

Starch Based Biodegradable Blends: A Review

Waham Ashaier Laftah*

¹Composites Center, Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, Malaysia.

¹ College of Oil and Gas Engineering, Basrah University for Oil and Gas, 61004 Basrah, Iraq.

Abstract: Starch based polymer bio-blends are biodegradable polymeric materials of cellulosic-based biomaterials, which can be degraded by microorganisms and enzymes. The combination of starch with polyolefin produces a single material that has the biodegradation properties of starch and the mechanical, thermal and barrier properties of polyolefin. Starches such as rice, tapioca and sago starch and polyolefin such as polyethylene and polypropylene have been used to prepare bio-blend using different processing methods. The review has shown that the bio-blends obtained from starch and polyolefin have improved biodegradation and in some instances enhanced the mechanical properties.

Keywords: Starch; bio-blends; biofilm; packaging application

1. INTRODUCTION

Scientists, manufacturers and consumers have defined biodegradability in various ways. The American Society for Testing and Materials (ASTM) define biodegradable plastics as plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and physical forces in the environment at a rate that leads to fragmentation or disintegration of the structure. The biological factor refers to the biological surroundings (including biological agents responsible for the deterioration of polymeric substances) in which the polymers are present. Biological agents such as bacteria, fungi and enzymes consume substances as food thereby changing the original form of the materials. Biodegradation is a relatively rapid process in the presence of chemicals and other physical forces such as moisture, temperature and oxygen. Generally, the main factors that affect the biodegradation of polymers are the polymer structure, polymer morphology, radiation, chemical treatment and molecular weight. Biodegradable polymers and biopolymers are the best alternative to petroleum-based polymers in various applications due to their biodegradability, biocompatibility and the rising cost of petroleum-based plastics. Biodegradable polymers have been classified as natural biodegradable polymers, polymers with hydrolysable backbones and polymers with carbon backbones. The natural biodegradable polymer refers to polymers that are formed naturally during the growth cycles of all organisms. The natural biopolymers are divided into three groups: polysaccharides, polypeptides of natural origin and bacterial polyesters. Examples of the polysaccharides are starch, cellulose, chitin and chitosan. Cellulose and starch are the most abundant of the naturally occurring polymers as such have gained much attention in the field of material science.

Cellulose has received more attention as compared to other biopolymers because it can be consumed by many microorganisms and is often used in textiles without additives. Starch is a polymer that occurs widely in plants such as potatoes, corn and rice as water insoluble granules. Starch has been widely used as a raw material in film production because of the increasing prices and decrease in the availability of the conventional film-forming resins. The low permeability characteristic of starch films makes them attractive materials for food packaging [1, 2].

Polymers with hydrolyzable backbones e.g. polyesters, polycaprolactones, polyamides, polyurethanes, polyanhydrides and poly(amide-enamines) are susceptible to biodegradation. Polyesters, which are the most popular, are classified as aliphatic and aromatic polyesters based on the composition of their main chain. Polymers such as polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), polyglycolic acid (PGA) and polylactic acid (PLA) belong to the aliphatic polyester family while derivatives of Polybutylene terephthalate (PBT) are in the aromatic family. The Polyester polymers are derived either from renewable resources or petroleum-based products. The advantage of the biodegradable polymers as compared to others is that it can be processed by most conventional plastics processing techniques. The products can be produced using film extrusion, injection molding, blow molding and thermoforming. The applications of biodegradable polymers have been focused on three major areas: medical, agricultural and packaging. However, due to their specialized nature and greater unit value, the medical and packaging applications have developed faster than agriculture.

Plastics (synthetic polymers) are petroleum-based products that are derived from fossil fuel such as naphtha and natural gas. Plastic materials are considered to be an essential part of modern life due to specific features of strength, lightweight, less expensive, easily process able and energy efficient. With their inert properties, plastics are widely used as packaging materials as they maintain the purity and freshness of the content. Synthetic plastics have important properties such as ease of forming, heat seal ability, flexibility, impact strength, lightweight, low cost, good tensile and tear strength and good barrier properties to oxygen [3]. Figure 1 shows packaging as the largest single sector of plastics use in the UK. Plastic is the material of choice in nearly half of all packaged goods. The packaging industry is the leading user of plastics accounting for about 40% of the total world plastic production.

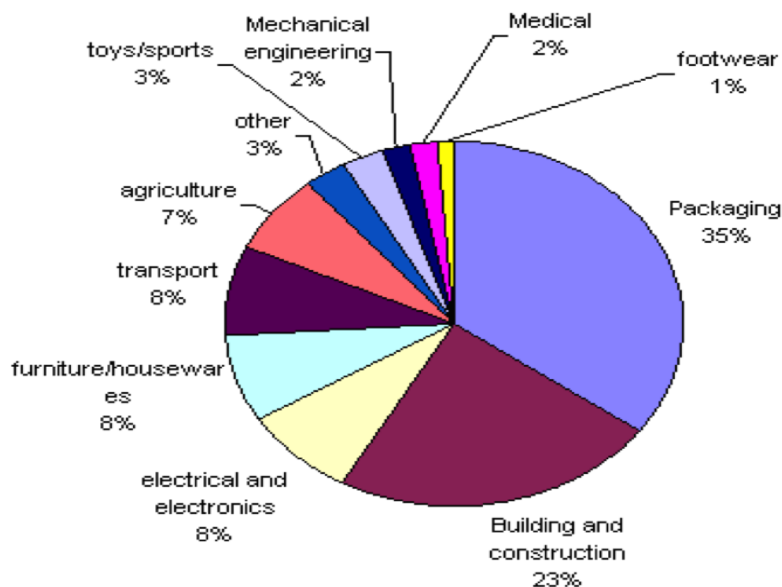


Figure 1: Major uses of plastics in the UK.

The most widely used polymeric materials are durable and inert in the presence of microbes thus leading to long-term performance. Emphasis on environmental pollution problems for solid waste management, pending legislation and the need for environmentally friendly plastics has risen [4]. The recent trends in the preservation of the environment have also created public interest on the heavy usage of plastics as packaging materials in consumer industries [5]. Also, the petrochemical-based plastics have

very low water vapor transmission rate and most importantly, they are totally non-biodegradable thus leading to environmental pollution, which poses serious ecological problems [3, 6]. Table 1 shows the microbial resistance of commodity plastics used in packaging applications. The relative proportion of plastic waste increases everyday on account of their low degradability [5].

Table 1: Microbial resistance of synthetic polymers used in packaging applications

Polymers	Microbial resistance
Polyethylene	Very high
Polypropylene	Very high
Polyvinyl chloride	Very high
Polyvinylidene chloride	High
Polyvinyl acetate	Moderate
Polyvinyl alcohol	High
Polystyrene	High
Polymethyl methacrylate	High
Polytetrafluoroethylene	High
Polytrifluorochloroethylene	High
Cellulose acetate	High
Polyamides	Low
Polyethylene terephthalate	Fair
Silicone	High
Phenol formaldehyde	High

The conventional methods of plastic waste management such as land filling, recycling and incineration have proved inadequate [7, 8]. Non-degradable plastic packaging is the reason behind shortening the life expectancy of commercial landfills, increasing operational cost, contaminating the environment and posing threats to animals and marine life. In view of the above, different

types of polymeric materials that are compatible with the environment or eco-friendly have been developed. Research on biodegradable plastics based on starch began in the 1970s and continues today at various laboratories all over the world. Various processing techniques have been developed for continuous production of extrusion blown film and injection-molded articles containing 50% or more

starch [3, 9]. The blends of starch or protein and synthetic polymers are an attractive choice in order to replace more readily common thermoplastics in commodity application. Starch blends are process able in existing standard equipment and they provide comparable mechanical properties and stability to the non-degradable thermoplastics [10].

2. DEGRADATION

Degradation is defined as a process that leads to change in the properties of the materials. It reduces the ability of the material to perform its intended function. Heat, light, short-wavelength electromagnetic radiation, radioactive emissions, chemicals and interaction with

bacteria and fungi are the main cause of materials degradation. Degradation is categorized into chemical, mechanical, physical and biological. Figure 2 shows the summary of various models of environmental polymer degradation. Materials degradation such as thermal damage or chemical reactions that are either entirely physical or chemical in nature coexists with combined forms of materials degradation e.g. corrosive water. Environmental conditions also exert a strong effect on materials degradation. The three basic degradation mechanisms identified so far are scission of intermonomer linkages in the backbone, scission of side chain linkage in the backbone and ionically catalyzed attack on the side chains [11].

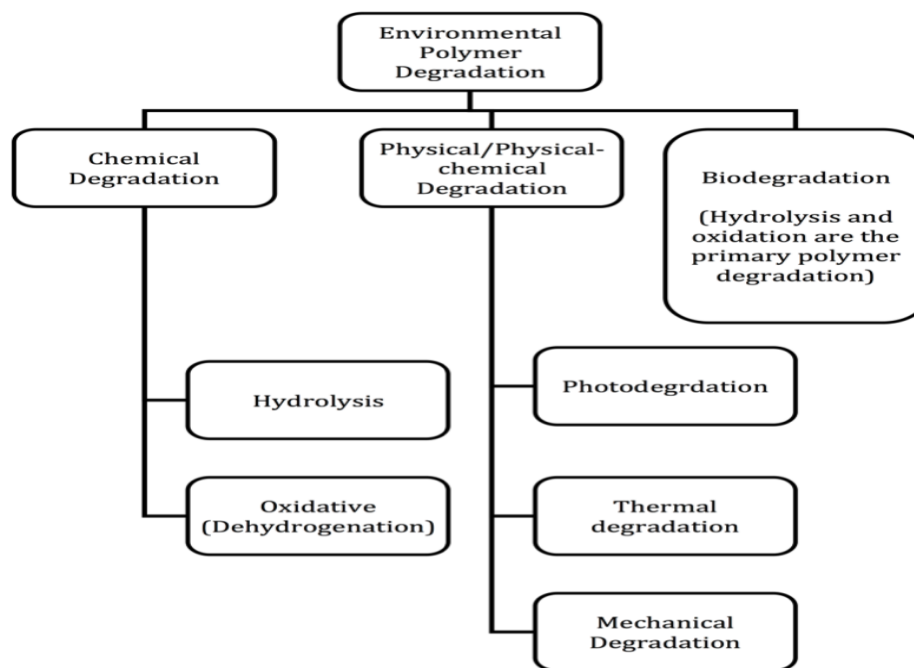


Figure 2: Environmental polymer degradation

The degradation of polymers proceeds by one or more mechanisms, which includes biodegradation, photo-oxidation or thermal degradation depending on the polymer environment and the desired application. The

combination of different factors such as sunlight, heat and humidity also has synergistic effects on the degradation [12, 13]. The possible degradation processes or agents for polymer and elastomers are shown in Table 2 [14].

Table 2: Degradation process for polymers and elastomers

Chemical	Mechanical	Physical	Biological
<ul style="list-style-type: none"> • Oxidative degradation • Reaction with air pollutants • Reaction of olefinic double bonds • Ozonization and ozone cracking • Ionic degradation 	<ul style="list-style-type: none"> • Fracture • Fatigue • Wear abrasion • Erosion 	<ul style="list-style-type: none"> • Photo oxidation by UV • Thermal degradation • Ultrasonic degradation • Radiation damage • Radiolysis 	<ul style="list-style-type: none"> • Enzymatic attack by microorganism • Attack by mammals and insects

3. BIODEGRADATION

This process is interpreted by the general public as the same as other processes of polymer degradation such as photo degradation, oxidation and hydrolysis though they lead to very different end products. It is often conceived that the breakdown of plastics into small invisible fragments is biodegradation but in reality, these fragments may remain in the environment over a significant period of time. Biodegradable polymers when placed in bioactive environments will compost or breakdown to CO₂ and water under the action of bacteria and fungi [15]. There are two major steps in biodegradation process. The first step involves the depolymerization or chain cleavage of the polymer oligomers while the second step is the

mineralization of these oligomers. The depolymerization step, which normally occurs outside the microorganism, involves the endo and exo-enzymes. The endo-enzymes cause random scission on the main chain while the exo-enzymes cause sequential cleavage of the terminal monomer in the polymer chain. After the depolymerization step, small-sized oligomeric fragments are formed and transported into the cell where they are mineralized. Mineralization is defined as the conversion of the polymer into biomass, minerals, water, alkanes (CH₄), nitrogen gas (N₂) and carbon dioxide (CO₂). The pathways for polymer biodegradation are shown in Figure 3.

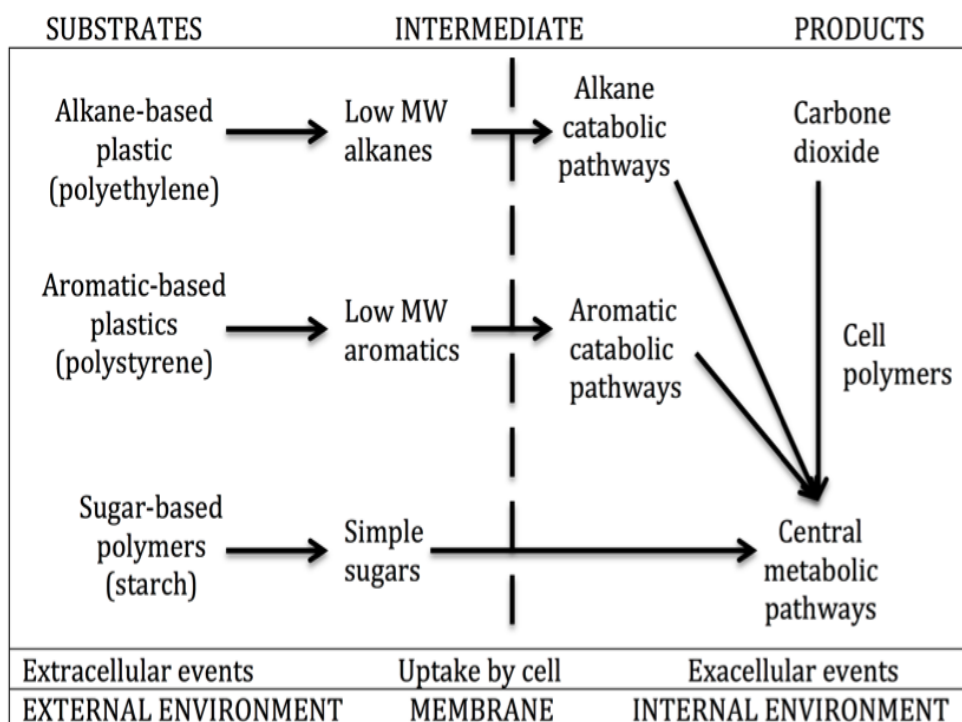


Figure 3: Pathways for polymer biodegradation

There are various standard test methods available to evaluate the biodegradability of plastics as listed in Table 3. Most of these test methods measure the percent conversion of the carbon from the designed biodegradable plastics to CO₂ and CH₄ in aerobic and anaerobic environments respectively. The absence of polymer and

residue in the environment indicates complete biodegradation process whereas incomplete biodegradation may leave polymer and/or residue as a result of polymer fragmentation or metabolism in the biodegradation process [11].

Table 3: Standard Methods for estimating biodegradation of plastics materials

Test	Environment	Property Measured
ASTM D 5209-92	Aerobic sewage sludge	CO ₂
ASTM D 5210-92	Anaerobic sewage sludge	CO ₂ /CH ₄
ASTM D 5247-92	Aerobic specific microorganism	Molecular weight
ASTM D 5271-93	Activated sewage sludge	O ₂ /CO ₂
ASTM D 5338-92	Controlled composting	CO ₂
ASTM D 5509-94	Simulated compost	Physical properties
ASTM D 5511-94	High solids anaerobic digestion	CO ₂ /CH ₄
ASTM D 5512-94	Simulated compost using external heater reactor	Physical properties
ASTM D 5525-94	Simulated landfill	Physical properties
ASTM D 5526-94	Accelerated landfill	CO ₂ /CH ₄
MITI test	Mixed microbial	O ₂

4. STARCH

Starch is a carbohydrate component occurring in granular form in the organs of plants. It is made up of carbon, hydrogen and oxygen in the ratio 6:10:5 (C₆H₁₀O₅). Granular starch is deposited in the seeds, tubers, roots and stem piths of plants as reserve food supply for periods of dormancy, germination and growth.

Microscopic observation revealed that starch is composed of tiny white granules ranging from 2 to 100 µm in diameter. The size and shape of the granules are peculiar to each variety of starch. Figure 4 shows schematically the appearance of various starches.

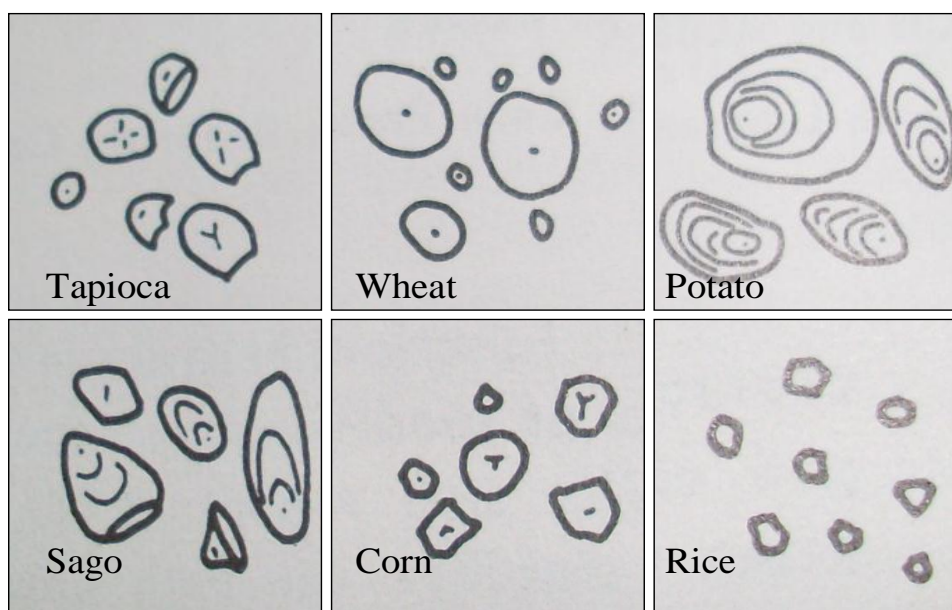


Figure 4: Microscopic appearance of various starch granules

Irrespective of the source, all starches occur in nature as tiny granules each with its inherent characteristic, size and shape. The

sources of starch can be identified from its microscopic appearance. Table 4 shows the size and shape of starches from different origins.

Table 4: Starch granule properties

Starch	Type	Size (µm)	Size (average)	Shape
Corn	Cereal	3-26	15	round, polygonal
Potato	Tuber	5-100	33	oval, spherical
Wheat	Cereal	2-35	15	round, lenticular
Tapioca	Root	4-35	20	oval, truncated
Waxy Maize	Cereal	3-26	15	round, polygonal
Sorghum	Cereal	3-26	15	round, polygonal
Rice	Cereal	3-8	5	polygonal, angular
Sago	Pith	5-65	30	oval, truncated
Arrowroot	Root	5-70	30	oval, truncated
Amylomaize	Cereal	3-24	12	round, deformed
Sweet Potato	Root	5-25	15	polygonal

Starches are considered as condensation polymers of glucose consisting of anhydroglucose units. The glucose units are linked through glucosidic bonds that are hydrosable in the presence of enzymes or acid but stable under alkaline conditions. Most starches are a mixture of amylose and amylopectin each with a wide range of molecular sizes. Starches of different origin have different amylose-amylopectin ratios. In each case, the repeating unit is identical but the two polymers are different in chemical structure, physical properties, water solubility and susceptibility to enzyme hydrolysis [16, 17]. The molecular weights of amylose and amylopectin in starch are normally in the order of several hundred thousand and several millions respectively. The commonly used starches have an amylose content of 25% even though starches containing varying amylose content have been used on special applications [10]. Cereal grains such as corn, wheat, sorghum rice; tubers like potato; roots such as tapioca, sweet potato, arrowroot and the pith of sago palm are commercial sources of starch. The starch industry uses a combination of grinding and wet purification techniques to manufacture starch with purity of about 99 %. The manufacturing process involves separating the starch from constituents such as fibers, proteins, sugars and salts from the milled raw material [18]. Starch granules are insoluble in water below 50 °C. When a suspension of starch in water

is heated beyond a critical temperature (gelatinization temperature), the granules absorb water and swell to many times their original size. When heating is continued, the swollen starch aggregates. The mass viscous aqueous medium is termed starch paste. The process involving the transformation of starch into starch paste is referred to as gelatinization. True solubilization of all the starch molecules occurs when the pastes are allowed to go through retro gradation phenomenon which is manifested in the formation of gel or precipitate [19]. The most important practical property of starch is its ability to produce a viscous paste when heated in water. Also, the hydro colloidal properties of starch make it suitable for great variety of applications. Starch and its derivatives are widely used in the manufacture of plastics [20], foods [21], paper [22], textiles [23], production of super absorbent polymers [24] and adhesive materials [25].

4.1 Chemical Composition of Starch

Starch granules usually contain 10-29 % (w/w) moisture and small amounts of protein, fatty materials, phosphorus and traces of inorganic materials. Table 5 shows the average chemical composition of various commercial starches [26].

Table 5: Average chemical composition of starch granules

Starch	Moisture %	Lipids %	Proteins %	Ash %	Phosphorus %
Corn	13	0.6	0.35	0.1	0.015
Potato	19	0.05	0.06	0.4	0.08
Wheat	14	0.8	0.4	0.15	0.06
Tapioca	13	0.1	0.1	0.2	0.01
Waxy Maize	13	0.2	0.25	0.07	0.007
Sorghum	13	0.7	0.3	0.08	-
Rice	-	0.8	0.45	0.5	0.1
Sago	-	0.1	0.1	0.2	0.02
Amylomaize	13	0.4	-	0.2	0.07
Sweet Potato	13	-	-	0.1	-

The moisture content of starch products depends on the relative humidity (RH) of the atmosphere in which they have been stored. The equilibrium moisture content of starch is also dependent on the type of starch product. Under normal atmospheric conditions, most commercial native starches contain 10-20 % (w/w) moisture. The equilibrium moisture content of all starches is low at a low atmospheric relative humidity. At RH zero, the moisture content of starches is near zero while at RH 20 %, the moisture content of all starches is about 5-6 % (w/w). Normal water of hydration in starch granules is located on carbon 6 of the glucose units [27].

The presence of lipids in the common cereal starches has a profound effect on the physical properties of these starches. The lipids exist as amylose-lipid inclusion complex in the granules. The amylose-lipid complexes are insoluble but their dissociation temperature is indicative of the strength of bonding which probably depends on the type of complexing agent. The amylose-lipid complexes limit the swelling and solubilization of the cereal starch

granules. At elevated temperatures above 125 °C, the organized amylose-lipid structure of the cereal starches granules is disrupted thus solubilizing the amylose fraction. The presence of fatty substances in corn starch products can result in rancid products during storage [28]. The quantity of proteins as shown in Table 5 includes real proteins, peptides, amides, amino acids, nucleic acids and enzymes that may be present in the starch granules. The tuber (potato) and root (tapioca) starches contain only a small amount of proteins (0.1 % w/w or lower) as compared to the common cereal starches (corn and wheat) which contain 0.3-0.5 % w/w proteins [26].

4.2 Chemical Structure of Amylose and Amylopectin

Most starches are mixture of amylose and amylopectin, each with a wide range of molecular sizes. Starches of different origin have different amylose – amylopectin ratios as presented in Table 6. In addition, the table shows the average degree of polymerization (DP) of both fractions in various starches [29].

Table 6: Amylose and amylopectin content and degree of polymerization of various starches

Starch	Amylose % (w/w)	Amylopectin % (w/w)	Average DP, amylose	Average DP, amylopectin
Corn	28	72	800	2000000
Potato	21	79	3000	2000000
Wheat	28	72	800	2000000
Tapioca	17	83	-	2000000
Waxy Maize	0	100	-	2000000
Sorghum	28	72	-	-
Rice	13	83	-	-
Sago	27	73	-	-
Arrowroot	20	80	-	-
Amylomaize	50-80	20-50	-	-

4.2.1 Amylose

Amylose is a linear polymer containing up to 6000 glucose units, connected by α (1,4) linkages. Enzyme studies indicate perhaps trace amount of branching in the amylose molecules or in a portion. The branched amylose molecules may contain 3-20 chains, with an average chain length of about 500 glucose units. The ratio of amylose to amylopectin is fairly constant for much higher amylose content, compared with the tuber and root starches, which contain only about 20% amylose [30]. Amylose covers a range of degrees of polymerization, depending upon the source of starch. The amylose molecules of potato and

tapioca starch have a substantially higher molecular weight than corn and wheat amylose. The amylose fraction of potato starch has a degree of polymerization ranging from 1000 to 6000 glucose units [31]. Amylose forms inclusion complexes with iodine and various organic compounds, such as butanol fatty acids, various surfactants, phenols and hydrocarbons. These complexes by forming a helix coil around the complexing agent. The complex of amylose with iodine gives a characteristic blue color, which used to establish the presence of amylose containing starch. Figure 5 shows the linear structure chain of amylose molecules.

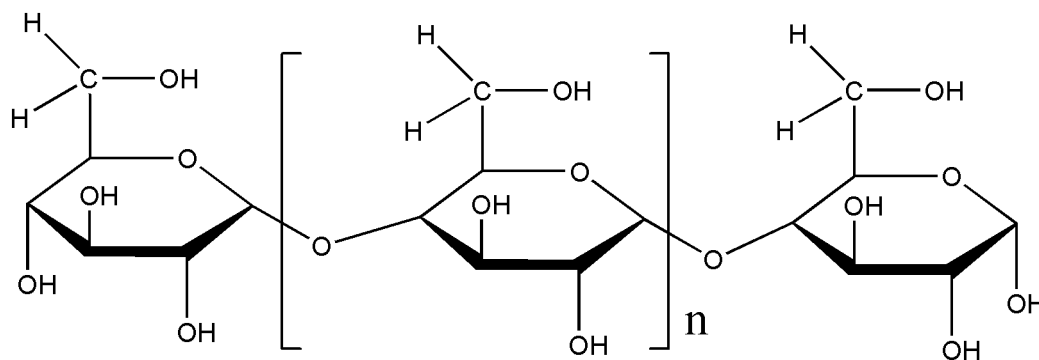


Figure 5: Linear chain structure of amylose molecules.

4.2.2 Amylopectin

Amylopectin has highly branched structure, consisting of short amylose chains, with DP ranging from

10 to 60 glucose units. The average DP of these chains is about 2,000,000. The chains are connected to each other by α (1,6) linkage as shown in Figure 6.

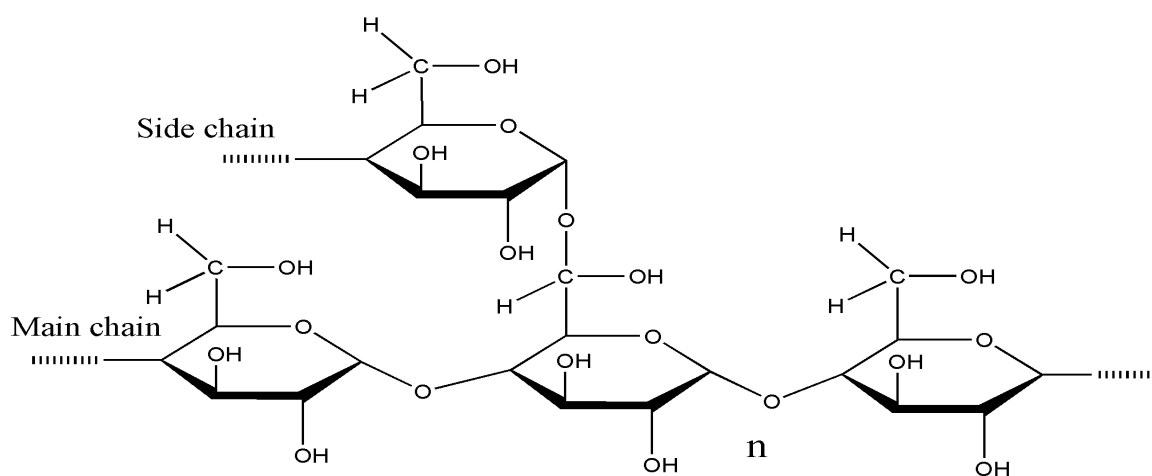


Figure 6: Structure of amylopectin branching.

The glucose units with α (1,6) linkage are the branching points of the amylopectin molecule and make about 5 % of the total glucose units in amylopectin. The average lengths of the outer chains of amylopectin before reaching a branch point are about 12 glucose units while the average chain lengths of the inner branches are about 8 glucose units. Only one glucose unit separates the portions of the branches, which suggests the presence of region dense branching. Probably amylopectin has cluster type structure. The branch points are arranged in tiers of some kind. The molecular weight of amylopectin is about 1000 times as high as the molecular weight of amylose [32].

4.3 Biosynthesis of Starch

The formation of starch in plant leaves is facilitated by the presence of water, carbon dioxide and chlorophyll under the influence sunlight. During active photosynthesis the starch accumulates in the leaves in the form of tiny granules. At night, the starch in the leaves is partly broken down by enzymes and transported to other parts of the plants to form sugars (mainly sucrose). Some of these sugars are reconverted into starch in the seeds, tubers and roots of the plants. The true mechanism for the biosynthesis of amylose and amylopectin is not entirely clear. The enzymes phosphorylase, starch synthetase and

branching enzymes are involved in starch biosynthesis. Phosphorylase has the capacity to lengthen the existing chains of glucose units but can also catalyze the degradation of these chains. For many years phosphorylase is believed to be solely responsible for the chain extension in starch biosynthesis. The discovery of another enzyme that can transfer glucose units to suitable polysaccharide resulted in the reconsideration of the above beliefs. Most of scientists think that starch synthetase is the true chain-lengthening enzyme in normal starch biosynthesis. The branching enzyme is responsible for the synthesis of branching points in the amylopectin molecules [33, 34]. The development of starch granules commences with the accumulation of poorly organized material of unknown chemical composition. At certain moment, there is deposition of a little amount of insoluble polysaccharide which acts as nucleus for further starch deposition. This nucleus is the botanical center (hilum) around which the granules grow. The initial growth gives nearly spherical granules. As the granules enlarge, they often become elongated or flattened. The starch molecular chains grow in an orientation perpendicular to the growing surface of the starch granule. As the dissolved glucose units are linked to the growing starch polymer, they simultaneously solidify [35].

4.5 Structure and Organization of Starch Granules

Starch granules viewed under polarized light usually show a strong interference cross-centered through the hilum. This suggests a radial organization of some sort. The characteristic x-ray diffraction pattern of starch granules proves that there are areas of crystallinity in the starch granules. The starch molecules are arranged in the granules in a radial fashion towards the hilum. Whenever the linear segments of the starch molecules are parallel to one another the hydrogen bond forces pull the chains together into associated crystalline bundles or micelles and the crystallinity is essentially due to the amylopectin component [36]. The large amylopectin molecule participates in the crystalline micelles as well as in the less organized regions. The starch granules are organized into more or less crystalline regions and amorphous regions. The transition between these regions is gradual. The regions of micellar crystallinity hold the granules together. The radial orientation of the micelles is responsible for their optical polar and the x-ray spectrum. The orientation of the crystalline micelles perpendicular to the granule surface implies that the molecular axes of the starch molecules are also arranged in this fashion. The amorphous regions are those where chain folding or multiple branching occur thus preventing the formation of the ordered polymer structures [37]. The areas of crystallinity in the various native starches comprise about 25-50 % of the total volume of the starch granules. In the tuber and root starches, only the amylopectin molecules constitute the crystalline structure. The amylose in these starches is present in the amorphous state and can be readily leached out preferentially from the granule. The amylopectin fraction is the most important element of crystalline structure in the cereal starches. A portion of the amylose molecules in the common cereal starches is present as a complex with fatty substances. This complex forms a weak crystalline structure and could be involved in the structural network of the granules. The amylose-fat complex provides some reinforcement of the cereal starch granules that could retard granule swelling [38].

4.6 Disruption of Starch Granule

Native starches are insoluble in water below their gelatinization temperature as such can be easily extracted from their plant source in aqueous system. Also, native starches can be chemically modified in water suspension and recovered in purified form by filtration, washing with water and then dried. Starch granules are insoluble in cold

water due to the hydrogen bonds formed either directly with the neighboring alcoholic OH groups of the individual starch molecules or indirectly via water bridges. The hydrogen bond forces though weak are so many in starch granules when they dissolve in cold water (10 -15 % increase in diameter). The granules shrink back to their original dimensions on drying. When starch granules are heated in water progressively to higher temperatures a point is reached where the polarization crosses starts to fade at the hilum and this rapidly extends to the periphery of the granule. Simultaneously, the granule starts to swell irreversibly. The term "gelatinization" is applied to this loss of polarization and concurrent initiation of swelling. The initial swelling takes place in the amorphous regions of the granule thus disrupting the weak bonding between the starch molecules and hydrating them. The tangential swelling disrupts the orderly radial organization of the micelles and the granule loses its polarization. As the temperature of the aqueous starch mixture rises more hydration occurs in the amorphous regions and the hydrogen bonds in the crystalline regions begin to be disrupted. The granules continue to expand to a greatly swollen reticulated network still held together by persistent micelles that have not been disrupted. Portions of the amylose molecules leach out into the aqueous substrate. The viscosity increases to a maximum, which corresponds to the largest hydrated swollen volume of the granules. Extensive swelling is associated with disruption of the crystalline areas. In the first stages of gelatinization, the shorter micelles dissociate followed by the longer micelles at higher temperatures. As heating and agitation of the mixtures continues, the swollen starch granules begin to rupture and collapse yielding a viscous colloidal dispersion of swollen granule fragments, hydrated starch aggregates and dissolves molecules [39, 40]. Gelatinization of starch granules in water is detected by the loss of their polarization crosses, increase in optical transmittances and rise in viscosity. Measurement of loss birefringence is the most sensitive, accurate and reproducible technique for measuring the gelatinization temperature of starch granules. Another procedure is the use of Kofler hot-stage microscope. Table 7 shows examples of Kofler and differential scanning calorimetry [41] gelatinization temperature ranges of various starches. The recorded temperatures correspond to the loss of birefringence by 5, 50 and 95 % of the granules [29, 42].

Table 7: Gelatinization characteristic of native starch

Starch	Kofler gelatinization temperature range (°C)	DSC gelatinization temperature range (°C)
Corn	62-67-72	70-89
Potato	56-63-68	57-87
Wheat	58-61-64	50-86
Tapioca	59-64-69	68-92
Waxy Maize	63-68-72	68-90
Sorghum	68-74-78	-
Rice	68-74-78	-
Sago	60-66-72	-

4.7 Swelling and Gelatinization of Starch

The properties of starch that has been gelatinized are related to factors such as size, proportion and kind of crystalline organization and ultra-structure of the starch granule. In its stable granular state, starch molecules exist as spherulites held together by Van der Waals' forces or hydrogen bonds. These granules exhibit a typical birefringence. Native starch granules swell when they absorb water through hydrogen bonding with their free hydroxyl groups but still retain their order and crystallinity [43]. As a first step in a majority of starch applications, the crystal structure of the granule is disrupted by gelatinization. Heating starch granules in water makes them to absorb water and swell. The birefringence properties of the granules are lost at the gelatinization temperature due to the irreversible breakdown of the hydrogen bonds and Van

der Waals' forces that maintain the spatial molecular relationships in the crystalline and amorphous regions [44, 45]. This kind of reaction destroys the crystallinity of starch progressively. Gelatinization is an irreversible order-disorder transition which involves the disruption of molecular organization within the starch granules upon heating in the presence of plasticizers [46]. The amorphous regions swell first leading to disruption of the radial organization, then the crystalline regions begin to disrupt, the granule still being held together. Some amylose will leach out into the water resulting in increase in viscosity until the largest hydrated swollen volume of the granules is reached. The swollen granules begin to rupture and then collapse [47, 48]. The viscous dispersion of granule fragments and dissolved molecules will finally become viscous starch solution as illustrated in Figure 7.

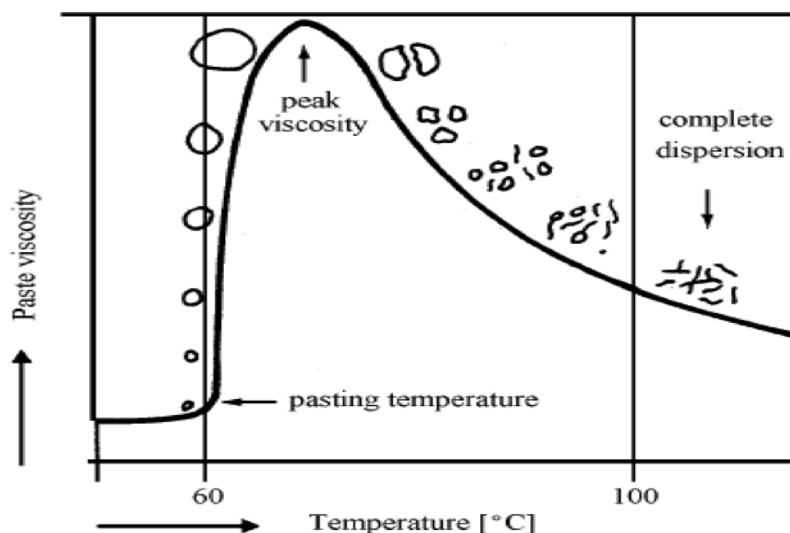


Figure 7: Swelling, disruption and dispersion of a starch granule during gelatinization

The process is irreversible and can be seen by the loss of birefringence of the starch granules which indicates that the crystalline structure of the starch has been disrupted. If the process of gelatinization is allowed to continue, pasting will occur. Pasting is said to occur when the largest percentage of granules are swollen, but still intact. This is known as peak viscosity when the mixture

reaches its maximum viscosity. During this process, amylose leaches out of the starch granules followed by the release of some amylopectin as heating continues. After pasting, the starch granules begin to breakdown causing an increase in the release of both amylose and amylopectin. At this point the structural integrity of the granules is lost [45, 49].

In summary, it can be concluded that starch phase transitions are three stage processes during which the following structural events take place:

1- Water absorbed by the starch granules facilitates increased starch polymer mobility in the amorphous regions.

2- Starch polymers in the amorphous regions rearrange and form new intermolecular interactions

3- Further increase in hydrothermal effects increases the polymers mobility, lost in intermolecular interactions and the overall granular structure.

The energy absorbed by granules not only melts crystallite structures during gelatinization but also facilitates "rearrangement" or formation of new bonds among molecules at lower temperatures before gelatinization [50].

5. DEVELOPMENT OF BIODEGRADABLE PACKAGING MATERIALS

The demand for plastic packaging increases based on good opportunity for both flexible and rigid packaging. Flexible packaging advances have been fueled by rapid growth of pouches and protective packaging. The rapidly expanding stand-up pouch segment enables flexible packaging to gain share in a number of rigid packaging applications. In rigid plastic packaging the best opportunities are anticipated for trays, tubs and cups. Plastics have gained a unique position in food packaging technology for a number of reasons which include:

- a) Higher strength, elongation and barrier properties against waterborne organisms
- b) Light and water resistance
- c) Low cost and energy effectiveness

Despite the continuous growth of polymer materials in food packaging applications, the visibility of plastics in the environment when discarded has triggered further research on plastic waste management. Estimates have shown that 2% of all plastics eventually reach the environment thus contributing considerably to ecological problems. The accumulation of plastic waste needs immediate solution. With the growing concern about environmental pollution, biodegradable plastics have been intensively studied in recent years. They have also been commercialized into products such as garbage bags, composting yard waste bags, grocery bags and agricultural mulches. The growing interest in biodegradable polymers was initiated over the past thirty years. It started off in the field of medicine and agriculture in the production of degradable fibers for sutures and mulch films and controlled pesticide release respectively. Biodegradable plastics are materials that can undergo a degradation process known as biodegradation. Biodegradation results in a change in the chemical structure of the plastic materials. The change is usually caused by the biological activity of microbes in the environment leading to naturally occurring metabolic end products [2, 51].

Biodegradable plastics are generally defined as plastics with similar properties to the conventional plastics but can be decomposed after disposal in the environment

by the activities of microorganisms. The end products produced are CO₂ and H₂O. Biodegradable plastics can be utilized in hygiene products, household goods, horticultural products, agriculture, medical products and many more. The biodegradable polymers are divided into two categories which are naturally occurring biodegradable polymers and the synthetic biodegradable polymers [7]. The naturally occurring polymers are polymers formed in nature during the growth cycles of all organisms. Their synthesis generally involves enzyme-catalyzed chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes. This type of polymers includes polysaccharides such as starch, cellulose, chitin/chitosan, pullulan, levan, konjac and elsinan. The basic units in these compounds are simple sugars such as glucose, fructose and maltose. Certain polyesters such as polyhydroxyalkanoates are also considered as naturally occurring biodegradable polymers. The synthetic biodegradable polymers are polymers with hydrolysable backbone or polymers that are sensitive to photo degradation e.g. poly (glycolic acid), poly (glycolic acid-co-lactic acid), polycaprolactone, polyether-polyurethane and poly (amide-enamide).

Biodegradable packaging covers all types of packaging materials such as rigid and semi rigid containers, flexible materials and foamed materials. In the rigid container applications, bottles are the most common package type but plastics are also widely used in tubs, tubes, drums, bins, trays and others shape. The flexible packaging includes wraps, pouches, bags, sacks, envelopes and similar packages. The foamed materials include cushioning. Plastics have become an essential everyday item with its use growing broadly in line with global economy. Thus, the state of the packaging industry is linked to the state of the world economy. As the world market for global packaging increased, the accumulation of waste also increased. Until recently, the majority of packaging plastics production was based on non-renewable materials [52, 53]. The use of polyolefin plastics in packaging applications is commonplace because these materials are inexpensive, easy to fabricate, have good barrier properties, hydrophobic and are available with a wide range of physical and mechanical properties. The various polyethylene, polypropylene, blends and copolymers of them plus polystyrene collectively account for more production than all the other packaging plastics combined because of this versatility and on the basis of cost/benefit analysis. Also, carrier bags made of HDPE, trash bags made of LDPE, clear films of LDPE for food wrapping and clear clothing bags made of oriented polypropylene are few examples of many that can be cited. To replace the traditional plastics with the biodegradable polymers in packaging, the polymers have to meet the following: be inexpensive, light, strong, tough, flexible, impact resistance, easy to fabricate, inert, recyclable, high wet strength, safe during use and after disposal. More specific characteristics arise from specific uses such as safe for food contact, durable in outdoor applications (a year or more). Plastics packaging may be required to be transparent in order to display the goods contained in it or

opaque in the case of garbage bags. Most packaging protects the contents from mechanical damage as such have significantly reduced waste through breakage. Besides that, plastics packaging should have good barrier properties against permeation by water and water-borne microbes. To produce biodegradable polymers, the conventional plastics have been blended with starch which initiates slow disintegration of the product in nature. Although the incorporation of starch as an additive in synthetic plastic is slightly attractive, the overall degradability of the final polymer is questionable. Another alternative to produce the biodegradable polymers is derived from synthetic or natural materials or blends of both [54, 55].

The first high-profile biodegradable plastic used in packaging is polyhydroxybutyrate-valerate (PHBV). It is a natural polyester copolymer produced by certain bacteria. Despite its similar properties with polypropylene, PHBV was shortly used in Europe for shampoo bottles due to its high cost. The utilization of 100 % starch for truly biodegradable plastics has received considerable attention during the past two decades due to its renewability, low cost, availability, and easy chemical and mechanical modification. In many packaging applications, starch is used as thermoplastic starch (TPS). TPS is a relatively new concept and considered one of the main research hints for the manufacturing. Starch becomes thermoplastic in the presence of hydroxyl-rich plasticizers such as glycerol and water. At high temperatures (90 – 180°C) and shearing, starch melts and fluidizes thus enabling its use in injection, extrusion and blowing equipment [56]. To obtain a thermoplastic starch, it is necessary that the starch maintains its semi-crystal granular structure. The starch also has to behave in a similar way like that of a melted thermoplastic obtained through mono- or twin-screw extrusion. The incorporation of plasticizing agents such as glycerol and water can lower the glass transition temperature and melting temperature of the starch. Starch alone is a poor choice as replacement for plastics because of its poor mechanical properties and high water susceptibility. Recently, one of the most promising new generation biodegradable plastics is based on polylactic acid (PLA). PLA has become the predominant biopolymer in the market for packaging applications. The food and drug administration approved the use of PLA in fabricating articles that will have contact with food. Currently, PLA is being commercialized and used as food-packaging polymer for short shelf-life products such as containers, drinking cups, salad and sundry cups, and overwrap and lamination film. Pure PLA can degrade to carbon dioxide, water and methane in the environment over a period of several months to tow years as compared to other petroleum-based plastics which need 500 – 1000 years. However, the low deformation at break and high price of PLA limit its applications [57-59].

6. POLYMER BIO-BLENDS BASED ON THERMOPLASTIC STARCH

Research on biodegradable plastics based on starch started in the year 1970. Starch was then added to

plastics mainly to increase the rate of biodegradation of the plastic products. The blends of polymers with additives that are readily consumed by microorganisms e.g. polyethylene and starch are considered biodegradable materials [51]. Starch satisfies the requirements of adequate thermal stability, minimum interference with melt properties and disturbance of product quality. The extensive search for potential biodegradable fillers for thermoplastics led to the discovery of starch as a cost effective additive. Bio-composites based on starch have been prepared using extrusion method with the addition of processing aid to enhance the compatibility of the raw blended materials [12]. Many studies on the utilization of starch in conventional plastics especially LDPE have been conducted. LDPE/rice and potato starch film have been prepared by varying the starch and water content. The mechanical, water vapor transmission rate (WVTR) and gas permeability (GP) properties of the films were investigated. High starch contents promoted brittleness, which resulted in low tensile strength and modulus but high GP and WVTR. The blends with increased water content exhibited improved percentage elongation. This was attributed to the water plasticization of the composite matrix. The degradation of samples that were tested by immersion in bioreactors and burial in soil showed a substantial decrease in mechanical strength, tensile and flexural modulus and percentage elongation [4]. A reactive blend of LLDPE/corn starch with anhydride functional polymer was prepared using maleic anhydride as a cross-linker. Maleic anhydride (MA) was grafted onto LLDPE in xylene using dicumyl peroxide. The blending of MA-g-LLDPE/corn starch was carried out in a torque rheometer. Several methods have been used to processed blends of LDPE/corn starch [1, 68,69].

Numerous studies have shown that the addition of dry starch granules (GS) to low density polyethylene (LDPE) follows the general trend of filler effects on the polymer properties. The modulus increased due to the stiffening effect of the GS and elongation decreased as the starch content is increased [60, 61]. Ductile films have been prepared with low starch loading, but the films became paper-like when the starch content exceeded 15%. As observed in mineral fillers, the addition of GS to PE results in severe reduction of the tensile strength (TS) and elongation at break (Eb) while the elastic modulus (E) increases. However, the improvement of TS and Eb can be achieved through modification of the non-polar polyolefin and the polar granular starch interface [51].

Otey and co-workers developed granular starch/acrylic acid copolymer (GS/EAA) cast films, which had good transparency, flexibility and mechanical properties. The blown films of the GS/EAA blends compounded with LDPE and polyvinyl alcohol (PVOH) were extruded in a further step. The addition of LDPE led to the reduction of both TS and Eb. However, incorporating PVOH increased the Eb of the starch-based films [62, 63]. The addition of a plasticizer such as glycerol can further improve the ductility of GS. Reports have shown that mixtures of TPS with other polymers have the potential to

behave in a manner similar to the conventional polymer-polymer blends. The melt blending of TPS has been studied with polyethylene and biodegradable polyesters such as polycaprolactone, polyesteramide, polylactic acid, poly(butylene adipate-co-terephthalate), poly(butylene succinate adipate and poly(hydroxy ester ether). The tensile properties of these blends decreased significantly as TPS content increased. The E_b is the property most adversely affected by the presence of TPS particles. Typically, ductile polymers such as polyethylene and polycaprolactone become fragile when 20–30 wt% TPS is added to them [64, 65].

Erlanson and his colleagues compared the susceptibility of pure LDPE, LDPE mixed with starch and LDPE mixed with starch and pro-oxidant manganese stearate (MB); LDPE/MB to thermo and photo-oxidation. They found that LDPE/MB is more susceptible to thermal degradation and photodegradation as compared to the other two materials. At any appreciable rate, the reduction in molecular weight of the material took place before the material degrades. This was attributed to the pro-oxidant, which promotes photo-oxidation on PE chain, thus reducing the molecular weight of the PE chain followed by cleavage [66, 67]. Various properties of starch based LDPE matrix film such as physico-mechanical, optical, morphological. Baldev et al studied thermal and biodegradation. They employed solution blending followed by thermo press and extrusion methods to prepare the films. For the solution cast LDPE/starch films, tensile strength and elongation at break decreased gradually to about 63.6% deviation and 84.6% deviation respectively as starch concentration increased.

The extruded films however showed better mechanical properties as compared to those of thermo-pressed films due to unidirectional molecular alignment. The reduction in percent transmittance and increase haze with starch addition were mainly due to the scattering of light radiation by the starch particles. Another reason for the drop in transmittance is because LDPE/starch is an immiscible blend. The rate of biodegradation of the LDPE/starch films also depends on the starch content. The melt temperature and crystallization temperature did not change due to the presence of starch and there was gradual decrease in enthalpy due to the decreasing concentration of LDPE in the LDPE/starch system. The images of Scanning Electron Microscopy (SEM) indicated that LDPE/starch systems have two-phase morphology. The extruded films

had layer like structures with uniform dispersion of starch in the LDPE matrix [68]. Also, biodegradable composites of low-density polyethylene films have been prepared based on cassava mesocarp carbohydrate and its modified form as fillers. The tensile strength of the films decreased with increase in the amount of the filler incorporated. The modification of the cassava mesocarp carbohydrate enhanced the compatibility of the blend by reducing the variance in the hydrophobicity [69].

Various plasticizers from monohydroxyl alcohol and glycol group have been used as plasticizer together with cornstarch to obtain thermoplastic starch via melts processing technique. The quantity and type of plasticizer did not affect appreciably the crystallinity of the processed samples but influenced the mechanical properties of the TPS in two opposite ways i.e. softening effect due to plasticizing of the amorphous phase and stiffening due to antiplasticization effect. Monohydroxyl alcohols and the higher molecular weight glycols are not suitable to plasticize starch as compared to the short glycols and sorbitol [70].

The mechanical properties of compression-molded starches with glass temperature below room temperature are strongly dependent on the water content of the compound. Varying the water content of the compound will lead to a large change in strain and stress at break. Also, the mechanical properties of the blends are dependent on starch source, the composition of the native starch and the structure of the constituting polysaccharide [71].

The use of urea and formamide as mixed plasticizer for thermoplastic wheat flour has been investigated. The scanning electron microscopy showed that the wheat flour granules transfer to a continuous phase as displayed in Figure 8. The thermoplastic starch with low plasticizer content had relatively good water-resistant. Thermoplastic starch with 30 % plasticizer weight had relatively good mechanical properties [72]. Plasticizer containing amide groups for thermoplastic starch (TPS) has been used to suppress the retrogradation of TPS. The formamide plasticize TPS had good flexibility at over a wide range of water contents. The strains of the urea plasticized TPS increased up to 65 % at high water content (42 %). A small percent of urea could react with starch at the given TPS processing conditions [73].

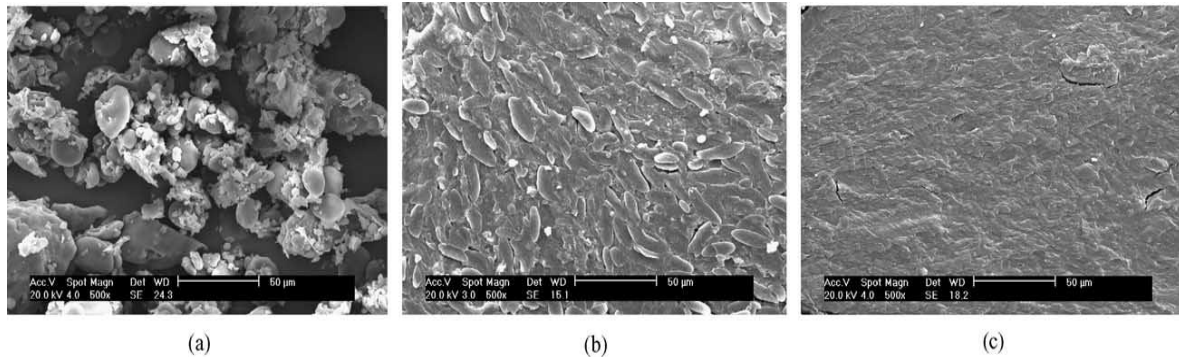


Figure 8: SEM micrograph of native wheat flour granules (a) and the fracture face of TPF containing 25% (b) and 30% (c) weight content of plasticizer.

Enrione and co-workers studied the sorption behavior of mixtures of glycerol and starch. Waxy maize starch, rice and wheat starch were thermo mechanically extruded in the presence of glycerol and hermetically packed, quenched in liquid nitrogen, freeze dried, ground and sieved to certain particle diameter. The sorption isotherms of samples were ascertained using dynamic vapor sorption. The Brunaur-Emmet-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) model showed a significantly higher monolayer for waxy maize starch than for rice and wheat. When glycerol was added during extrusion, each starch showed relative humidity below 60 %. The presence of glycerol decreased the equilibrium of moisture content. The low monolayer and temperature dependent constant values from BET and GAB suggest that fewer sorption sites are available for water molecules and hence the reduction in the heat sorption of the monolayer [74]. Huang and co-workers studied ethanolamine as plasticizer and observed that it yields thermoplastic starch material with better properties as compared to glycerol. They reported that ethanolamine plasticized thermoplastic starch successfully restrained the re-crystallization of traditional thermoplastic starch plasticized by glycerol which was proved by XRD. The mechanical properties of ethanolamine plasticized starch such as Young's modulus, breaking energy and water absorption improve. However, the thermograms of Differential Scanning Calorimetry [41] and Thermal Gravimetric Analysis (TGA) showed quite similar profiles between ethanolamine and glycerol

plasticized starch [75]. Shi et al prepared soft rubbery glycerol plasticized thermoplastic starch for soft tissue engineering application by plasticizing the cornstarch with high glycerol content. The XRD results suggest that high glycerol content promotes formation of single V-type helical structure but inhibits B-type double helix structure as shown in Figure 9. DMTA measurement showed that the onset temperature of the upper transition thermoplastic starch with less glycerol content increased more quickly than that of the high glycerol content. The stress-strain measurement exhibited slow change when the glycerol content was over 40 wt%. The FTIR showed decrease in peak of the hydroxyl group stretching as glycerol content increased. They concluded that the high glycerol content could prevent ageing effectively [76]. In another study, Shi et al reported the characterization of citric acid and glycerol co-plasticized thermoplastic starch prepared by melt blending. The one part of citric acid that reacted with starch was considered as internal plasticizer while the other part of citric acid played a role as an external plasticizer. The carboxyl groups in the citric acid changed the properties of the materials and also supply the potential reactive points for grafting and cross-linking modification. The intrinsic viscosity measurement, laser light scattering and FTIR showed that the molecular weight of starch decreased as the citric acid percentage increased. They also found that citric acid enhanced the thermal stability of the material, changed the crystal type and reduced the crystallinity as compared to glycerol thermoplastic starch[77].

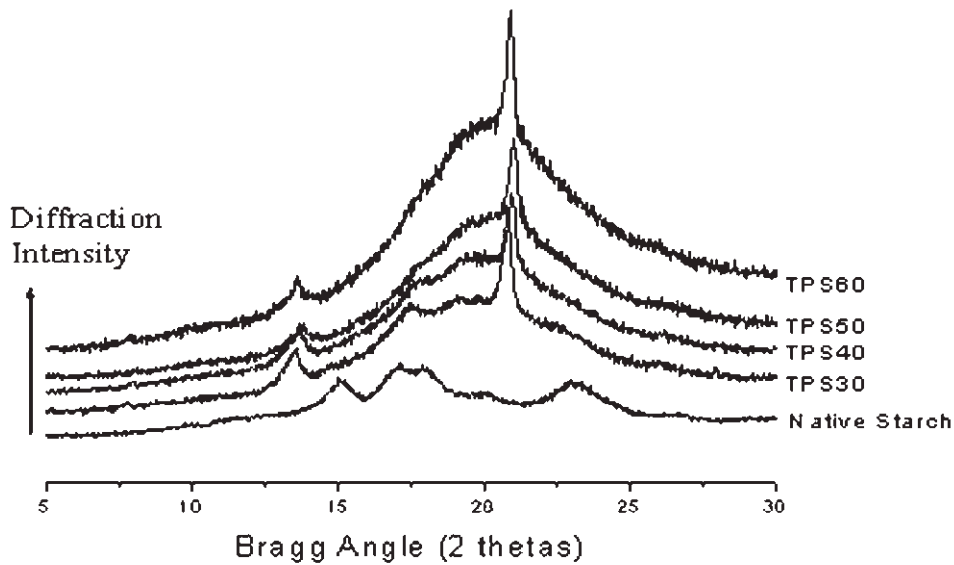


Figure 9: XRD diffractogram of native starch and glycerol-plasticized thermoplastic starch with different glycerol content within 24 h after preparation.

Teixeira and his colleagues studied the effect of glycerol/sugar/water and sugar/water mixtures on the plasticization of thermoplastic tapioca starch. The reported that the addition of 2 wt% sugar to starch-glycerol system causes reduction in the glass transition temperature (T_g). The storage modulus also reduced as such inhibits the formation of V_H -type crystal structures in the resulting TPS. The use of only sugar and water as plasticizers in the TPS caused considerable reduction in the subsequent water uptake [78]. Córdoba and co-workers studied the plasticizing effect of alginate on thermoplastic starch/glycerin blends. Cornstarch and cornstarch alginate were used to produce thermoplastic starch without water. Their finding proved that addition of alginate to thermoplastic cornstarch caused plasticizing effect and a significant decrease in plasticization energy when the alginate content was increased from 0 % to 15%. The glass transition temperature decreased by 20 °C when the alginate content was increased [79]. The difference in physical properties of wheat starch and wheat flour based thermoplastic starch using thermogravimetric, calorimetric, X-ray diffraction, Leblanc et al carried out mechanical and morphological analyses. They observed that there was no significant difference between the wheat flour based and wheat starch based materials. However, there was one clear difference for the strain to break value that decreased by about 30 % for the wheat flour based materials [80].

The cross linking method has recently been used to improve compatibility between starch molecules and polyolefin using maleic anhydride as compatibilizer. Anhydride groups can react with hydroxyl groups in starch to produce chemical bonding and improve dispersion of the starch interfacial adhesion and subsequently the mechanical properties of the resultant blends. Liu and his colleagues investigated the effect of polyethylene grafted maleic anhydride (PE-g-MA) on the thermal, morphological and

tensile properties of blends of low-density polyethylene and cornstarch. The results indicated that the miscibility between granular corn starch and LDPE improved when PE-g-MA compatibilizer was added. The improved miscibility was attributed to the chemical reaction between the hydroxyl groups in starch and anhydride groups in PE-g-MA and also the physical interaction between PE-g-MA and LDPE. They also showed that it is possible to produce a biofilm blend with high percentage of granular cornstarch with LDPE while keeping comparable tensile properties [81]. Wattanachant and co-workers studied the effect of cross linking reagent and propylene oxide levels for the preparation of hydroxypropylated cross-linked sago starch with good thickening properties such as non-gelling, resistant to heat, acid and shear and good stability at low temperatures. The mixture of phosphate salts at 2% sodium trimetaphosphate and 5% sodium tripolyphosphate is more efficient in cross-linking than phosphorus oxychloride or epichlorohydrin for preparing the hydroxypropylation-cross linked sago starch. Greatly altered sago starch is obtained by hydroxypropylation with 10–12% propylene oxide, followed by cross linking with a mixture of 2% sodium trimetaphosphate and 5% sodium tripolyphosphate [82].

CONCLUSION

Bio-blends based on starch are eco-friendly class of materials, which can be used sufficiently as food packaging. The incorporation of starch materials in the backing based materials enhances the mechanical and biodegradation properties of the materials and lead to make the blends environmentally friendly biomaterials.

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