10 wt % nano-composite film is 6.3 nm.

Figure 4.5.6: XRD pattern of starch-glycerin-MMT nano-composite film.
4.5.3 XRD analysis for starch-glycerin-kaolinite nano-composite film

Figure 5.7 shows that, kaolinite clay gives more than are crystalline peak. Starch-glycerin film displayed amorphous peaks. In corporation of glycerin and kaolinite clay into starch granule, starch peak turns to broader. With variation of clay percentage, starch-glycerin-kaolinite 2 wt% nano-composite film peaks showed amorphous peak. Peak crystallinity increases with increasing percentage of kaolinite clay. The average crystallite size was found for starch-clay-kaolinite 10 wt% nano-composite film was 25.6 nm.

Figure 4.5.7: XRD pattern of starch-kaolinite nano-composite film.
From all of the above observations, the following network structures can be proposed for starch-clay nano-composite film.

![Network Structures](image)

**Figure 4.5.8**: Proposed structure of starch-clay nano-composite films.

### 4.6 THERMOGRAVIMETRIC ANALYSIS (TGA)

#### 4.6.1 TG-DTA of Hectorite clay

The thermal stability of the starch-glycerin and the corresponding nano-composite film are shown in Figure 4.6.1. In TGA, two parameters were measured: the temperature of thermal degradation at 20% weight loss and the yield of ash residue at 900°C, respectively. About 78% starch decomposed at 292°C and the remaining ash residue after decomposition is 22%. Hectorite granules decomposed at 720°C with ash residue 83%. Starch-glycerin film exhibits maximum decomposition temperature of 296°C and ash residue of 19%. The weight loss observed between ambient temperature and 200°C is due to the loss of water molecules and plasticizers. The second stage of weight loss occurred between 200°C-400°C due to the starch decomposition. It is clear from Figure 4.6.1 starch-glycerin-hectorite nano-composites
film exhibits better thermal stability compared with starch-glycerin film. The film decomposed at 316°C and ash residue of 9%. Figure 4.6.2 displayed Derivative of TGA for starch granules, hectorite granules, starch-glycerin film and starch-glycerin-hectorite nano-composite film.

Figure 4.6.1: TGA curve for starch, hectorite, starch-glycerin film and starch-glycerin-hectorite nano-composite film.

Figure 4.6.2: DTG curve for starch, hectorite, starch starch-glycerin film and starch-glycerin-hectorite nano-composite film.
Figure 4.6.3: DTA curve for starch, hectorite, starch-glycerin film and starch-glycerin-
hectorite nano-composite film.

4.6.2 TG-DTA of Montmorillonite clay

The degradation of starch and its nano-composite films occurred in three steps. The first range (50°C–200°C) is associated with the loss of water, whereas the second range (200–350 °C) corresponds to the degradation of starch and the third degradation step (400 °C –900 °C) is assigned to the degradation of the clay. Figure 4.6.4 shows TGA curves for the starch-glycerin-MMT nano-composites films. Starch decomposed at 292 °C, the ash residue at 550 °C is 22%. MMT granules decomposed at approximately 400°C with 10% weight loss. Starch-glycerin film exhibits maximum decomposition temperature of 260°C. The weight loss observed between ambient temperature and 200°C is related to the loss of water molecules and plasticizers. The second stage of weight loss occurred between 200°C and 400°C is due to the starch decomposition. From Figure 4.6.4, starch-glycerin-MMT nano-composites film exhibits better thermal stability compared to starch-glycerin film. The film decomposed at 296 ° C and ash residue of 19%. One can see from these data that almost all the nanocomposites exhibit an increase in the onset and mid-point temperature of degradation relative to virgin starch-glycerin films and they increases as the amount of the clay increases. This indicates that starch-glycerin- MMT nano-composites films have enhanced thermal
stability. Starch-glycerin-montmorillonite nano-composite film decomposed at 306 °C and charred residue of 14%.

Figure 4.6.4: TGA curve for starch, MMT, starch-glycerin film and starch-glycerin-MMT nano-composite film.

Figure 4.6.5: DTG curve for starch, MMT, starch-glycerin film and starch-glycerin-MMT nano-composite film.
Figure 4.6.6: DTA curve for starch, MMT, starch-glycerin film and starch-glycerin-MMT nano-composite film.

4.6.3 TG-DTA of Kaolinite clay

The thermal degradation of kaolinite occurred with 20% weight loss at 900°C. Starch decomposed at 292°C, the ash residue at 550°C is 22%. Kaolinite granules decomposed at 470°C and the ash residue at 550°C is 88%. Starch-glycerin film exhibits maximum decomposition temperature at 296°C. The weight loss observed between ambient temperature and 200°C is due to the loss of water molecules and plasticizers from the samples. The second stage of weight loss occurred between 200°C-400°C is due to the decomposition of starch. It is clear from Fig. 2.7 that starch-glycerin-kaolinite nano-composite films exhibits better thermal stability compared with starch-glycerin film. The film decomposed about 296°C with 19% weight loss. The stronger hydrogen bonds interactions among Starch, glycerin, and kaolinite in nano-composites films are responsible for this degradation behavior. FTIR analysis also testifies this observation. Therefore, the high thermally stable kaolinite based nano-composite film could be obtained. Starch-glycerin-kaolinite nano-composite film decomposed at 311°C and ash residue 13%.
Figure 4.6.7: TGA curve for starch, kaolinite, starch-glycerin film and starch-glycerin-kaolinite nano-composite film.

Figure 4.6.8: DTG curve for starch, kaolinite, starch-glycerin film and starch-glycerin-kaolinite nano-composite film.
4.7 WATER ABSORPTION TEST

The effect of plasticizer and clay incorporation into nano-composite film on water uptake percentage of various types of starch-clay-nano-composite films are shown in Figure 4.7.1 to 4.7.5. The water absorption decreases with the plasticizer addition and further decreases with the addition of clay. Water uptake percentage increases with the increase of time. It is also found that the water absorption is approximately same for starch-glycerin-hectorite, starch-glycerin-montmorillonite and starch-glycerin-kaolinite nano-composite film (Figure 7.5). In the case of different types of plasticizer such as glycerin, ethylene glycol, sorbitol and formamide, water absorption was almost same except sorbitol. Sorbitol has less water absorption capacity.

Figure 4.7.1 shows that, the presence of plasticizer (glycerol) may affect the film properties. Amylopectin of starch was found to be more sensitive to glycerol plasticization than amylase. The properties of plasticized films were not improved by the presence of glycerol and
remained constant when amylose content was >40%. But water absorption significantly decreased about more than 60 percent because in potato starch amylose percentage is about 30% in the most cases. In addition, the presence of mineral clay may affect the starch network structure and crystallinity of amylose films.

Figure 4.7.2 showed water uptake properties for starch based nano-composite films. Starch film uptakes water readily upto 125% but showed different behavior with addition of plasticizer and hectorite clay. Starch-glycerin film absorbed about 90% water and decreases water absorption properties with increasing clay content 2 -5%. Water absorption increases with 10 wt % hectorite clay slightly than 2 and 5 percent.

![Graph showing water uptake properties](image)

Figure 4.7.1: Percentage of water absorption with time for starch-water, starch-glycerine film, starch-ethylene glycol film, starch-sorbitol film, starch-formamide film.
Figure 4.7.2: Percentage of water absorption with time for starch-water film, starch-glycerine film, starch-glycerine-hectorite 10% nano-composite film d) starch-glycerine-hectorite 5% nano-composite film e) starch-glycerine-hectorite 2% nano-composite film.

Water absorption of the starch-plasticizer-MMT nano-composite films were significantly lower than that of films made from starch with water in Figure 7.3. Water absorption decreased significantly with the addition of 2–10% MMT. It was obvious that the addition of plasticizer improves the water barrier properties of the films, which indicated that improvement in film properties depending on the formation of intercalation or exfoliation network structure.
Figure 4.7.3: Percentage of water absorption with time for starch-water film, starch-glycerine film, starch-glycerine-MMT 10% nano-composite film, starch-glycerine-MMT 5% nano-composite film, starch-glycerine-MMT 2% nano-composite film.

Generally, water absorption through a hydrophilic film depends on both diffusivity and solubility of water molecules in the film matrix. When the nano-composite structure is formed, the impermeable clay layers mandate a tortuous pathway for water molecules to traverse the film matrix, thereby increasing the effective path length for diffusion. The decreased diffusivity due to the homogeneous mixing of clay with starch in starch-plasticizer-MMT composite film reduced the water absorption. Figure 4.7.3 shows the effect of 0–10% MMT on water absorption of starch-MMT nano-composite films. Water uptake decreased sharply as clay content increased 2 to 10%. Water absorption of starch with 10% clay for 24 hour was ≈70% which is lower than the water absorption of the starch only film.

Water absorption was an important index to evaluate application of nano-composites. The results of water absorption experiments of the starch-glycerin and its nano-composites with kaolinite clay contents are shown in Figure 7.4. It is apparent that the presence of kaolinite significantly decreased the water uptake of nano-composites, especially with 5 wt% clay contents. The results obtained here provide that the water resistance of starch-glycerine-kaolinite nano-composite film was better than that of starch-kaolinite film. The strong hydrogen bonds formed among starch, glycerin, and kaolinite, which prevented water
molecules to penetrate into the materials, and thereby, enhance the water resistance of the corresponding nanocomposite film.

Figure 4.7.4 suggests that the water resistance of starch-glycerine-kaolinite nano-composite film is obviously higher than starch-glycerine film. Therefore, conclusions can be drawn that the addition of the kaolinite platelets and the strong structure significantly reduced the diffusion of water molecules in the materials, improving the water resistance of starch films.

Figure 4.7.4: Percentage of water absorption with time for starch/water film, starch-glycerine film, starch-glycerine-kaolinite 10% nano-composite film, starch-glycerine-kaolinite 5% nano-composite film, starch-glycerine-kaolinite 2% nano-composite film.
The picture of starch-clay nano-composite film before and after water absorption is given below.

Figure 4.7.5: a) As prepared starch-clay nano-composite film b) Starch-clay nano-composite film after equilibriated water absorption (each bar 12mm).

In summary, only starch film showed highest water absorption capacity. It decreases with the addition of different plasticizer and further decreases with addition of different type of clays. The water uptake percentage followed the order given below, starch > starch-plasticizer film > starch-glycerin-MMT nano-composite film > starch-glycerin-kaolinite nano-composite film > starch-glycerin-hectorite nano-composite film.

4.8 BIODEGRADABILITY OF STARCH-CLAY NANO-COMPOSITES FILMS

4.8.1 Soil bury test

Starch-clay nano-composites films are completely biodegradable under soil burial test. From the biodegradability test of the Starch-clay nano-composite films was found that Starch-clay nano-composite films lost weight because of composting time and the weight loss rapidly increased up to 38% upon composting for 4 weeks. It was found that the addition of starch resulted in a faster rate of enzymatic biodegradation. In the burial test, the composite gradually degraded, because a more rapid decreases in the percentage weight loss of the film by bacteria and fungi during the natural soil burial test. For all the samples, the weight reduction rapidly reduced until the sixth week. From the tenth week onwards, there was a small amount of weight reduction for all the samples.

Figure 4.8.1: Bio-degradable Starch-clay nano-composite film.
CHAPTER FIVE

CONCLUSION
5.1 CONCLUSION

The aim of this research work was to produce biodegradable starch-clay nano-composite film. For that reason, natural biodegradable polymer starch granules were successfully extracted from potato. Different types of plasticizers and various nano-clays were used with native starch to enhance the mechanical strength of starch based nano-composite films. DLS analysis was used to measure the hydrodynamic radius of starch and different types of clays such as hectorite, montmorillonite and kaolinite. Starch-clay nano-composites films could successfully prepared by solution casting method.

From tensile strength analysis, it was observed that glycerin is the most effective plasticizer for starch-plasticizers composite film, which increases the tensile strength readily compared to sorbitol, ethylene glycol. For that reasons, glycerin is constantly used as plasticizers for starch-clay nano-composite films. All types of clays such as hectorite, montmorillonite and kaolinite can significantly improve the mechanical properties of starch-clay nano-composite films. But starch-glycerin-hectorite nano-composite films exhibits very soft and flexible properties. Intercalated/exfoliated nano-composites are formed by homogenous mixing of starch and clay in the starch-clay nano-composite film for optimum percentage of clay. In other cases, phase separation occurs due to irregular distribution of clay particles inside the starch-clay nano-composite films network.

The clay particles homogeneously disperse into starch-clay nano-composite films but heteroginity exists for starch-plasticizer composite films. Starch-glycerin film exhibits a layer by layer morphology. EDS provides rapid qualitative and quantitative analysis of elemental composition. From this analysis, we can conclude that the clay particles are successfully incorporated into the starch-clay nano-composite films.

Suitable interaction of hydrogen bond and formation of intercalation or exfoliation network are responsible for these interesting phenomena. FTIR and ATR method provide the information about different interaction in the films. Starch absorption peaks shifted towards lower wave number due to addition of different plasticizers, especially for glycerin, suggesting the strong hydrogen bond interaction.
Starch is semicrystalline structure. Introducing the nano-clay into starch-glycerin-hectorite nano-composite film gives amorphous structure which indicates proper mixing of elements. Sometimes small amount of clay such as 2 wt % does not homogeneously mixed with starch and crystallite peaks of clay exists into nano-composite film. This observation represents the phase separation of clay sheets in the films. Amorphous peak facilitate the biodegradable characteristics of polymeric materials. Crystalline peaks of starch turns into amorphous for starch based nano-composite film which is evidence for the superior mechanical and biodegradable properties of starch based nano-composite films.

Thermal stability and water resistivity of starch based nano-composite films are increased significantly. These films are completely biodegradable under soil burial test.

Starch-clay nano-composite films can potentially be used in the field of alternative of synthetic plastic materials, plastic bag, DDS, smart sensor, fuel cell and so on.
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