MECHANICAL AND THERMAL PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE) COMPOSITES WITH THERMOPLASTIC STARCH AND STARCH DICARBOXYLIC ACID

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BY

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DECLARATION

I declare that the work in this dissertation entitled 'Mechanical and thermal properties of low density polyethylene (LDPE) composites with thermoplastic starch and starch dicarboxylic acid' has been carried out by me in the Department of Textile Science and Technology, Ahmadu Bello University, Zaria, Nigeria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other University.

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Name of Student _____ Signature _____ Date

CERTIFICATION

This dissertation entitled MECHANICAL AND THERMAL PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE) COMPOSITES WITH THERMOPLASTIC STARCH AND STARCH DICARBOXYLIC ACID by MUHAMMAD BUKHARI MUSA meets the regulations governing the award of the degree of doctor of philosophy (Polymer and fibre Technology) of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

The Mechanical and thermal properties of low density polyethylene (LDPE) composites with thermoplastic starch and starch dicarboxylic acid have been studied. Thermoplastic starch (TPS) and Starch dicarboxylic acid compound (SDCA) were prepared from potato starch. These modified starches indicated reduced crystallinity and better thermal stability as compared to native starch. The complexation of the plasticizer with the starch also resulted in a shift of the O-H and C-H bands on the FT-IR spectra indicating replacement of Hydroxyl bonds between the starch polymer chains with weaker hydrogen bonds between the starch and the plasticizer. The FT-IR spectrum of the starch dicarboxylic acid compound suggested partial ester formation between the starch and the dicarboxylic acid. The SEM micrographs of the TPS showed the broken down of the polygonal shaped granules of the starch to patches of various sizes, but on the SDCA micrograph, the starch granules appeared swollen which could be attributed to the gelatinizing action of the dicarboxylic acid on the starch granules. The modified starch obtained were each melt blended with low density polyethylene to obtain LDPE/TPS and LDPE/SDCA composites. Various investigations suggested immiscibility between the composite components i.e the LDPE (matrix) and the TPS or SDCA as fillers. It was shown that the complexation of the LDPE with the TPS/SDCA has taken place on the amorphous region and therefore the crystalline region is not affected. These composites have slightly better thermal stability as compared to LDPE, but their mechanical properties were not so good. The water absorbency studies indicated that LDPE/SDCA composites are more susceptible to water attack than the LDPE/TPS, similarly the biodegradation studies revealed that the LDPE/SDCA composite are more prone to soil degradation as compared to the LDPE/TPS composites.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
BMC	Bulk molding compound
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EP	Epoxy
FT – IR	Fourier transform infrared spectroscopy
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear Low density polyethylene
MDPE	Medium density polyethylene
MF	Melamine – formaldehyde
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
PEX	Cross linked polyethylene
PMMA	Polymethyl methacrylate

Pp	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RIM	Reaction Injection molding
SDCA	Starch – dicarboxylic Acid compound

LIST OF ABBREVIATIONS

SEM	Scanning electron microscopy
SMC	Sheet molding compound
STA	Starch
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPS	Thermoplastic Starch
UF	Urea – formaldehyde
UP	Unsaturated polyester
WAXD	Wide angle X – ray diffraction
XLPE	Cross linked polyethylene
XRD	X – ray diffraction

CHAPTER ONE

INTRODUCTION

1.1 PLASTIC

A plastic material is any of a wide range of synthetic or semi-synthetic organic solids that are moldable. Plastics are typically organic polymers of high molecular mass, but they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals, but many are partially natural.

Almost invariably, organic polymers mainly comprise plastics. The vast majority of these polymers are based on chains of carbon atoms alone or with oxygen, sulfur, or nitrogen as well. The backbone is that part of the chain on the main "path" linking a large number of repeat units together. To customize the properties of a plastic, different molecular groups "hang" from the backbone (usually they are "hung" as part of the monomers before linking monomers together to form the polymer chain). The structure of these "side chains" influence the properties of the polymer. This fine tuning of the properties of the polymer by repeating unit's molecular structure has allowed plastics to become an indispensable part of the twenty-first century world.

Most plastics contain other organic or inorganic compounds blended in. The amount of additives ranges from zero percentage for polymers used to wrap foods to more than 50% for certain electronic applications. The average content of additives is 20% by weight of the polymer. Fillers improve performance and/or reduce production costs. Stabilizing additives include fire retardants to lower the flammability of the material. Many plastics contain fillers, relatively inert and inexpensive materials that make the product cheaper

by weight. Typically fillers are mineral in origin, e.g., chalk. Some fillers are more chemically active and are called reinforcing agents. Since many organic polymers are too rigid for particular applications, they are blended with plasticizers, oily compounds that confer improved rheology. Colourants are of course common additives, although their weight contribution is small. Many of the controversies associated with plastics are associated with the additives.

1.1.1GENERAL PROPERTIES OF PLASTICS

Plastics possess a wide variety of useful properties and are relatively inexpensive to produce. They are lighter than many materials of comparable strength, and unlike metals and wood, plastics do not rust or rot. Most plastics can be produced in any color. They can also be manufactured as clear as glass, translucent (transmitting small amounts of light), or opaque (impenetrable to light).

Plastics have a lower density than that of metals, so plastics are lighter. Most plastics vary in density from 0.9 to 2.2 g/cm^3 (0.45 to 1.5 oz/cu in), compared to steel's density of 7.85 g/cm^3 (5.29 oz/cu in). Plastic can also be reinforced with glass and other fibers to form incredibly strong materials. For example, nylon reinforced with glass can have a tensile strength (resistance of a material to being elongated or pulled apart) of up to 165 Mega Pascal (24,000 psi). Plastics have some disadvantages, when burned, some plastics produce poisonous fumes. Although certain plastics are specifically designed to withstand temperatures as high as 288° C (550° F), in general plastics are not used when high heat resistance is needed. Because of their molecular stability, plastics do not easily

break down into simpler components. As a result, disposal of plastics creates a solid waste problem(Richardson, 2009).

1.1.2 Classification

1.1.2.1 Thermoplastics and thermosetting polymers

All plastics, whether made by addition or step – growth polymerization, can be divided into two groups: thermoplastics and thermosetting plastics. These terms refer to the different ways these types of plastics respond to heat. Thermoplastics can be repeatedly softened by heating and hardened by cooling. Thermosetting plastics, on the other hand, harden permanently after being heated once. The reason for the difference in response to heat between thermoplastics and thermosetting plastics lies in the chemical structures of the plastics. Thermoplastic molecules, which are linear or slightly branched, do not chemically bond with each other when heated. Instead, thermoplastic chains are held together by weak van der Waals forces (weak attractions between the molecules) that cause the long molecular chains to clump together like piles of entangled spaghetti. Thermoplastics can be heated and cooled, and consequently softened and hardened, repeatedly, like candle wax. For this reason, thermoplastics can be remolded and reused almost indefinitely. Examples include polyethylene, polypropylene, polystyrene, polyvinyl chloride, and polytetrafluoroethylene (PTFE).

Thermosetting plastics consist of chain molecules that chemically bond, or cross-link, with each other when heated. When thermosetting plastics cross-link, the molecules create a permanent, three-dimensional network that can be considered one giant molecule. Once cured, thermosetting plastics cannot be remelted, in the same way that

cured concrete cannot be reset. Consequently, thermosetting plastics are often used to make heat-resistant products, because these plastics can be heated to temperatures of 260° C (500° F) without melting. The vulcanization of rubber is a thermosetting process. Before heating with sulfur, the polyisoprene is a tacky, slightly runny material, but after vulcanization the product is rigid and non-tacky as the case for vehicle tires, conveyor belts, pump housings and piping used in the handling of abrasive sludges etc.

The different molecular structures of thermoplastics and thermosetting plastics allow manufacturers to customize the properties of commercial plastics for specific applications. Because thermoplastic materials consist of individual molecules, properties of thermoplastics are largely influenced by molecular weight. For instance, increasing the molecular weight of a thermoplastic material increases its tensile strength, impact strength, and fatigue strength (ability of a material to withstand constant stress). Conversely, because thermosetting plastics consist of a single molecular network, molecular weight does not significantly influence the properties of these plastics. Instead, many properties of thermosetting plastics are determined by adding different types and amounts of fillers and reinforcements, such as glass fibers(Richardson, 2009).

1.1.2.2 Other classifications

Other classifications are based on qualities that are relevant for manufacturing or product design. Examples of such classes are the thermoplastic and thermoset, elastomer, structural, biodegradable, and electrically conductive. Plastics can also be classified by various physical properties, such as density, tensile strength, glass transition temperature, and resistance to various chemical products.

1.1.2.2.1 Biodegradable Plastics

Due to their molecular stability, plastics do not easily break down into simpler components. Plastics are therefore not considered biodegradable. However, researches are going on to develop biodegradable plastics that will disintegrate upon exposure to sunlight (e.g., ultra-violet radiation), water or dampness, bacteria, enzymes, wind abrasion, and in some instances rodent pest or insect attack are also included as forms of biodegradation or environmental degradation. Some modes of degradation require that the plastic be exposed at the surface, whereas other modes will only be effective if certain conditions exist in landfill or composting systems.

Biodegradable polymers may thus be defined as those which undergo microbially induced chain scission leading to photodegradation, oxidation, and hydrolysis, which can alter the polymer during the degradation process. The biopolymers may be obtained from renewable resources and also can be synthesized from petroleum – based chemicals. Blending of two or more biopolymers can produce a new biopolymer designed for specific requirements(Mohanty et al, 2005).

1.1.2.2.2 Natural and synthetic plastics

Most plastics are produced from petrochemicals. Motivated by the finiteness of petrochemical reserves and possibility of global warming, bioplastics are being developed. Bioplastics are made substantially from renewable plant materials such as cellulose and starch.

1.1.2.2.3 Crystalline vs amorphous

Some plastics are partially crystalline and partially amorphous in molecular structure, giving them both a melting point (the temperature at which the attractive intermolecular forces are overcome) and one or more glass transitions (temperatures above which the extent of localized molecular flexibility is substantially increased). The so-called semi-crystalline plastics include polyethylene, polypropylene, poly (vinyl chloride), polyamides (nylons), polyesters and some polyurethanes. Many plastics are completely amorphous, such as polystyrene and its copolymers, poly (methyl methacrylate), and all thermosets.

1.1.3 Processing of Plastics

The process of forming plastic resins into plastic products is the basis of the plastics industry. Many different processes are used to make plastic products, and in each process, the plastic resin must be softened or sufficiently liquefied to be shaped. Although some processes are used to manufacture both thermoplastics and thermosetting plastics, certain processes are specific to forming thermoplastics.

1.1.3.1 Injection Molding

Injection molding uses a piston or screw to force plastic resin through a heated tube into a mold, where the plastic cools and hardens to the shape of the mold. The mold is then opened and the plastic cast removed. Thermoplastic items made by injection molding include toys, combs, car grills, and various containers

1.1.3.2 Extrusion

Extrusion is a continuous process, as opposed to all other plastic production processes, which start over at the beginning of the process after each new part is removed from the mold. In the extrusion process, plastic pellets are first heated in a long barrel. In a manner similar to that of a pasta-making or sausage-stuffing machine, a rotating screw then forces the heated plastic through a die (device used for forming material) opening of the desired shape. As the continuous plastic form emerges from the die opening, it is cooled and solidified, and the continuous plastic form is then cut to the desired length. Plastic products made by extrusion include garden hoses, drinking straws, pipes, and ropes. Melted thermoplastic forced through extremely fine die holes can be cooled and woven into fabrics for clothes, curtains, and carpets.

1.1.3.3 Blow molding

Blow molding is used to form bottles and other containers from soft, hollow thermoplastic tubes. First a mold is fitted around the outside of the softened thermoplastic tube, and then the tube is heated. Next, air is blown into the softened tube (similar to inflating a balloon), which forces the outside of the softened tube to conform to the inside walls of the mold. Once the plastic cools, the mold is opened and the newly molded container is removed. Blow molding is used to make many plastic containers, including soft-drink bottles, jars, detergent bottles, and storage drums.

1.1.3.4 Blow Film Extrusion

Blow Film Extrusion is the process used to make plastic garbage bags and continuous sheets. This process works by extruding a hollow, sealed-end thermoplastic tube through a die opening. As the flattened plastic tube emerges from the die opening, air is blown inside the hollow tube to stretch and thin the tube (like a balloon being inflated) to the desired size and wall thickness. The plastic is then air-cooled and pulled away on take-up rollers to a heat-sealing operation. The heat-sealer cuts and seals one end of the thinned, flattened thermoplastic tube, creating various bag lengths for products such as plastic grocery and garbage bags. For sheeting (flat film), the thinned plastic tube is slit along one side and opened to form a continuous sheet.

1.1.3.5 Calendering process

The calendering process forms continuous plastic sheets that are used to make flooring, wall siding, tape, and other products. These plastic sheets are made by forcing hot thermoplastic resin between heated rollers called calenders. A series of secondary calenders further thins the plastic sheets. Paper, cloth, and other plastics may be pressed between layers of calendered plastic to make items such as credit cards, playing cards, and wallpaper.

1.1.3.6 Thermoforming

Thermoforming is a term used to describe several techniques for making products from plastic sheets. Products made from thermoformed sheets include trays, signs, briefcase shells, refrigerator door liners, and packages. In a vacuum-forming

process, hot thermoplastic sheets are draped over a mold. Air is removed from between the mold and the hot plastic, which creates a vacuum that draws the plastic into the cavities of the mold. When the plastic cools, the molded product is removed. In the pressure-forming process, compressed air is used to drive a hot plastic sheet into the cavities and depressions of a concave, or female, mold. Vent holes in the bottom of the mold allow trapped air to escape.

1.1.3.7 Thermosetting plastics

Thermosetting plastics are manufactured by several methods that use heat or pressure to induce polymer molecules to bond, or cross-link, into typically hard and durable products.

1.1.3.7.1 Compression molding

Compression molding forms plastics through a technique that is similar to the way a waffle iron forms waffles from batter. First, thermosetting resin is placed into a steel mold. The application of heat and pressure, which accelerate cross-linking of the resin, softens the material and squeezes it into all parts of the mold to form the desired shape. Once the material has cooled and hardened, the newly formed object is removed from the mold. This process creates hard, heat-resistant plastic products, including dinnerware, telephones, television set frames, and electrical parts.

1.1.3.7.2 Laminating

The laminating process binds layers of materials, such as textiles and paper, together in a plastic matrix. This process is similar to the process of joining sheets of wood to make plywood. Resin-impregnated layers of textiles or paper are stacked on hot plates, then

squeezed and fused together by heat and pressure, which causes the polymer molecules to cross-link. The best-known laminate trade name is Formica, which is a product consisting of resin-impregnated layers of paper with decorative patterns such as wood grain, marble, and colored designs. Formica is often used as a surface finish for furniture, and kitchen and bathroom countertops. Thermosetting resins known as melamine and phenolic resins form the plastic matrix for Formica and other laminates. Electric circuit boards are also laminated from resin-impregnated paper, fabric, and glass fibers.

1.1.3.7.3 Reaction Injection Molding (RIM)

Strong, sizable, and durable plastic products such as automobile body panels, skis, and business machine housings are formed by reaction injection molding. In this process, liquid thermosetting resin is combined with a curing agent (a chemical that causes the polymer molecules to cross-link) and injected into a mold. Most products made by reaction injection molding are made from polyurethane.

1.1. 3.7.4 Forming both types of Plastics

Certain plastic fabrication processes can be used to form either thermoplastics or thermosetting plastics.

1.1.3.7.5 Casting

The casting process is similar to that of molding plaster or cement. Fluid thermosetting or thermoplastic resin is poured into a mold, and additives cause the resin to solidify. Photographic film is made by pouring a fluid solution of resin onto a highly polished

metal belt. A thin plastic film remains as the solution evaporates. The casting process is also used to make furniture parts, tabletops, sinks, and acrylic window sheets.

1.1.3.7.6. Expansion Processes

Thermosetting and thermoplastic resins can be expanded by injecting gases (often nitrogen or methyl chloride) into the plastic melt. As the resin cools, tiny bubbles of gas are trapped inside, forming a cellular plastic structure. This process is used to make foam products such as cushions, pillows, sponges, egg cartons, and polystyrene cups.

Foam plastics can be classified according to their bubble, or cell, structure. Sponges and carpet pads are examples of open-celled foam plastics, in which the bubbles are interconnected. Flotation devices are examples of closed-celled foam plastics, in which the bubbles are sealed like tiny balloons. Foam plastics can also be classified by density (ratio of plastic to cells), by the type of plastic resin used, and by flexibility (rigid or flexible foam). For example, rigid, closed-celled polyurethane plastics make excellent insulation for refrigerators and freezers.

1.1.4 IMPORTANT TYPES OF PLASTICS

A wide variety of both thermoplastics and thermosetting plastics are manufactured. These plastics have a spectrum of properties that are derived from their chemical compositions. As a result, manufactured plastics can be used in applications ranging from contact lenses to jet body components.

1.1.4.1 Thermoplastics

Thermoplastic materials are in high demand because they can be repeatedly softened and remolded. The most commonly manufactured thermoplastics are presented in this section in order of decreasing volume of production.

1.1.4.1.1. Polyethylene

Polyethylene (PE) resins are milky white, translucent substances derived from ethylene (CH_2=CH_2). Polyethylene, with the chemical formula $[-CH_2-CH_2-]_n$ (where *n* denotes that the chemical formula inside the brackets repeats itself to form the plastic molecule) is made in low- and high-density forms. Low-density polyethylene (LDPE) has a density ranging from 0.91 to 0.93 g/cm3 (0.60 to 0.61 oz/cu in). The molecules of LDPE have a carbon backbone with side groups of four to six carbon atoms attached randomly along the main backbone. LDPE is the most widely used of all plastics, because it is inexpensive, flexible, extremely tough, and chemically resistant. LDPE is molded into bottles, garment bags, frozen food packages, and plastic toys. High-density polyethylene (HDPE) has a density that ranges from 0.94 to 0.97 g/cm3 (0.62 to 0.64 oz/cu in). Its molecules have an extremely long carbon backbone with no side groups. As a result, these molecules align into more compact arrangements, accounting for the higher density of HDPE. HDPE is stiffer, stronger, and less translucent than low-density polyethylene. HDPE is formed into grocery bags, car fuel tanks, packaging, and piping.

1.1.4.1.2. Polyvinyl Chloride

Polyvinyl chloride (PVC) is prepared from the organic compound vinyl chloride (CH_2=CHCl). PVC is the most widely used of the amorphous plastics. PVC is lightweight, durable, and waterproof. Chlorine atoms bonded to the carbon backbone of its molecules give PVC its hard and flame-resistant properties.

In its rigid form, PVC is weather-resistant and is extruded into pipe, house siding, and gutters. Rigid PVC is also blow molded into clear bottles and is used to form other consumer products, including compact discs and computer casings. PVC can be softened with certain chemicals. This softened form of PVC is used to make shrink-wrap, food packaging, rainwear, shoe soles, shampoo containers, floor tile, gloves, upholstery, and other products. Most softened PVC plastic products are manufactured by extrusion, injection molding, or casting.

1.1.4.1.3. Polypropylene

Polypropylene is polymerized from the organic compound propylene (CH_3-CH=CH_2) and has a methyl group (-CH_3) branching off of every other carbon along the molecular backbone. Because the most common form of polypropylene has the methyl groups all on one side of the carbon backbone, polypropylene molecules tend to be highly aligned and compact, giving this thermoplastic the properties of durability and chemical resistance. Many polypropylene products, such as rope, fiber, luggage, carpet, and packaging film, are formed by injection molding.

1.1.4.1.4. Polystyrene

Polystyrene, produced from styrene ($C_6H_5CH=CH_2$), has phenyl groups (six-member carbon ring) attached in random locations along the carbon backbone of the molecule. The random attachment of benzene prevents the molecules from becoming highly aligned. As a result, polystyrene is an amorphous, transparent, and somewhat brittle plastic. Polystyrene is widely used because of its rigidity and superior insulation properties. Polystyrene can undergo all thermoplastic processes to form products such as toys, utensils, display boxes, model aircraft kits, and ballpoint pen barrels. Polystyrene is also expanded into foam plastics such as packaging materials, egg cartons, flotation devices, and styrofoam.

1.1.4.1.5. Polyethylene Terephthalate

Polyethylene terephthalate (PET) is formed from the reaction of terephthalic acid ($HOOC\text{-}C_6H_4\text{-}COOH$) and ethylene glycol ($HOCH_2\text{-}CH_2OH$), which produces the PET monomer $[\text{-}OOC\text{-}C_6H_4\text{-}COO\text{-}CH_2CH_2\text{-}]_n$. PET molecules are highly aligned, creating a strong and abrasion-resistant material that is used to produce films and polyester fibers. PET is injection molded into windshield wiper arms, sunroof frames, gears, pulleys, and food trays. This plastic is used to make the trademarked textiles Dacron, Fibre V, Fortrel, and Kodel. Tough, transparent PET films (marketed under the brand name Mylar) are magnetically coated to make both audio and video recording tape.

1.1.4.1.6. Acrylonitrile Butadiene Styrene

Acrylonitrile butadiene styrene (ABS) is made by copolymerizing (combining two or more monomers) the monomers acrylonitrile (CH_2CHCN) and styrene ($C_6H_5CH=CH_2$). Acrylonitrile and styrene are grafted onto polybutadiene rubber $[-CH=CH-CH=CH-]_n$, which allows these monomers to form chains by attaching to the rubber molecules. The advantage of ABS is that this material combines the strength and rigidity of the acrylonitrile and styrene polymers with the toughness of the polybutadiene rubber. Although the cost of producing ABS is roughly twice the cost of producing polystyrene, ABS is considered superior for its hardness, gloss, toughness, and electrical insulation properties. ABS plastic is injection molded to make telephones, helmets, washing machine agitators, and pipe joints. This plastic is thermoformed to make luggage, golf carts, toys, and car grills. ABS is also extruded to make piping, to which pipe joints are easily solvent-cemented.

1.1.4.1.7. Polymethyl Methacrylate

Polymethyl methacrylate (PMMA), more commonly known by the generic name acrylic, is polymerized from the hydrocarbon compound methyl methacrylate ($C_4O_2H_8$). PMMA is a hard material and is extremely clear because of the amorphous arrangement of its molecules. As a result, this thermoplastic is used to make optical lenses, watch crystals, aircraft windshields, skylights, and outdoor signs. These PMMA products are marketed under familiar trade names, including Plexiglas, Lucite, and Acrylite. Because PMMA can be cast to resemble marble, it is also used to make sinks, countertops, and other fixtures.

1.1.4.1.8 Polyamide

Polyamides (PA), known by the trade name Nylon, consist of highly ordered molecules, which give polyamides high tensile strength. Some polyamides are made by reacting dicarboxylic acid with diamines (carbon molecules with the ion $–NH_2$ on each end), as in nylon-6,6 and nylon-6,10. (The two numbers in each type of nylon represent the number of carbon atoms in the diamine and the dicarboxylic acid, respectively.) Other types of nylon are synthesized by the condensation of amino acids. Polyamides have mechanical properties such as high abrasion resistance, low coefficients of friction (meaning they are slippery), and tensile strengths comparable to the softer of the aluminum alloys. Therefore, nylons are commonly used for mechanical applications, such as gears, bearings, and bushings. Nylons are also extruded into millions of tons of synthetic fibers every year. The most commonly used nylon fibers, nylon-6,6 and nylon-6 (single number because this nylon forms by the self-condensation of an amino acid) are made into textiles, ropes, fishing lines, brushes, and other items.

1.1.4.2Thermosetting Materials

Because thermosetting plastics cure, or cross-link, after being heated, these plastics can be made into durable and heat-resistant materials. The most commonly manufactured thermosetting plastics are presented below in order of decreasing volume of production.

1.1.4.2.1. Polyurethane

Polyurethane is a polymer consisting of the repeating unit $[\text{-R-OOCNH-R'-}]_n$, where R may represent a different *alkyl group* than R'. Alkyl groups are chemical groups obtained by removing a hydrogen atom from an *alkane*—a hydrocarbon containing all carbon-

carbon single bonds. Most types of polyurethane resin cross-link and become thermosetting plastics. However, some polyurethane resins have a linear molecular arrangement that does not cross-link, resulting in thermoplastics. Thermosetting polyurethane molecules cross-link into a single giant molecule. Thermosetting polyurethane is widely used in various forms, including soft and hard foams. Soft, open-celled polyurethane foams are used to make seat cushions, mattresses, and packaging. Hard polyurethane foams are used as insulation in refrigerators, freezers, and homes.Thermoplastic polyurethane molecules have linear, highly crystalline molecular structures that form an abrasion-resistant material. Thermoplastic polyurethanes are molded into shoe soles, car fenders, door panels, and other products.

1.1.4.2.2. Phenolics

Phenolic (phenol-formaldehyde) resins, first commercially available in 1910, were some of the first polymers made. Today phenolics are some of the most widely produced thermosetting plastics. They are produced by reacting phenol (C_6H_5OH) with formaldehyde (HCOH). Phenolic plastics are hard, strong, inexpensive to produce, and they possess excellent electrical resistance. Phenolic resins cure (cross-link) when heat and pressure are applied during the molding process. Phenolic resin-impregnated paper or cloth can be laminated into numerous products, such as electrical circuit boards. Phenolic resins are also compression molded into electrical switches, pan and iron handles, radio and television casings, and toaster knobs and bases.

1.1.4.2.3. Melamine-Formaldehyde and Urea-Formaldehyde

Urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins are composed of molecules that cross-link into clear, hard plastics. Properties of UF and MF resins are similar to the properties of phenolic resins. As their names imply, these resins are formed by condensation reactions between urea (H_2NCONH_2) or melamine ($C_3H_6N_6$) and formaldehyde (CH_2O). Melamine-formaldehyde resins are easily molded in compression and special injection molding machines. MF plastics are more heat-resistant, scratch-proof, and stain-resistant than urea-formaldehyde plastics are. MF resins are used to manufacture dishware, electrical components, laminated furniture veneers, and to bond wood layers into plywood. Urea-formaldehyde resins form products such as appliance knobs, knife handles, and plates. UF resins are used to give drip-dry properties to wash-and-wear clothes as well as to bond wood chips and wood sheets into chip board and plywood

1.1.4.2.4. Unsaturated Polyesters

Unsaturated polyesters (UP) belong to the polyester group of plastics. Polyesters are composed of long carbon chains containing $[-OOC-C_6H_4-COO-CH_2-CH_2]_n$. Unsaturated polyesters (an *unsaturated* compound contains multiple bonds) cross-link when the long molecules are joined (copolymerized) by the aromatic organic compound styrene. Unsaturated polyester resins are often premixed with glass fibers for additional strength. Two types of premixed resins are bulk molding compounds (BMC) and sheet molding compounds (SMC). Both types of compounds are doughlike in consistency and may contain short fiber reinforcements and other additives. Sheet molding compounds are

preformed into large sheets or rolls that can be molded into products such as shower floors, small boat hulls, and roofing materials. Bulk molding compounds are also preformed to be compression molded into car body panels and other automobile components.

1.1.4.2.5. Epoxy

Epoxy (EP) resins are named for the epoxide groups (cycl-CH_2OCH; *cycl* or *cyclic* refers to the triangle formed by this group) that terminate the molecules. The oxygen along epoxy's carbon chain and the epoxide groups at the ends of the carbon chain give epoxy resins some useful properties. Epoxies are tough, extremely weather-resistant, and do not shrink as they cure (dry). Epoxies cross-link when a catalyzing agent (hardener) is added, forming a three-dimensional molecular network. Because of their outstanding bonding strength, epoxy resins are used to make coatings, adhesives, and composite laminates. Epoxy has important applications in the aerospace industry. All composite aircraft are made of epoxy. Epoxy is used to make the wing skins for the F-18 and F-22 fighters, as well as the horizontal stabilizer for the F-16 fighter and the B-1 bomber. In addition, almost 20 percent of the Harrier jet's total weight is composed of reinforcements bound with an epoxy matrix (Plastics, 2011). Because of epoxy's chemical resistance and excellent electrical insulation properties, electrical parts such as relays, coils, and transformers are insulated with epoxy.

1.1.4.2.6. Reinforced Plastics Reinforced plastics, called composites, are plastics strengthened with fibers, strands, cloth, or other materials. Thermosetting epoxy and polyester resins are commonly used as the polymer matrix (binding material) in

reinforced plastics. Due to a combination of strength and affordability, glass fibers, which are woven into the product, are the most common reinforcing material. Organic synthetic fibers such as aramid (an aromatic polyamide with the commercial name Kevlar) offer greater strength and stiffness than glass fibers, but these synthetic fibers are considerably mor expensive.

The Boeing 777 aircraft makes extensive use of lightweight reinforced plastics. Other products made from reinforced plastics include boat hulls and automobile body panels, as well as recreation equipment, such as tennis rackets, golf clubs, and jet skis (Anonymous, 2011).

1.1.5 Recycling plastics

All plastics can be recycled. Thermoplastics can be remelted and made into new products. Thermosetting plastics can be ground, commingled (mixed), and then used as filler in moldable thermoplastic materials. Highly filled and reinforced thermosetting plastics can be pulverized and used in new composite formulations. Chemical recycling is a depolymerization process that uses heat and chemicals to break plastic molecules down into more basic components, which can then be reused. Another process, called pyrolysis, vaporizes and condenses both thermoplastics and thermosetting plastics into hydrocarbon liquids.

Collecting and sorting used plastics is an expensive and time-consuming process. Once plastic products are thrown away, they are collected and then separated by plastic type. Most modern automated plastic sorting systems are not capable of differentiating

between many different types of plastics. However, some advances are being made in these sorting systems to separate plastics by color, density, and chemical composition. For example, x-ray sensors can distinguish PET from PVC by sensing the presence of chlorine atoms in the polyvinyl chloride material (Richardson, 2009). If plastic types are not segregated, the recycled plastic cannot achieve high remolding performance, which results in decreased market value of the recycled plastic. Other factors can adversely affect the quality of recycled plastics. These factors include the possible degradation of the plastic during its original life cycle and the possible addition of foreign materials to the scrap recycled plastic during the recycling process. For health reasons, recycled plastics are rarely made into food containers. Instead, most recycled plastics are typically made into items such as carpet fibers, motor oil bottles, trash carts, soap packages, and textile fibers (Richardson, 2009).

1.2 Glycerol

Glycerol or Glycerin, colorless, odorless, sweet-tasting alcohol, $C_3H_8O_3$, with a specific gravity of 1.26. It boils at 290° C (554° F) and melts at 18° C (64.4° F) as given by the manufacturers (Kanto chemical Co. inc). Liquid glycerol resists freezing but may crystallize at low temperatures. It forms a solution with water in any proportion, and dissolves in alcohol in all proportions, but is insoluble in ether and many other organic solvents. The term *glycerol* refers specifically to the compound, the formula of which is given above, whereas *glycerin* may also refer to glycerite (glycerol in solution) or other solutions of or preparations made from glycerol. Simple fats and oils are esters of fatty acids and glycerol. Obtained as a by-product of soap manufacture, after fats and oils have

been treated with alkali to form the soap, crude glycerol is purified by distillation. Glycerol may be synthesized from the petroleum products allyl alcohol, C_3H_6O, or propylene, C_3H_6, or by the catalytic action of hydrogen on sugar at high temperature and pressure (Glycerol, 2009). .

1.3 STARCH

The word "**starch**" is derived from Middle English *sterchen*, meaning to stiffen. "amylum" is Latin for starch, from the Greek αμυλον, "amylon" which means "not ground at a mill". The root amyl is used in biochemistry for several compounds related to starch (Starch, 2012).

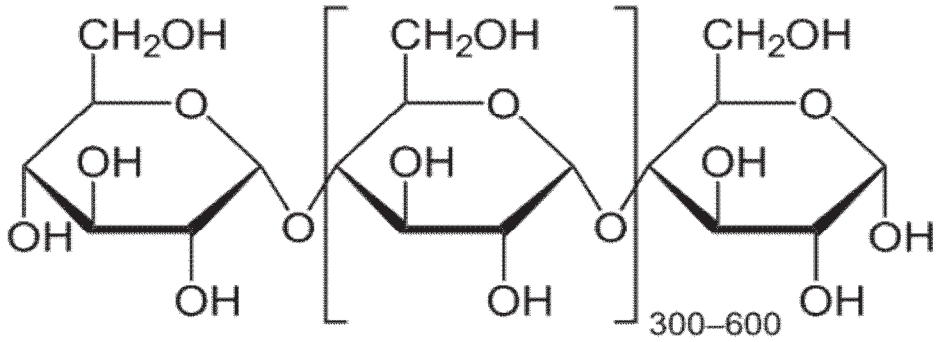
Starch or **amylum** is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as an energy store. It is the most common carbohydrate in the human diet and is contained in large amounts in such staple foods as potatoes, wheat, maize (corn), rice, and cassava. Pure starch is a soft white, tasteless and odorless powder that is insoluble in cold water, alcohol or other solvents. The basic chemical formula of the starch molecule is $(C_6H_{10}O_5)_{n.}$ Starch is a polysaccharide comprising glucose monomers joined in α 1,4 linkages. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Amylose is a much smaller molecule than amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin (Brown, & Poon, 2005). Glycogen, the glucose store of animals, is a more branched version of amylopectin. Starch is processed to produce many of the sugars in processed foods. Dissolving starch in warm water gives wheatpaste, which can be used as

a thickening, stiffening or gluing agent. The biggest industrial non-food use of starch is as adhesive in the papermaking process.

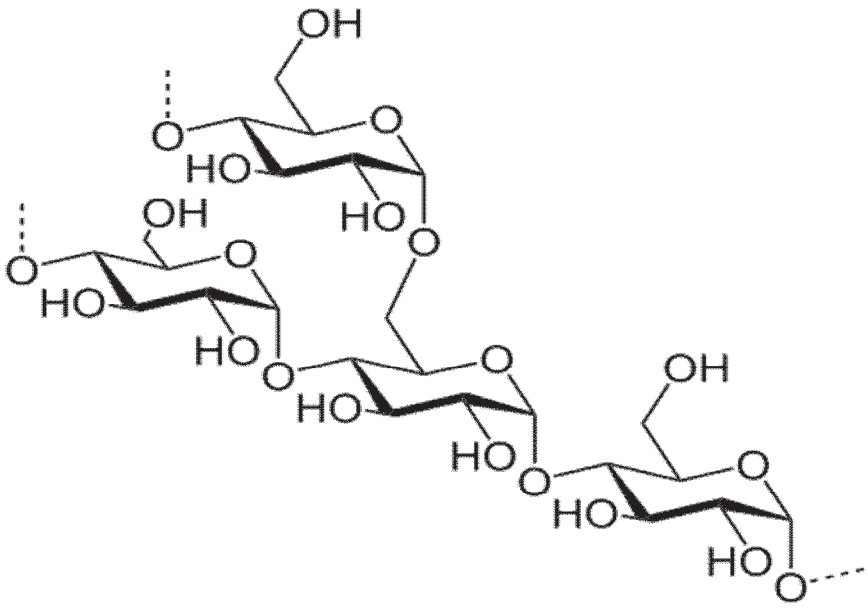
Starch molecules arrange themselves in the plant in semi-crystalline granules. Each plant species has a unique starch granular size: rice starch is relatively small (about 2μm) while potato starches have larger granules (up to 100μm).

Starch becomes soluble in water when heated. The granules swell and burst, the semi-crystalline structure is lost and the smaller amylose molecules start leaching out of the granule, forming a network that holds water and increasing the mixture's viscosity. This process is called starch gelatinization. During cooking the starch becomes a paste and increases further in viscosity. During cooling or prolonged storage of the paste, the semi-crystalline structure partially recovers and the starch paste thickens, expelling water. This is mainly caused by retrogradation of the amylose. This process is responsible for the hardening of bread or staling, and for the water layer on top of a starch gel (syneresis). Some cultivated plant varieties have pure amylopectin starch without amylose, known as *waxy starches*. The most used is waxy maize, others are glutinous rice and waxy potato starch. Waxy starches have less retrogradation, resulting in a more stable paste. High amylose starch, amylomaize, is cultivated for the use of its gel strength and for use as a resistant starch (a starch that resists digestion) in food products (Starch, 2012).

1.3.1 STRUCTURE



Amylose molecules



Amylopectin molecules

1.3.2 HYDROLYSIS

The enzymes that break down or hydrolyze starch into the constituent sugars are known as amylases. Alpha-amylases are found in plants and in animals. Human saliva is rich in amylase, and the pancreas also secretes the enzyme. Individuals from populations with a high-starch diet tend to have more amylase genes than those with low-starch diets

(Perry, 2007). It is possible that turning to a high-starch diet was a significant event in human evolution(Myers, 2008).

1.3.3 DEXTRINIZATION

If starch is subjected to dry heat, it breaks down to form dextrins, also called "pyrodextrins" in this context. This break down process is known as dextrinization. (Pyro)dextrins are mainly yellow to brown in color and dextrinization is partially responsible for the browning of toasted bread.

1.3.4 STARCH SUGARS

Starch can be hydrolyzed into simpler carbohydrates by acids, various enzymes, or a combination of the two. The resulting fragments are known as dextrins. The extent of conversion is typically quantified by *dextrose equivalent* (DE), which is roughly the fraction of the glycosidic bonds in starch that have been broken. These starch sugars are by far the most common starch based food ingredient and are used as sweetener in many drinks and foods. They include:

- Maltodextrin, a lightly hydrolyzed (DE 10–20) starch product used as a bland-tasting filler and thickener.
- Various glucose syrups (DE 30–70), also called corn syrups in the US, viscous solutions used as sweeteners and thickeners in many kinds of processed foods.
- Dextrose (DE 100), commercial glucose, prepared by the complete hydrolysis of starch.

- High fructose syrup, made by treating dextrose solutions with the enzyme glucose isomerase, until a substantial fraction of the glucose has been converted to fructose. In the United States, high fructose corn syrup is the principal sweetener used in sweetened beverages because fructose has better handling characteristics, such as microbiological stability, and more consistent sweetness/flavor.
- Sugar alcohols, such as maltitol, erythritol, sorbitol, mannitol and hydrogenated starch hydrolysate, are sweeteners made by reducing sugars.

1.3.4 CHEMICAL TESTS

1.3.4.1 Iodine test:

Iodine solution is used to test for starch; a dark blue color indicates the presence of starch. The details of this reaction are not yet fully known, but it is thought that the iodine (I_3^- and I_5^- ions) fit inside the coils of amylose, the charge transfers between the iodine and the starch, and the energy level spacings in the resulting complex correspond to the absorption spectrum in the visible light region. The strength of the resulting blue color depends on the amount of amylose present. Waxy starches with little or no amylose present will color red

1.3.4.2 Starch, 800x magnified, under polarized light

Starch indicator solution consisting of water, starch and iodine is often used in redox titrations: in the presence of an oxidizing agent the solution turns blue, in the presence of reducing agent the blue color disappears because triiodide (I_3^-) ions break up into three iodide ions, disassembling the starch-iodine complex. A 0.3% w/w solution is the

standard concentration for a starch indicator. It is made by adding 3 grams of soluble starch to 1 liter of heated water; the solution is cooled before use (starch-iodine complex becomes unstable at temperatures above 35 °C).

Each species of plant has a unique type of starch granules in granular size, shape and crystallization pattern. Under the microscope, starch grains stained with iodine illuminated from behind with polarized light show a distinctive Maltese cross effect (also known as extinction cross and birefringence) (Starch, 2012).

1.3.5 FOOD

Starch is the most common carbohydrate in the human diet and is contained in many staple foods. The major sources of starch intake worldwide are the cereals (rice, wheat, and maize) and the root vegetables (potatoes and cassava) (Anne-Charlotte Eliasson 2004). Many other starchy foods are grown, some only in specific climates, including acorns, arrowroot, arracacha, bananas, barley, breadfruit, buckwheat, canna, colacasia, katakuri, kudzu, malanga, millet, oats, oca, polynesian arrowroot, sago, sorghum, sweet potatoes, rye, taro, chestnuts, water chestnuts and yams, and many kinds of beans, such as favas, lentils, mung beans, peas, and chickpeas.

Widely used prepared foods containing starch are bread, pancakes, cereals, noodles, pasta, porridge and tortilla. Digestive enzymes have problems digesting crystalline structures. Raw starch will digest poorly in the duodenum and small intestine, while bacterial degradation will take place mainly in the colon. When starch is cooked, the

digestibility is increased. Hence, before humans started using fire, eating grains was not a very useful way to get energy.

Starch gelatinization during cake baking can be impaired by sugar competing for water, preventing gelatinization and improving texture.

1.3.6 Use as food additive

As an additive for food processing, food starches are typically used as thickeners and stabilizers in foods such as puddings, custards, soups, sauces, gravies, pie fillings, and salad dressings, and to make noodles and pastas.

Gummed sweets such as jelly beans and wine gums are not manufactured using a mold in the conventional sense. A tray is filled with native starch and leveled. A positive mold is then pressed into the starch leaving an impression of 1000 or so jelly beans. The jelly mix is then poured into the impressions and put into a stove to set. This method greatly reduces the number of molds that must be manufactured. Resistant starch is starch that escapes digestion in the small intestine of healthy individuals. High amylose starch from corn has a higher gelatinization temperature than other types of starch and retains its resistant starch content through baking, mild extrusion and other food processing techniques. It is used as an insoluble dietary fiber in processed foods such as bread, pasta, cookies, crackers, pretzels and other low moisture foods. It is also utilized as a dietary supplement for its health benefits. Published studies have shown that Type 2 resistant corn helps to improve insulin sensitivity (Maki et al, 2012), increases satiety (Bodinham, 2001) and improves markers of colonic function (Nugent, 2005). It has been suggested

that resistant starch contributes to the health benefits of intact whole grains (Higgins, 2012).

In the pharmaceutical industry, starch is also used as an excipient, as tablet disintegrant or as binder.

1.3.7 STARCH INDUSTRY

The starch industry extracts and refines starches from seeds, roots and tubers, by wet grinding, washing, sieving and drying. Today, the main commercial refined starches are cornstarch, tapioca, wheat and potato starch. To a lesser extent, sources include rice, sweet potato, sago and mung bean. Historically, Florida arrowroot was also commercialized. To this day, starch is extracted from more than 50 types of plants. Untreated starch requires heat to thicken or gelatinize. When a starch is pre-cooked, it can then be used to thicken instantly in cold water. This is referred to as a pregelatinized starch**.**

1.3.8. INDUSTRIAL APPLICATIONS

1.3.8.1 Papermaking

Papermaking is the largest non-food application for starches globally, consuming millions of metric tons annually. In a typical sheet of copy paper for instance, the starch content may be as high as 8%. Both chemically modified and unmodified starches are used in papermaking. In the wet part of the papermaking process, generally called the "wet-end", the starches used are cationic and have a positive charge bound to the starch

polymer. These starch derivatives associate with the anionic or negatively charged paper fibers / cellulose and inorganic fillers. Cationic starches together with other retention and internal sizing agent help to give the necessary strength properties to the paper web to be formed in the papermaking process (wet strength), and to provide strength to the final paper sheet (dry strength). In the dry end of the papermaking process, the paper web is rewetted with a starch based solution. The process is called surface sizing (Anonymous 2012). Starches used have been chemically, or enzymatically depolymerized at the paper mill or by the starch industry (oxidized starch). The size - starch solutions are applied to the paper web by means of various mechanical presses (size press). Together with surface sizing agent the surface starches impart additional strength to the paper web and additionally provide water hold out or "size" for superior printing properties. Starch is also used in paper coating as one of the binders together with a mixture of pigments, binders and thickeners. Coated paper has improved smoothness, hardness, whiteness and gloss and thus improves printing characteristics.

1.3.8.2 Corrugated board adhesives

Corrugated board adhesives are the next largest application of non-food starches globally. Starch glues are mostly based on unmodified native starches, plus some additive such as borax and caustic soda. Part of the starch is gelatinized to carry the slurry of uncooked starches and prevent sedimentation. This opaque glue is called a SteinHall adhesive. The glue is applied on tips of the fluting. The fluted paper is pressed to paper called liner. This is then dried under high heat, which causes the rest of the uncooked starch in glue to swell/gelatinize. This gelatinizing makes the glue a fast and strong adhesive for corrugated board production (Starch, 2012).

1.3.8.3 Clothing starch

Clothing or laundry starch is a liquid that is prepared by mixing a vegetable starch in water (earlier preparations also had to be boiled), and is used in the laundering of clothes. Starch was widely used in Europe in the 16th and 17th centuries to stiffen the wide collars and ruffs of fine linen which surrounded the necks of the well-to-do. During the 19th century and early 20th century, it was stylish to stiffen the collars and sleeves of men's shirts and the ruffles of girls' petticoats by applying starch to them as the clean clothes were being ironed. Aside from the smooth, crisp edges it gave to clothing, it served practical purposes as well. Dirt and sweat from a person's neck and wrists would stick to the starch rather than to the fibers of the clothing, and would easily wash away along with the starch. After each laundering, the starch would be reapplied. Today, the product is sold in aerosol cans for home use (Starch, 2012).

1.3.8.4 Other

Another large non-food starch application is in the construction industry, where starch is used in the gypsum wall board manufacturing process. Chemically modified or unmodified starches are added to the stucco containing primarily gypsum. Top and bottom heavyweight sheets of paper are applied to the formulation, and the process is allowed to heat and cure to form the eventual rigid wall board. The starches act as a glue for the cured gypsum rock with the paper covering, and also provide rigidity to the board. Starch is used in the manufacture of various adhesives or glues for book-binding, wallpaper adhesives, paper sack production, tube winding, gummed paper, envelope adhesives, school glues and bottle labeling. Starch derivatives, such as yellow dextrins, can be modified by addition of some chemicals to form a hard glue for paper work; some of those forms use borax or soda ash, which are mixed with the starch solution at 50–70 °C to create a very good adhesive. Sodium silicate can be added to reinforce these formulae.

- Starch is also used to make some packing peanuts, and some drop ceiling tiles.
- Textile chemicals from starch are used to reduce breaking of yarns during weaving; the warp yarns are sized. Starch is mainly used to size cotton based yarns. Modified starch is also used as textile printing thickener.
- In the printing industry, food grade starch is used in the manufacture of anti-set-off spray powder used to separate printed sheets of paper to avoid wet ink being set off.

- Starch is used to produce various bioplastics, synthetic polymers that are biodegradable. An example is polylactic acid.
- For body powder, powdered corn starch is used as a substitute for talcum powder, and similarly in other health and beauty products.
- In oil exploration, starch is used to adjust the viscosity of drilling fluid, which is used to lubricate the drill head and suspend the grinding residue in petroleum extraction.
- Glucose from starch can be further fermented to biofuel corn ethanol using the so called wet milling process. Today most bioethanol production plants use the dry milling process to ferment corn or other feedstock directly to ethanol.
- Hydrogen production can use starch as the raw material, using enzymes.

1.3.9 Sources of starch

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca(cassava), and rice. Amylopectin (without amylose) can be isolated from 'waxy' maize starch whereas amylose (without amylopectin) is best isolated after specifically hydrolyzing the amylopectin with pullulanase Genetic modification of starch crops has recently led to the development of starches with improved and targeted functionality. Cassava crop is abundantly planted in Nigeria an thus easily available in various forms; raw cassava tubers, alabo flour, Gari, etc.

1.3.10 Modification of starch

Among maize, carbohydrate polymers, starch is currently enjoying increased attention owing to its usefulness in various applications. Starches from various plant sources, such as wheat, rice, potato and cassava have received extensive attention in relation to structural
and physico-chemical properties (Singh, 2008).

Starch is being modified so that it obtains the characteristics that deviate from the native starch. It does not matter whether or not the change has come about in a physical or (bio)chemical manner.

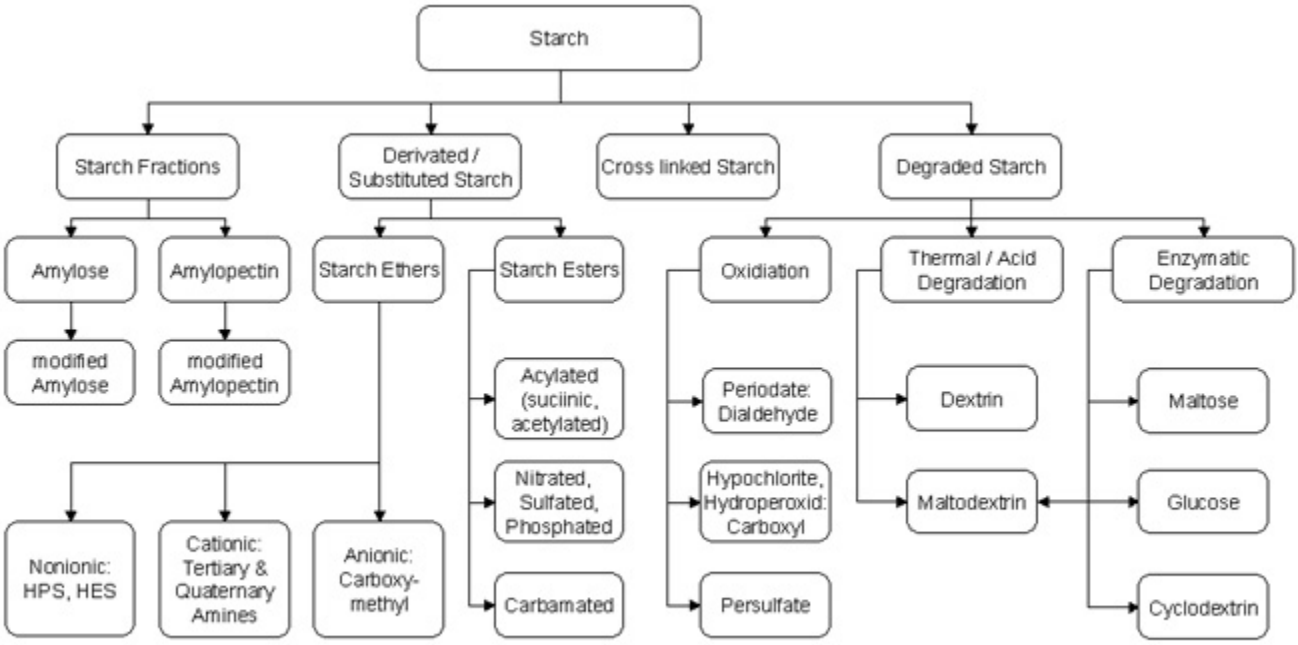
Some starch/water mixtures are very viscous, clear and stay that way even when they remain stagnant for quite some time; other starches hardly dissolve or give turbid, very finely refined suspensions. Starches with a high amylose content are most satisfactory as a gelling means (many H-bridges can be formed), but are therefore not satisfactory when a solution is desired that can be stirred.

For most applications the flow behaviour of the native (thus non-modified) starch is unsuitable. The viscosity is too low in the desired consumption concentration when native starch is used (wallpaper paste) or too high (gumming) or the solution is not cohesive enough, or too long (pudding). In some cases specific characteristics are desired, such as a high sweetening force (glucose=dextrose), an interaction with positive of even negative particles cq. Polymers.

A **modified starch** is thus a starch that has been physically or chemically modified to allow the starch to function properly under conditions frequently encountered during processing or storage, such as high heat, high shear, low pH, freeze/thaw and cooling. Native starch has a granular structure, is insoluble to water and in this form used in only a few specific applications. For normal applications starch is converted into another, mostly water-soluble form. Modifications are performed with the aim for the following properties (Zuckerforschung):

- Change gelatinisation or cooking properties
- Decrease the retro gradation tendency for gel formation
- Increase hydrophilic properties
- Confer hydrophobic properties
- Introduce ionic substituents
- Adjust viscosity by changes to the molecular weight increase of shear stability
- Improvement of film forming
- Enhancement of adhesive force

1.3.10.1 Types of starch modification Starch can be changed by chemical, physical and enzymatic treatments. Modifications give starch its specific and desired properties. Derivatisation technologies aim for modifications of the natural starch properties or for the establishment of new ones for utilisation of starch in different applications. Thus starch molecules are degraded, chemically modified by introduction of functional groups or changed by hydrothermal technology.



Various combinations of these technologies are possible and have already been realised on an industrial scale.

The following basic modification types are available and may also be combined.

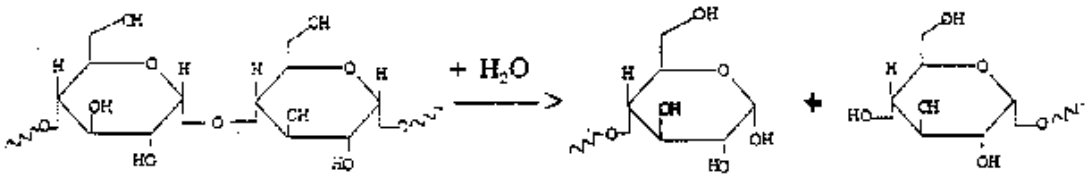
(i) Depolymerisation

(ii) Cross linking

(iii) Substitution

1.3.10.2 Depolymerisation

With the term depolymerisation we denote the reduction of the polymer, in this case the starch. A more common name for depolymerisation is breaking down



The breaking down can occur both chemically, biochemically (enzymes) and physically. At a high temperature starch appears to depolymerize. Increase of entropy supplies the driving force. The main reason to break down a starch is to reduce the viscosity. A low viscosity is desired when a high consumption concentration is needed in an application. The viscosity increases at higher concentrations; solutions of native potato starch higher than 10% can hardly be processed due to the high viscosity.The choice of the breaking down method does not only determine the maximum level of break-down but also influences other product characteristics such as stability.

1.3.10.3 Cross linking

Cross linking is said to occur when two polymers (due to a reaction) are compounded. The cross linking can occur between molecules in a solution or in the starch grain. The effect of cross linking is considerable. This can easily be imagined by keeping in mind that 1 cross link can signify the doubling of the molecule weight.

The main effects caused by cross linking are:

- increasing the gelatinization temperature
- changing the viscosity

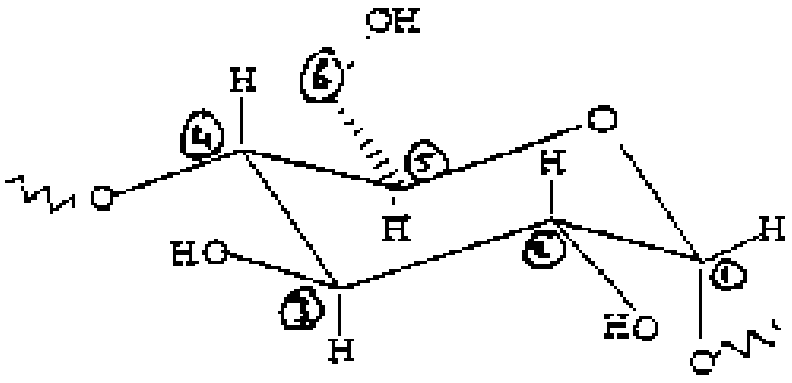
- changing the character of starch solutions

- reducing the sensitivity to stirring forces.

Cross linking in the grain, strengthens the internal grain structure. Increasing the temperature causes the grains to swell. The areas with a crystal structure mainly determine the solidity of grains and thus the gelatinization temperature. By cross linking a second kind of solidity is brought into the structure, which we can adjust to any level. It is even possible to take cross linking that far that the grain will not swell again under any condition. With a less far cross linked starch the grain swells to a maximum value while heated. Through cross linking the grain remains an entity for a longer period. This increases the viscosity maximum (the grains are less quickly destroyed by rubbing) and the temperatute at which the maximum is found shifts to a higher value.

1.3.10.4 Substitution

Besides changes to the polymer chain (cross linking or breaking down), the building stone of the polymer can also be changed. The building stone of starch is the glucose molecule



As shown above, the glucose unit has 3 hydroxyl groups. It is a (poly) alcohol and can therefore enter into all the reactions which are common for alcohols. In reaction equations the starch is represented as Z-OH when the alcohol group is of importance, or as AHG-O-AHG when the glucosidic compound between the glucose units plays a role.

In the structure given above, an H atom of a hydroxyl group may be replaced by a group R. The R-group can be anionic (negatively charged), cationic (positive) or not charged, hydrophobic (apolar) or hydrophilic (polar). In reality the H of the hydroxyl group of the 2nd carbon atom is the most reactive one. The least reactive is the OH-group of the third carbon atom. In practice it appears that by far not all OH groups have to be replaced. It is not even necessary to provide all glucose units with a substituent. For a large part of the products the **substitution degree** is lower than 0.1. This means that only 1 in 10 glucose molecules in the starch may contains a substituent (this corresponds with 1 in 30 OH groups). It will become clear that by making an appropriate choice of the R group, the starch will get the characteristics which are necessary for a certain application (Singh, 2008).

1.3.10.5 Plasticized starch

Plasticizers or **dispersants** are additives that increase the plasticity or fluidity of a material to which they are added; these include plastics, cement, concrete, wallboard, clay e.t.c. Plasticizers work by embedding themselves between the chains of polymers, spacing them apart (increasing the "free volume"), and thus significantly lowering the glass transition temperature for the material and making it softer.

Starch can be processed into thermoplastic materials in the presence of plasticizers using heat and shear. Flexibiliser and plasticiser such as sorbitol and glycerine are added to starch and processed thermo-plastically. By varying the amounts of these additives, the characteristic of the material can be tailored to specific needs. During the thermoplastic process, the strong action between hydroxy groups of starch molecules is substituted by hydrogen bonds formed between plasticizers and starch, thus the starch is plasticized. Traditionally polyols such as glycerol, glycol, xylitol, sorbitol, and Sugars were employed as plasticizers which had poor water resistance and were sensitive to vapor. Some small molecules containing –CO-NH– functional group like urea was also proved to be used as plasticizer for the native starch. It was, however, a solid with little internal flexibility and hence urea-plasticized TPS are rigid and brittle. Thermoplastic starches (TPS) from granular starch and plasticizers provide a renewable, biodegradable, and cost effective material, which is flowable like other conventional thermoplastics (Boo, 2008). However, thermoplastic starch (TPS) suffers from high water susceptibility, poor mechanical properties, and posses low degradation temperatures, which make them difficult to process (Carvalho, 2003).

1.4 polyethylene (PE)

1.4.1 polyethylene (PE), a plastic polymer of ethylene; light, versatile synthetic resin made from the polymerization of ethylene. Polyethylene is a member of the important family of polyolefin resins. It is the most widely used plastic in the world, being made into products ranging from clear food wrap and shopping bags to detergent bottles and automobile fuel tanks. It can also be slit or spun into synthetic fibres or modified to take on the elastic properties of a rubber (Britannica online).

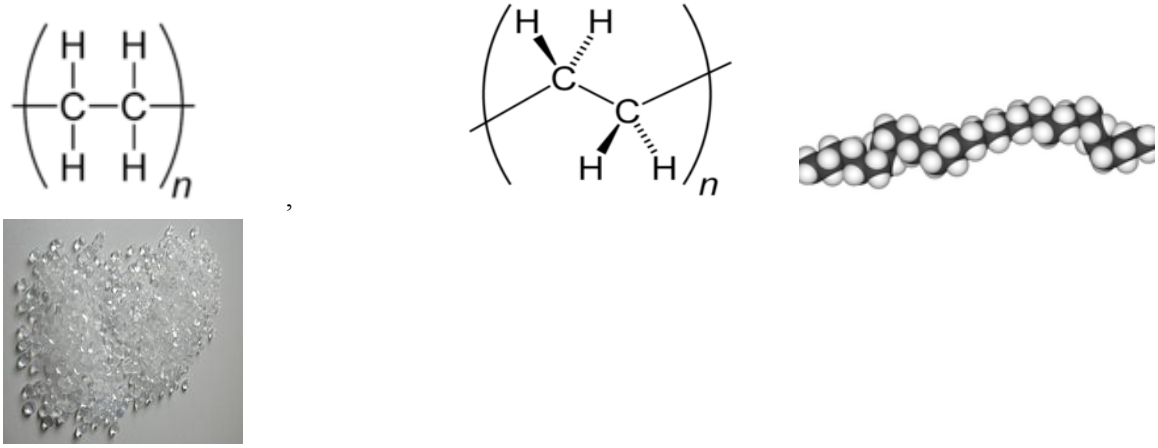


Plate I Polyethylene

1.4.2 Properties of polyethylene

1.4.2.1 Physical properties: Polyethylene is a thermoplastic polymer consisting of long hydrocarbon chains. Depending on the crystallinity and molecular weight, a melting point and glass transition may or may not be observable. The temperature at which these occur varies strongly with the type of polyethylene. For common commercial grades of medium- and high-density polyethylene the melting point is typically in the range 120 to 130 °C (248 to 266 °F). The melting point for average, commercial, low-density polyethylene is typically 105 to 115 °C.

1.4.2.2 Chemical properties:

Most LDPE, MDPE and HDPE grades have excellent chemical resistance, meaning that it is not attacked by strong acids or strong bases. It is also resistant to gentle oxidants and reducing agents. Polyethylene burns slowly with a blue flame having a yellow tip and gives off an odour of paraffin. The material continues burning on removal of the flame source and produces a drip.Crystalline samples do not dissolve at room temperature.

Polyethylene (other than cross-linked polyethylene) usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene, or in chlorinated solvents such as trichloroethane or trichlorobenzene

1.4.3 Types of polyethylene

Polyethylene is classified into several different categories based mostly on its density and branching. Its mechanical properties depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. With regard to sold volumes, the most important polyethylene grades are HDPE, LLDPE and LDPE.

1.4.3. 1 High-density polyethylene (HDPE)

HDPE is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. The lack of branching is ensured by an appropriate choice of catalyst (for example, chromium catalysts or Ziegler-Natta catalysts) and reaction conditions. HDPE is used in products and packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes. One third of all toys are manufactured from HDPE.

1.4.3. 2 Medium-density polyethylene (MDPE)

MDPE is defined by a density range of 0.926–0.940 g/cm^3. MDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts. MDPE has good shock and drop resistance properties. It also is less notch sensitive than HDPE,

stress cracking resistance is better than HDPE. MDPE is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures.

1.4.3. 3 Cross-linked polyethylene (PEX or XLPE)

PEX is a medium- to high-density polyethylene containing cross-link bonds introduced into the polymer structure, changing the thermoplast into an elastomer. The high-temperature properties of the polymer are improved, its flow is reduced and its chemical resistance is enhanced. PEX is used in some potable-water plumbing systems because tubes made of the material can be expanded to fit over a metal nipple and it will slowly return to its original shape, forming a permanent, water-tight, connection.

1.4.3. 4 Linear low-density polyethylene (LLDPE)

LLDPE is defined by a density range of 0.915–0.925 g/cm^3. LLDPE is a substantially linear polymer with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). LLDPE has higher tensile strength than LDPE, it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress cracking resistance but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. Cable covering, toys, lids, buckets, containers and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility and relative

transparency. Product examples range from agricultural films, saran wrap, and bubble wrap, to multilayer and composite films.

1.4.3. 5 Low-density polyethylene (LDPE)

LDPE is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. LDPE is created by free radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

1.5. Composites

1.5.1 Composite materials, often shortened to **composites** or called **composition materials**, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure .

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements

impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Engineered composite materials must be formed to shape. The matrix material can be introduced to the reinforcement before or after the reinforcement material is placed into the mould cavity or onto the mould surface. The matrix material experiences a melding event, after which the part shape is essentially set. Depending upon the nature of the matrix material, this melding event can occur in various ways such as chemical polymerization or solidification from the melted state. A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. For example, a glass-fiber reinforced plastic combines the high strength of thin glass fibers with the ductility and chemical resistance of plastic; the brittleness that the glass fibers have when isolated is not a characteristic of the composite. The opportunity to develop superior products for aerospace, automotive, and recreational applications has sustained the interest in advanced composites. Currently composites are being considered on a broader basis—for applications that include civil engineering structures such as bridges and freeway pillar reinforcement; and for biomedical products, such as prosthetic devices(Keith, 2009).

A variety of moulding methods can be used according to the end-item design requirements. The principal factors impacting the methodology are the natures of the chosen matrix and reinforcement materials. Another important factor is the gross quantity

of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher labour and tooling costs at a correspondingly slower rate. Many commercially produced composites use a polymer matrix material often called a resin solution. The reinforcement materials are often fibres but also commonly ground minerals.

1.5.2 Moulding methods

In general, the reinforcing and matrix materials are combined, compacted and processed to undergo a melding event. After the melding event, the part shape is essentially set, although it can deform under certain process conditions. For a thermoset polymeric matrix material, the melding event is a curing reaction that is initiated by the application of additional heat or chemical reactivity such as an organic peroxide. For a thermoplastic polymeric matrix material, the melding event is a solidification from the melted state. For a metal matrix material such as titanium foil, the melding event is a fusing at high pressure and a temperature near the melt point.

1.5.3 Failure

Shock, impact, or repeated cyclic stresses can cause the laminate to separate at the interface between two layers, a condition known as delamination. Individual fibres can separate from the matrix e.g. fibre pull-out.

Composites can fail on the microscopic or macroscopic scale. Compression failures can occur at both the macro scale or at each individual reinforcing fibre in compression buckling. Tension failures can be net section failures of the part or degradation of the composite at a microscopic scale where one or more of the layers in the composite fail in tension of the matrix or failure the bond between the matrix and fibres. Some composites are brittle and have little reserve strength beyond the initial onset of failure while others may have large deformations and have reserve energy absorbing capacity past the onset of damage. The variations in fibres and matrices that are available and the mixtures that can be made with blends leave a very broad range of properties that can be designed into a composite structure.

1.5.4 Testing

To aid in predicting and preventing failures, composites are tested before and after construction. Pre-construction testing may use finite element analysis (FEA) for ply-by-ply analysis of curved surfaces and predicting wrinkling, crimping and dimpling of composites (Waterman,2007). Materials may be tested after construction through several nondestructive methods including ultrasonics, thermography, shearography and X-ray radiography (Matzkanin, 2011).

The composite may be characterized using the following technics;

1.5.4. 1 Fourier transform spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint".

This is a measurement technique where by spectra are collected based on measurements of the **temporal coherence** of a **radioactive** source, using **time – domain** measurements of the **electromagnetic radiation** or other type of radiation.

1.5.4. 2 Transmission electron microscopy (**TEM**) This is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light, thus, objects may be observed to the order of a few angstrom (10^{-10} m). For example, you can study small details in the cell or different materials down to near atomic levels.

1.5.4. 3 Scanning Electron microscopy (SEM)

In a scanning electron microscope, a tightly focused electron beam moves over the entire sample to create a magnified image of the surface of the object in much the same way an electron beam scans an image onto the screen of a television. Electrons in the tightly focused beam might scatter directly off the sample or cause secondary electrons to be emitted from the surface of the sample. These scattered or secondary electrons are collected and counted by an electronic device. Each scanned point on the sample corresponds to a pixel on a television monitor; the more electrons the counting device

detects, the brighter the pixel on the monitor is. As the electron beam scans over the entire sample, a complete image of the sample is displayed on the monitor.

An SEM scans the surface of the sample bit by bit, in contrast to a TEM, which looks at a relatively large area of the sample all at once. Samples scanned by an SEM do not need to be thinly sliced, as do TEM specimens, but they must be dehydrated to prevent the secondary electrons emitted from the specimen from being scattered by water molecules in the sample.

Scanning electron microscopes can magnify objects 100,000 times or more. SEMs are particularly useful because, unlike TEMs and powerful optical microscopes, they can produce detailed three-dimensional images of the surface of objects

1.5.4. 4 X-Ray Diffraction

X-ray diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

1.5.4.5 Dynamic Mechanical analysis (DMA)

Dynamic Mechanical Analysis measures the mechanical properties of materials as a function of time, temperature and frequency. It is most useful for observing the viscoelastic nature of polymers. Two methods are currently used: One is the decay of free oscillations in which a force is applied to a sample and allowing it to oscillate after the force is removed, and the other technique is forced oscillation which involves the continued application of a force to the sample. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. Samples can be either solids or melts. Most solids are tested by linearly applied strains and melts or liquids are normally tested in shear.

The DMA measurement depend on the kind of sample under investigation, thus either of the following modes of measurement may be employed; flexure fixture, single cantilever, dual cantilever, 3 – point bending, tension, compression or shear fixtures. Because a sinusoidal force is being applied, the modulus may be expressed as an in-phase component, the storage modulus, and an out of phase component, the loss modulus,

The storage modulus, either E' or G', is the measure of the sample's elastic behavior. The ratio of the loss to the storage is the tan delta and is often called damping. It is a measure of the energy dissipation of a material.

1.5.4.6 Thermogravimetric Analysis(TGA)

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere, in other words

Thermogravimetric analysis TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. The technique is employed to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature.

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. There are two types of TGAs, a top-loading TGA which supports the sample pan above the balance via a "stem" support rod, and a bottom loading or hangdown, Pyris TGA, that supports the sample pan via a "hangdown" below the balance. Both styles take advantage of gravity to obtain very accurate and reproducible measurements. These instruments can quantify loss of water, loss of solvent, loss of plasticizer, decarboxylation, pyrolysis, oxidation, decomposition, weight % filler, amount of metallic catalytic residue remaining on carbon nanotubes, and weight % ash.

1.5.4.7 Differential Scanning Calorimetry (DSC) The Differential Scanning Calorimetry (DSC) is a thermoanalytical procedure in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a

function of time. The reference sample should have a well – defined heat capacity over the range of temperatures to be scanned.

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will be needed to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic process (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and studying polymer curing.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

1.6 Justification for the research

The employment of plastic material in a wide range of applications makes it one of the high demanding engineering materials. However, the disposal problems associated with conventional oil-based polymeric materials due to their inability to degrade constitute serious concern to environmentalist considering the huge amounts being turnout as waste all over the globe. The conventional methods of recycling and incineration are not without great challenges. The recycling option faces problem of high energy consumption and additional problem due to difficulty in collecting and sorting plastic types which is not cost effective and time consuming. Incineration of used plastics and polymeric materials gives hazardous and poisonous gases which could lead to diseases and ill-health conditions in human. It has thus become necessary to search for alternatives, to this end starch filled - thermoplastics were found to be most valuable. This is because starch is found abundantly in nature and its renewability, lowcost, and biodegrability. However, these composites did not show good mechanical properties due to the poor interfacial adhesion between the polymer matrix and the starch granules. To overcome the problem of the poor interfacial adhesion, modified starches and modified biodegradable matrix polymers are being studied.

In this Study, Mechanical and thermal properties of low density polyethylene (LDPE) composites with thermoplastic starch and starch dicarboxylic acid were investigated.

This project is designed to explore the use of local materials available in the country for the fabrication of materials that would find a lot of uses in everyday activities such as environmental friendly polyethylene bags and household utensils. The materials are also

such that they are environmentally friendly because of the biodegradable nature of the filler used; being modified starch.

1.7 The objectives of this research include:

To develop thermoplastic starch (TPS) from granular starch and polyol such as glycerol.

To develop starch – dicarboxylic acid compound[SDCA]

T o blend Thermoplastic polymer such as LDPE with TPS or SDCA

To characterized the TPS, SDCA, LDPE/TPS and LDPE/SDCA

To study the Mechanical and thermal properties of LDPE/TPS and LDPE/SDCA composites.

1.8 Limitation and constrains

This study would have cover investigations of mechanical and thermal properties of polyethylene – modified starches composites particularly using high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) as matrices and various modified starches as fillers and probably compare the results, however due to constraints of required equipment and materials in the country (Nigeria) and inadequate finance to carry out the work out side the country, the study is only limited to Mechanical and thermal properties of low density polyethylene (LDPE) composites with thermoplastic starch and starch dicarboxylic acid.

CHAPTER TWO

REVIEW OF LITERATURE

2.0 Literature Review

2.1 Introduction

Polymer materials and plastics are widely used in many applications because of their comprehensive properties and convenience in processing (Jie, et al 2007). However they are of great concern to environmentalist due to their negative environmental consequences and may deplete fossil fuel resources (Mohini, et al 2006). When buried in typical solid waste site, polymeric materials may have a long life time of hundreds of years (Musa, et al 2011) thus interfering with the soil fertility and causing erosion. The increasing demand for plastics gave birth to interest in biobased and biodegradable polymers as alternatives, based on renewable materials, predominantly from agro-forest resources (Mohini, et al 2006). To this end, starch – filled thermoplastics were found to be economically more active. Indeed, among the biomaterials tested for their suitability as biodegradable fillers, only raw starch meets the requirement of high thermal stability, minimum interference with flow properties, minimum disturbance of product (Nawang, et al 2001). Starch on mixing enhances the biodegradability of the synthetic polymer mainly because of the increase in polymer surface created after starch consumption by microorganisms (Hwan-Man, et al 2002). However, these composites did not show good mechanical properties due to the poor interfacial adhesion between the polymer matrix and the starch granules. To overcome the problem of the poor interfacial adhesion, modified starches and modified biodegradable matrix polymers are being studied.

In this Study, Mechanical and thermal properties of low density polyethylene (LDPE) composites with thermoplastic starch and starch dicarboxylic acid were investigated.

2.2Biodegradable polymer

The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those which undergo a significant change in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties, as measured by standard methods. Biodegradable plastics undergo degradation from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Plastics may also be designated as photodegradable, oxidatively degradable, hydrolytically degradable, or those which may be composted (Kolybaba et al, 2003).

In general, the likelihood of microbial attack on a material is dependent on the structure of the polymer. When examining polymer materials from a scientific standpoint, there are certain ingredients that must be present in order for biodegradation to occur. Most importantly, the active microorganisms (fungi, bacteria, actinomycetes, etc.) must be present in the disposal site. The organism type determines the appropriate degradation temperature, which usually falls between 20 to 60^{o}C (Huang et al. 1990). The disposal site must be in the presence of oxygen, moisture, and mineral nutrients, while the site pH must be neutral or slightly acidic (5 to 8) [Kolybaba et al, 2003].

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms .

Naturally occurring biopolymers are derived from four broad feedstock areas. Animal sources provide collagen and gelatine, Microbial biopolymer feedstocks are able to produce polylactic acid (PLA) and polyhydroxy alkanoates (PHA). The final category of agricultural feedstocks are the biopolymer that falls into the categories of hydrocolloids, and lipids and fats (Kolybaba et al, 2003).

Microbial biopolymer feedstocks produce biological polymers through microbial fermentation. The products are naturally degradable, environmentally friendly substitutes for synthetic plastics. A number of bacteria accumulate polyhydroxy alkanoates (PHAs) as intracellular carbon reserves when nutrient deficiencies occur. The biopolymers, which are microbially produced polyesters, have the same thermoplastic and water resistant qualities as synthetic plastics.

Polylactic acid is the second common biopolymer which is produced by microbial fermentation. It is produced by the condensation of lactic acid, which is obtained through fermentation processes. Wilkinson Manufacturing Co. (Fort Calhoun, Nebraska, USA) has recently introduced a commercially available thermoformed all-natural plastic

container using a corn-based PLA. The carbon stored in the plant starches is broken down to natural plant sugars. Fermentation and separation form the PLA. PHA and PLA are both considered synthetic polymers, as they are not found in nature. However, they are wholly biodegradable.

There are a number of other biological materials that have been examined and manipulated by biopolymer researchers. Wheat contains starch and gluten, both of which are employed by the biopolymer industry. Canola derivatives have potential as both polymers and plasticizers. Chitosan is obtained from the deacetylation of chitin, which is found in marine environments. Because it is insoluble in water, chitosan is dissolved in acidic solutions before being incorporated into biodegradable polymer films. The structural characteristics of soy proteins give them potential for industrial applications in plastics and reinforced composite materials (Park et al. 2002). As a general conclusion, it can be stated that many naturally occurring organisms (plant and animal) have potential to be modified and employed as biopolymers (Kolybaba et al, 2003).

Biopolymers that may be employed in packaging continue to receive more attention than those designated for any other application. All levels of government, particularly in China and Germany (Bastioli 2001), are endorsing the widespread application of biodegradable packaging materials in order to reduce the volume of inert materials currently being disposed of in landfills, occupying scarce available space. It is estimated that 41% of plastics are used in packaging, and that almost half of that volume is used to package food products (Kolybaba et al, 2003).

The renewable and biodegradable characteristics of biopolymers are what render them appealing for innovative uses in packaging. The end use of such products varies widely. For example, biodegradable plastic films may be employed as garbage bags, disposable cutlery and plates, food packaging, and shipping materials..

The biopolymer materials suited for packaging are often used in agricultural products. Young plants which are particularly susceptible to frost may be covered with a thin Ecoflex film. At the end of the growing season, the film can be worked back into the soil, where it will be broken down by the appropriate microorganisms. Agricultural applications for biopolymers are not limited to film covers. Containers such as biodegradable plant pots and disposable composting containers and bags are areas of interest (Huang et al 1990). The pots are seeded directly into the soil, and breakdown as the plant begins to grow. Fertilizer and chemical storage bags which are biodegradable are also applications that material scientists have examined. From an agricultural standpoint, biopolymers which are compostable are important, as they may supplement the current nutrient cycle in the soils where the remnants are added (Kolybaba et al, 2003).

The biopolymers used in medical applications must be compatible with the tissue they are found in, and may or may not be expected to break down after a given time period. It was reported that researchers working in tissue engineering are attempting to develop organs from polymeric materials, which are fit for transplantation into humans. The plastics would require injections with growth factors in order to encourage cell and blood vessel growth in the new organ. Work completed in this area includes the development of

biopolymers with adhesion sites that act as cell hosts in giving shapes that mimic different organs (Kolybaba et al, 2003).

Not all biopolymer applications in the field of medicine are as involved as artificial organs. The umbrella classification of bioactive materials includes all biopolymers used for medical applications. One example is artificial bone material which adheres and integrates onto bone in the human body. The most commonly employed substance in this area is called Bioglass.

Another application for biopolymers is in controlled release delivery of medications. The bioactive material releases medication at a rate determined by its enzymatic degradation PLA materials were developed for medical devices such as resorbable screws, sutures, and pins. These materials reduce the risk of tissue reactions to the devices, shorten recovery times, and decrease the number of doctor visits needed by patients (Kolybaba et al, 2003).

The automotive sector is responding to societal and governmental demands for environmental responsibility. Biobased cars are lighter, making them a more economical choice for consumers, as fuel costs are reduced. Natural fibres are substituted for glass fibres as reinforcement materials in plastic parts of automobiles and commercial vehicles. An additional advantage of using biodegradable polymer materials is that waste products may be composted. Natural fibres (from flax or hemp) are usually applied in formed interior parts. The components do not need load bearing capacities, but dimensional stability is important. Research and development in this area continues to be enthusiastic, especially in European countries (Kolybaba et al, 2003)). There are a number of novel

applications for biopolymers, which do not fit into any of the previous categories. One such example is the use of biopolymer systems to modify food textures. For example, biopolymer starch (gelatin-based) fat replacers possess fat-like characteristics of smooth, short plastic textures that remain highly viscous after melting. Research continues into high pressure being used to manipulate biopolymers into food products. The eventual goal is improved physical characteristics such as foaming, gelling, and water- or fat-binding abilities. Biopolymer materials are currently incorporated into adhesives, paints, engine lubricants, and construction materials. Biodegradable golf tees and fishing hooks have also been invented. The attraction of biopolymers in all of these areas is their derivation from renewable sources, slowing the depletion of limited fossil fuel stores (Kolybaba et al, 2003).

Many biopolymers are designed to be discarded in landfills, composts, or soil. The materials will be broken down, provided that the required microorganisms are present. Normal soil bacteria and water are generally all that is required, adding to the appeal of microbially reduced plastics.

Natural filler materials may be incorporated into synthetic plastic matrices as a rapidly biodegradable component. Often, granular starch is added to polyethylenes in order to increase the degradation rate of the plastic material. Starch can also be used in its gelatinized form. Heating the starch in the presence of water during extrusion or injection moulding causes the formation of a thermoplastic material that may be deformed during blending. This starch-based product is then blended with either natural or synthetic materials. Heating starch above its glass transition temperature breaks its molecular structure, allowing further bonding. Glycerol is often used as a plasticizer in starch

blends, to increase softness and pliability. Starch granules that have been plasticized with water and glycerol are referred to as plasticized starches. Plastic materials that are formed from starch-based blends may be injection molded, extruded, blown, or compression molded (Kolybaba et al, 2003).

2.3 Composite materials

A composite material is a substance that is made up of a combination of two or more different materials (Keith Kedward 2009) or a two – phase compact material with its components separated by interfaces, which can be natural or man made. The different components in a multi–phase composite may be present as macroscopically distinct phases, as incase of coating, sandwitch materials and laminates, or they may be mixed on microscopic scale, as in the case of dispersion, particulate and fibre composites. One of the phases called the reinforcement phase, is usually in form of fibres, sheets, or particles, which is stiff and strong. In second phase, matrix that embeds the reinforcement is usually weak and less stiff (Kogo, 2008).

A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. For example, a glass-fiber reinforced plastic combines the high strength of thin glass fibers with the ductility and chemical resistance of plastic; the brittleness that the glass fibers have when isolated is not a characteristic of the composite (Keith Kedward 2009)

CHAPTER THREE

MATERIALS AND METHODS

3.0 Materials and equipment

3.1 Materials

Low density Polyethylene, Plasticizer (Glycerol), and Oxalic acid (98% purity) all obtained from Sigma Aldrich, Potato Starch obtained from Kanto chemical Co. inc, Were used in this work

3.2 Equipment

Twin-screw co - rotating extruder HAAKE Rheomex OS PTW16, Compression molding machine (Carver Hydraulic press No 4533.4DIOBOO). Two roll mill (Mixing roll No. VP- 300), Scanning electron microscope Jeol JSM 7600F. Tensile tester Universal Tensile testing machine (UTM) WITHLAB WL2100. Weighing balance, Hardness testing instrument Universal Tensile testing machine (UTM) WITHLAB WL2100, Flexural testing instrument Universal Tensile testing machine (UTM) WITHLAB WL2100, Dynamic mechanical analyzer DMA Q800, Thermogravimetric Analysis equipment(TGA) symultanic thermal analyzer SDT Q600 V20.9 Build 20, Differential Scanning Calorimeter (DSC) symultanic thermal analyzer SDT Q600 V20.9 Build 20, Fourier transform spectroscope FT-IR Nicolet 6700. Were all employed during this work

3.3 Methodology

3.3.1 Preparation of Thermoplastic starch

Potato Starch (Analytical standard) obtained from Kanto chemical Co. inc, was plasticized using a one-stage process; The starch powder and liquid glycerol were manually mixed in the ratio 100 : 30 respectively (as determined during the preliminary work of this research), this mixture was then fed into a twin-screw co - rotating extruder HAAKE Rheomex OS PTW16 which is being driven by HAAKE Polylab OS Rheodrive16. The temperature profile used during the plasticization process are indicated in Table1. The screw diameter was 16mm, and L/D ratio was 25 running at11.6 rpm. The starch granules were fragmented. Under temperature and shearing, starch was destructured, plasticized, melted but also partially depolymerised. After the processing, plasticized starch (TPS) in sheet form was obtained.

Table 1: Temperature profile for the plasticization of starch

Zone	1	2	3	4	5	6	Die
Temperature(^{o}C)	160	165	165	165	170	170	165

3.3.2 Preparation of starch – Dicarboxylic acid compound

Oxalic acid pallets were thoroughly mixed with starch granules in the ratio 20 : 100 respectively (as determined during the preliminary work of this research), the mixture was then fed into a twin-screw co - rotating extruder HAAKE Rheomex OS PTW16 which was being driven by HAAKE Polylab OS Rheodrive16. The temperature profile

used during the plasticization process are indicated in Table 2. The screw diameter was 16mm, and L/D ratio was 25 running at 26.5 rpm. After the processing, a milky jelly paste Starch – Dicarboxylic acid compound (SDCA) was obtained, which solidified at ambient temperature.

Table 2: Temperature profile for the processing of starch – Dicarboxylic acid

Zone	1	2	3	4	5	6	Die
Temperature(^{o}C)	90	90	90	90	90	90	100

3.3.3 Preparation of the plasticized starch-polyethylene (LDPE/TPS) composite:

The plasticized starch was chopped into pieces by hand using a cutter then blended with thermoplastic polymer, i.e low density polyethylene as follows: The low density polyethylene in granulated form was thoroughly mixed with the plasticized starch and melt blended at 140^{o}C using the two roll mill (Mixing roll No. VP- 300). The blend was sandwitched in a Teflon sheet and then compressed at a pressure of 3 tons for 5minutes in between two steel plates of a compression molding machine(Carver Hydraulic press No 4533.4DIOBOO), at 140^{o}C. Flat sheets of composites were obtained using a covered 150mm X 150mm X 20mm metalic moulds filled with LDPE /TPS sandwitch. The composites are designated as LDPE /TPS composites and labeled, accordingly 7 different composites were prepared as follows;

Table 3: Preparation of LDPE/TPS composites

TPS	0	10	20	30	40	50	100
LDPE	100	90	80	70	60	50	0

3.3.4 Preparation of the polyethylene – starch Dicarboxylic acid (LDPE/SDCA) composite:

The Starch – Dicarboxylic acid compound was crushed into granular form using a hammer and then blended with the thermoplastic polymer, i.e low density polyethylene as follows: The low density polyethylene in granulated form was thoroughly mixed with the Starch – Dicarboxylic acid compound granules and melt blended at 120^{o}C with a two roll mill (Mixing roll No. VP- 300). The blend was sandwitched in a Teflon sheet and then compressed at a pressure of 3 tons for 10minutes in between two steel plates of a compression molding machine (Carver Hydraulic press No 4533.4DIOBOO), at 130^{o}C. Flat sheets of composites were obtained using a covered 150mm X 150mm X 20mm metalic moulds filled with LDPE /SDCA sandwitch. The composites are designated as LDPE /SDCA composites and labeled, accordingly 7 different composites were prepared as follows;

Table 4: Preparation of LDPE/SDCA composites

SDCA	0	10	20	30	40	50	100
LDPE	100	90	80	70	60	50	0

The molded samples were cut into square shape (15cm×15cm) from which the specimen(s) for all the tests where cutout as required. Specimens for test(s) and investigation(s) were conditioned at room temperature (28-30 ^{o}C) and relative humidity of 30±2% for 24hours.

It will be noted that the processing temperatures in the preparation of LDPE/SDCA was lowered as compared to that of LDPE/TPS because starch dicarboxylic acid compound (SDCA) could not with stand temperatures above 130 ^{o}C.

3.4 Characterization of the composites

The samples from LDPE, TPS, SDCA, LDPE/TPS composites, LDPE/SDCA composites were characterized using FT-IR, SEM, and XRD. Starch sample and 80/20 LDPE/STA composite were also studied for the purpose of comparism.

3.4.1 Fourier transform spectroscopy

Fourier transform infra-red spectroscopy (FT-IR Nicolet 6700) was used to investigate interaction between Low density polyethylene (LDPE) and starch derivatives i.e thermoplastic starch (TPS) and starch dicarboxylic acid compound (SDCA). The FT-IR spectra of the Starch, LDPE, TPS, SDCA, LDPE/TPS composites LDPE/SDCA composites and LDPE/STA composites were obtained on FT-IR Nicolet 6700 at Characterization conditions ATR acc (window ZnSe/diamond), resolution 8 and in a spectral range of 650 – 4000cm^{-1}.

3.4.2 Wide angle X – ray Measurements

X – Ray diffraction patterns of the conditioned samples were obtained using a Bruker AXS X-ray diffractometer with nickel – filtered CuKα rays ($\lambda = 1.542\ A^o$). The rotating-anode generator was operated at 40kV and 45mA. The measurement was performed at a diffraction angle 2θ range of ($0 – 40^o$). The aperture slits were set at 0.1^o and the scanning step was 0.02^o with a scan time of 300 seconds. The degree of crystallinity of the samples was estimated from the crystallograph.

3.4.3 Scanning Electron Microscopy

The morphology of the samples were studied using Scanning Electron Microscope Jeol JSM 7600F at an accelerating voltage of 5.0kV and magnification of 1000. Test samples were initially sputter – coated with gold (using Cressington sputter coater 108 auto) in order to prevent any electrical discharge during examination with the microscope.

3.5 Mechanical properties

The response to applied forces and deformation of polymeric materials contribute immensely to the behavior of polymer in processing. The mechanical properties cover a large number of effects, all of which combine to determine the particular character of the polymer.

3.5.1Tensile properties

Specimens for tensile testing were conditioned at temperature ($23 \pm 2\ ^oC$) and relative humidity of 50 ± 5 % for 24hours. The tensile properties were measured using

Universal tensile testing machine (UTM) WITHLAB WL2100 according to ASTM D638. Five replicates were tested for each sample, and the average values of the tensile strength, elongation at break and modulus were determined. The tests were carried out at temperature (23 ± 2 ^{o}C) using 30mm X 10mm X 0.1cm specimen(s) with a gauge length of 15mm.

The Young's modulus were determined from the slope of the linear portion of the load – elongation curves and the tensile strength is the stress at break. The elongation at break is the maximum extension at break.

3.5.2 Flexural Strength

The three point bending tests for the samples were carried out using Universal Tensile testing machine (UTM) (WITHLAB WL2100) according to ASTM D790. The flexural moduli were determined from the initial slope of the stress – strain curves. The test speed was 5mm/min, load cell capacity and support span were 200N and 25mm, respectively. The tests were carried out at temperature (23 ± 2 ^{o}C) and relative humidity of 50 ± 5 %. Five replicates were tested for each sample, and the average values determined.

3.5.3 Hardness Test

The samples hardness were measured using Asker Shore D (Durometer Hardness D type) in accordance with ASTM D2240. The tests were carried out at temperature (23 ± 2 ^{o}C) and relative humidity of 50 ± 5 %. Five replicates were tested for each sample, and the average values determined.

3.5.4 Dynamic Mechanical Analysis

Dynamic mechanical analysis of the samples were carried out in accordance with ASTM D4065 using a dynamic mechanical analyzer DMA Q800 over a temperature range of -140 ^{o}C to 100 ^{o}C at10Hz and a heating rate of 2 ^{o}C/min. The measurement was carried out using the dual cantilever bending mode.

3.6 Thermal Properties

Thermal properties (Thermogravimetric analysis and Differential Scanning Calorimetry of the samples were studied using symultanic thermal analyzer SDT Q600 V20.9 Build 20 under Nitrogen atmosphere.

3.6.1Thermogravimetric Analysis (TGA)

The Thermogravimetric analysis was performed using symultanic thermal analyzer SDT Q600 V20.9 Build 20. Samples were heated in the Nitrogen atmosphere in the temperature range of 25–600 ^{o}C with the temperature rate increase of 5^{o}C/min. Thermal degradation of the samples were investigated.

3.6.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was carried out using symultanic thermal analyzer SDT Q600 V20.9 Build 20 under Nitrogen atmosphere to measure the melting temperature (*Tm*) and the glass transition temperature (*Tg*). The samples were heated at a rate of 5°C per min from 25 °C to 600 °C.

3.7 Water absorption

Water absorption was carried out according to ASTM D570. The samples (each 50mm X 15mm X 01mm)were conditioned in an oven at 50^{o}C for 24hrs, then placed inside desiccators for 24hrs and finally weighed using a digital electrical balance correct to four decimal places. The weighed samples were each placed inside a plastic container and enough water added so that they were completely immersed using sinkers. The set up was allowed to stand for 56 days, the weight of the samples being measured at 7 days intervals, the percentage moisture uptake was calculated according to the equation below (Danjaji ,et al 2002)

$$\%M = \frac{W_w - W_d}{W_d} X100$$

Where M is the percentage moisture uptake, W_d and W_w are the weight of the sample before and after immersion in water, respectively.

3.8 Soil Burial Test

Soil burial testing was carried out at Seoul South Korea between the months of August 2012 and October 2012, by burying the samples (each 50mm X 25mm X 01mm) at an agricultural garden at a soil depth of about 15cm from the surface ground, and about 300mm in between each other. The samples were unearthed after 63 days, carefully washed thoroughly with tap water followed by distilled water and then allowed to dry in an open air for 7 days. The morphology of the samples was studied before and after the test using Scanning Electron Microscope Jeol JSM 7600F at an accelerating voltage of 5.0kV and magnification of 1000. Test samples were initially sputter – coated with gold

(using Cressington sputter coater 108 auto) in order to prevent any electrical discharge during examination with the microscope. The weight of the samples was also measured before and after the soil burial from which the percentage weight loss was determined.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Fourier transform spectroscopy (FT – IR)

The FT-IR spectra of the Starch, LDPE, TPS, SDCA, LDPE/TPS composites LDPE/SDCA composites and LDPE/STA composites were obtained and recorded (Figure 1a - p) on FT-IR Nicolet 6700.

The interpretation of the IR- absorption bands were largely based on Sinco. Thermo Scientific. FT-IR functional group Identification table. (USA) and also partly as provided by Volland (1999).

The starch spectrum (Figure 1a) is characterized by O-H band at 3297 cm^{-1}, C – H band at 2928 cm^{-1}, C – O bands at between 1000 – 1150 cm^{-1} and other bands corresponding to bending stretches. The influence of hydrogen bonding (band at 3500 cm^{-1}) resulted in the O – H stretch shift from 3350 cm^{-1}.

The TPS spectrum (Figure 1b) showed two new introduced stretch bands a C – H band at 2851 cm^{-1} and a C – O stretch at 1102 cm^{-1}, which results from the plasticizer. Table 5 shows the FT-IR major IR-absorption bands for starch, thermoplastic starch(TPS) and Starch dicarboxylic acid compound (SDCA).

It may be observed from Table 5 and figures 1a &1b that the plasticizer caused a shift slightly to the right of the O – H stretch and C – H stretch. This could be due to the fact that the bonds holding the starch molecules together are weakened as the strong action between hydroxyl groups of starch molecules are broken and substituted by hydrogen

bonds formed between the plasticizer and the starch during the plasticization process as a result of the heat and shear as the materials passed through the extrusion action. This agrees with the work of Xiao, et al (2004) who stated that the plasticizers could form the hydrogen bonds with starch, take the place of the strong action between hydroxyl groups of starch molecules, and make starch plasticizing.

The presence of the plasticizer occupying spaces between the starch polymer chains tempered with the bending vibrations thus, slightly increasing the wave number of the C – H bend.

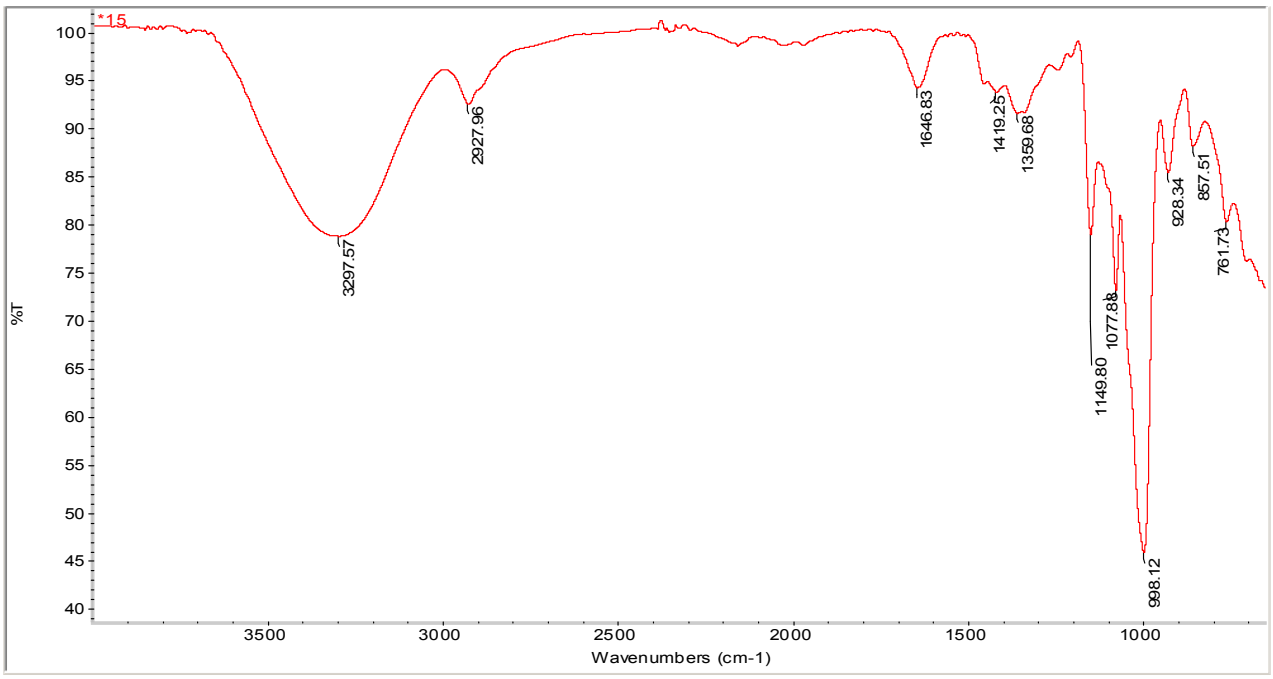


Figure 1(a) 100% Starch (STA) FT-IR Spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

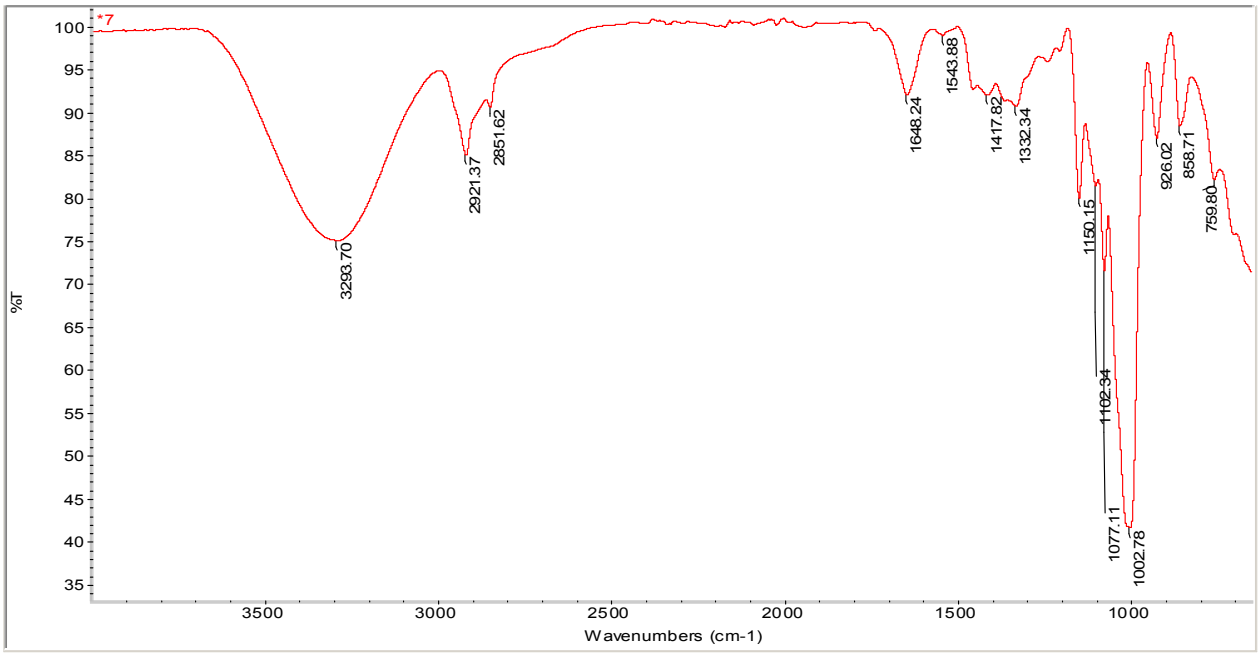


Figure 1(b) Thermoplastic Starch (TPS) FT-IR Spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

Figure 1c shows the appearance of ester bands; C = O stretch at 1738 cm^{-1} and C – O stretch at 1201 cm^{-1} indicating that there is a partial esterification when the starch reacts with the dicarboxylic (Oxalic) acid to form the SDCA. However the ester is only partially formed as indicated by the presence of O – H band at 3334 cm^{-1}.

The increase in the wave number of the O – H band is attributed to the hydrolyzing action of the carboxylic acid on the starch in the process of forming the SDCA. It could also be responsible for the high susceptibility of the SDCA to water and thus easier to degrade under microbial action as suggested in the soil burial test.

Zhang et al 2010 attributed the band at 1201 cm^{-1} to the coincidence of stretching vibration of hydroxyl group and C – O bond stretching. But the presence of C = O stretch at 1738 cm^{-1} in addition to the to the C – O stretch at 1201 cm^{-1} definitely suggests the association of -COOH group from the organic acid and –OH group from the starch to form an ester (O - C = O).

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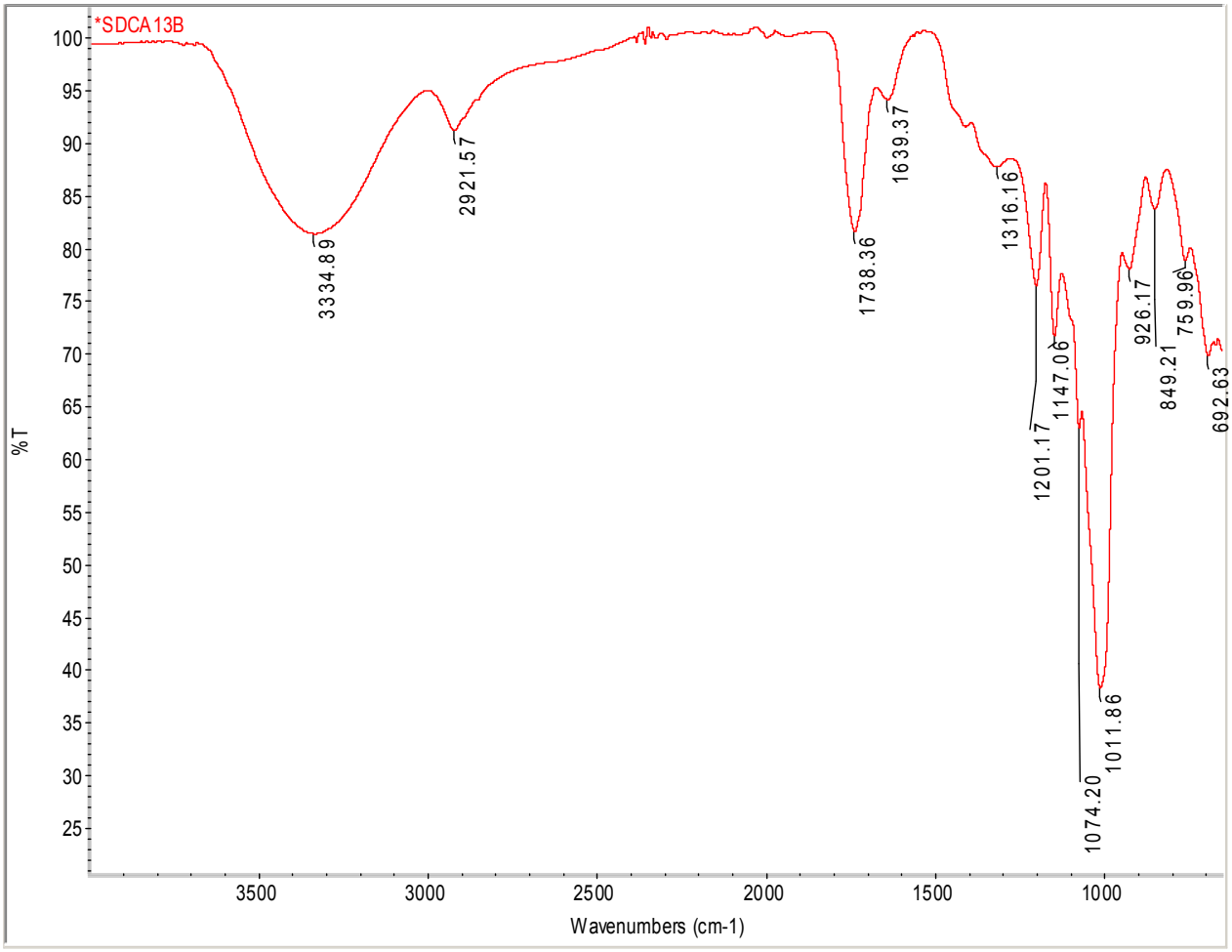


Figure 1(C) Starch – Oxalate (SDCA) FT-IR Spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

Table 5: FT-IR absorption for starch and it's derivatives

S/No	Functional Group	Absorption bands (cm^{-1})		
		Starch	TPS	SDCA
1	O – H stretch	3297	3293	3334
2	C - H stretch	2928	2851, 2921	2921
3	C – C stretch	1646	1648	1639
4	C – O stretch	998, 1077, 1150	1002, 1077,1102 1150	1011, 1074, 1147, 1201
5	C = O band (ester band)	_____	_____	1738
6	O – H bend	1419	1417	1418
7	C – H bend	928, 1359	926, 1332, 1543	926, 1316
8	C – C bend	761, 857	759, 858	692, 759, 850

From Table 5, the effect of the plasticizer (Glycerol) on potato starch is shown by the appearance of additional C-H and C-O stretches at 2851 cm^{-1} and 1102 cm^{-1} respectively, and decreasing O - H wave number rendering the thermoplastic starch (TPS) to hydrophobicity.

The Starch dicarboxylic acid (SDCA) exhibited higher O – H vibrational frequencies of IR radiation as compared to both the native starch and the thermoplastic starch, which is attributed to the hydrolyzing action of the dicarboxylic acid, rendering it more prone to water solubility, the partial ester formation is indicated by the C-O and C=O stretches at 1201 cm^{-1} and 1738 cm^{-1} respectively. The low value of the C – C stretch could be responsible for the brittleness properties of the SDCA as suggested be SEM (Plate IId).

The increase in wave number of the C – O band from 998 cm^{-1} (STA) to 1002 cm^{-1} (TPS) and 1011 cm^{-1} (SDCA) may be attributed to the resonance action of the acetal (O – C - O) group of the starch molecule during reaction of the starch with the plasticizer and the organic acid respectively.

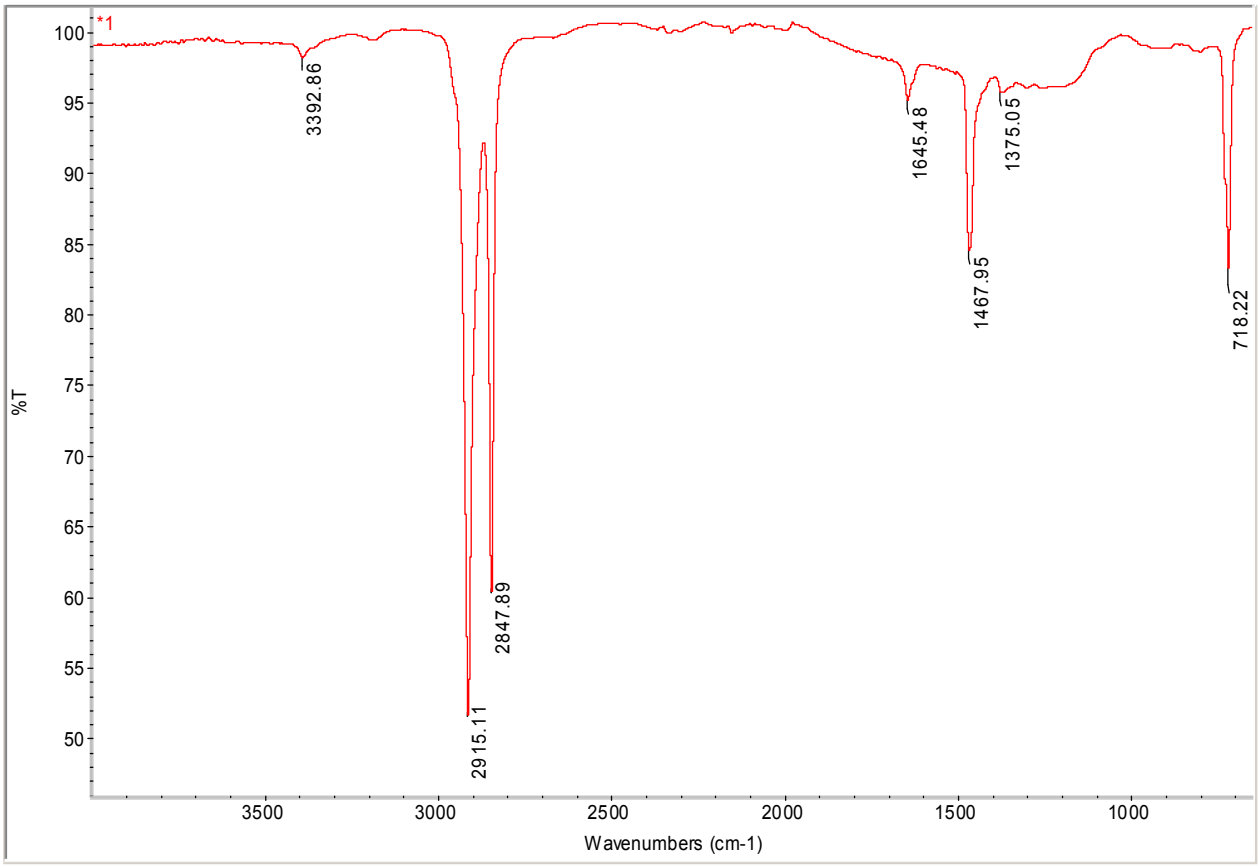


Figure 1(d) Low density polyethylene (LDPE) FT- IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

The LDPE spectrum(figure 1d) showed prominent C – H stretches at 2847cm^{-1} and 2915cm^{-1} regions representing both symmetric and asymmetric values. The C – H bending is indicated at between 1370 cm^{-1} – 1650 cm^{-1}. The weak band at 3392 cm^{-1} represents the C – C stretch, while the C – C bend is indicated at 718 cm^{-1}

Figures 1(e) to 1(i) are the FT- IR spectra of LDPE/TPS composites. The binding of TPS with LDPE is indicated by the appearance of an Alcohol absorption bands though initially weak (figure 1e) at 3188 cm^{-1} for the LDPE/TPS (90/10) as the concentration of the TPS increases in the composite, more absorption bands are introduced such that broad and prominent alcohol absorption bands are observed at 3390 cm^{-1}, 1250 cm^{-1} and 1019 cm^{-1} regional domains (figure 1i) for the LDPE/TPS (50/50). The major absorption bands of the LDPE remains. However, the weak C – C absorption band disappeared or overlapped by the stronger O – H absorption band.

The insignificant appearance of the absorption bands shown by the LDPE/TPS composites at low concentration of the TPS indicates low vibrational frequencies of the TPS molecules as they are being super imposed by the LDPE molecules, however as more molecules enters the system the TPS molecular vibrations increases and thus the phase separation between the two materials prevail more prominently as suggested by SEM micrographs plate II (e – i).

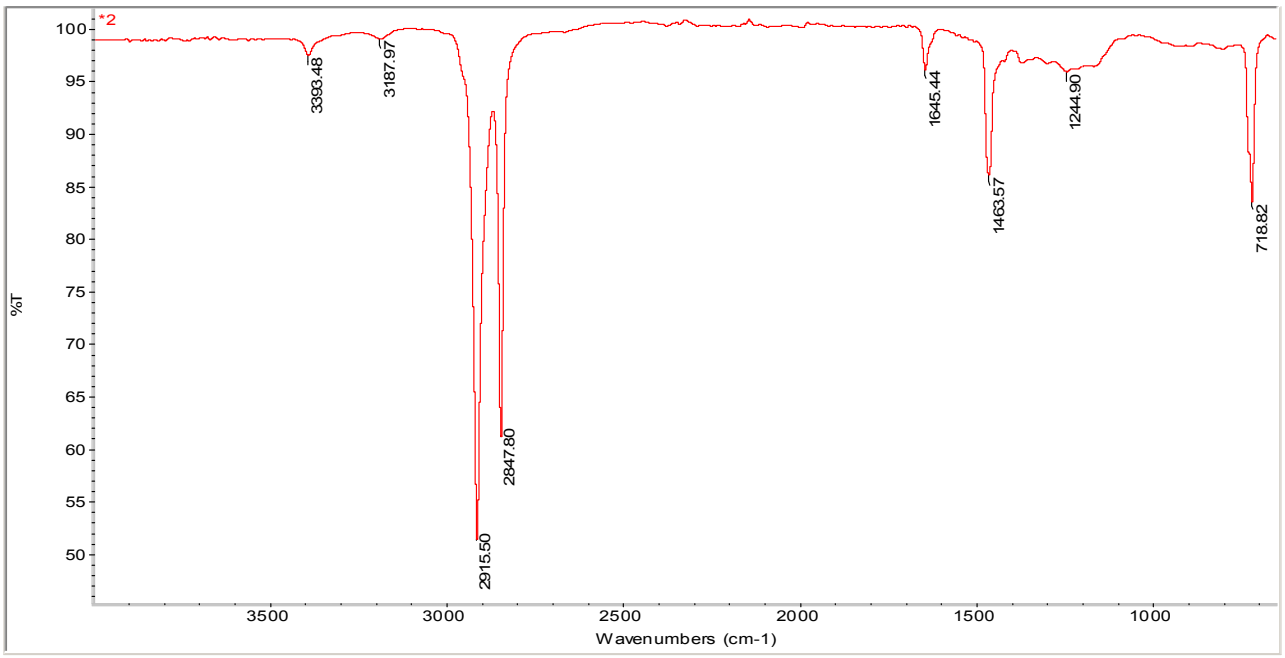


Figure 1(e) LDPE/TPS (90/10) FT-IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

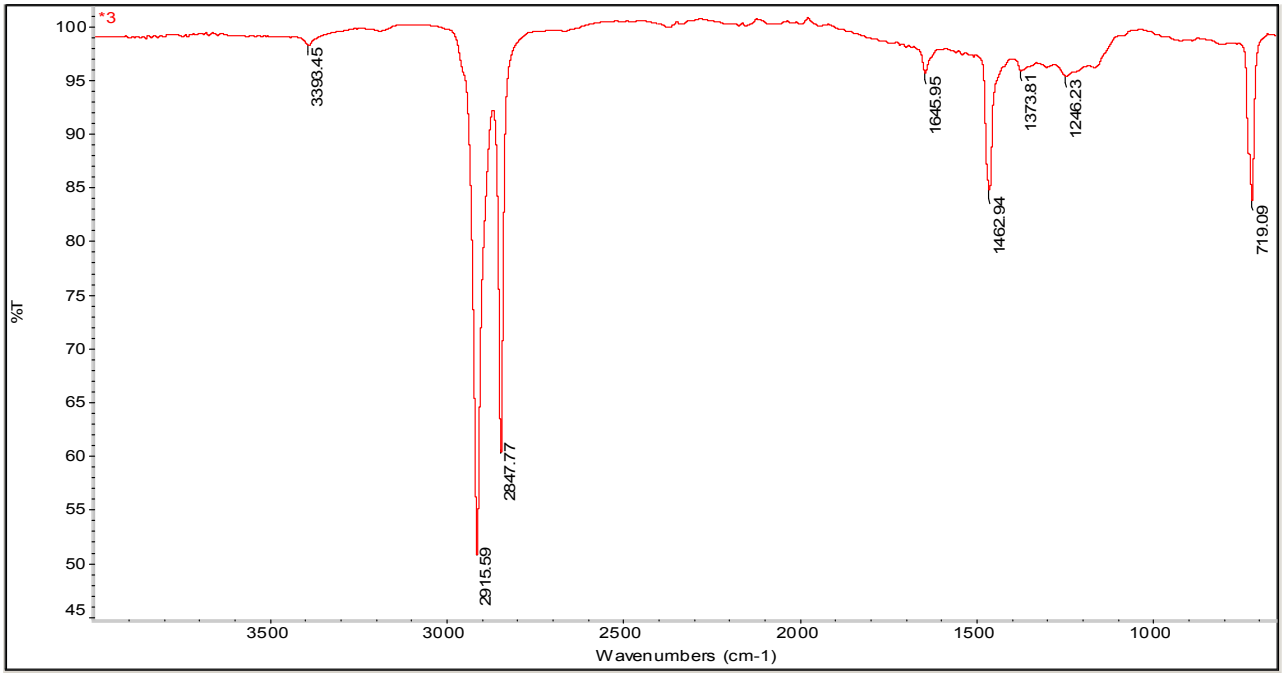


Figure 1(f) LDPE/TPS (80/20) FT-IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

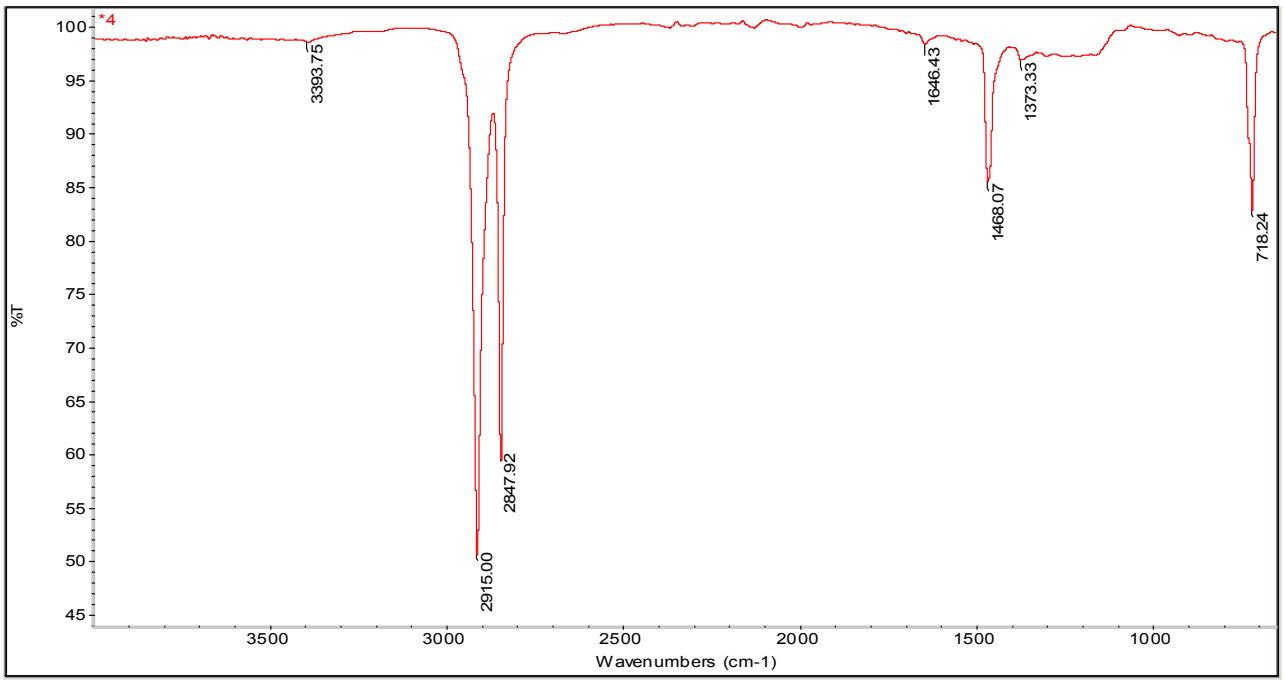


Figure 1(g) LDPE/TPS (70/30) FT-IR spectrum(showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

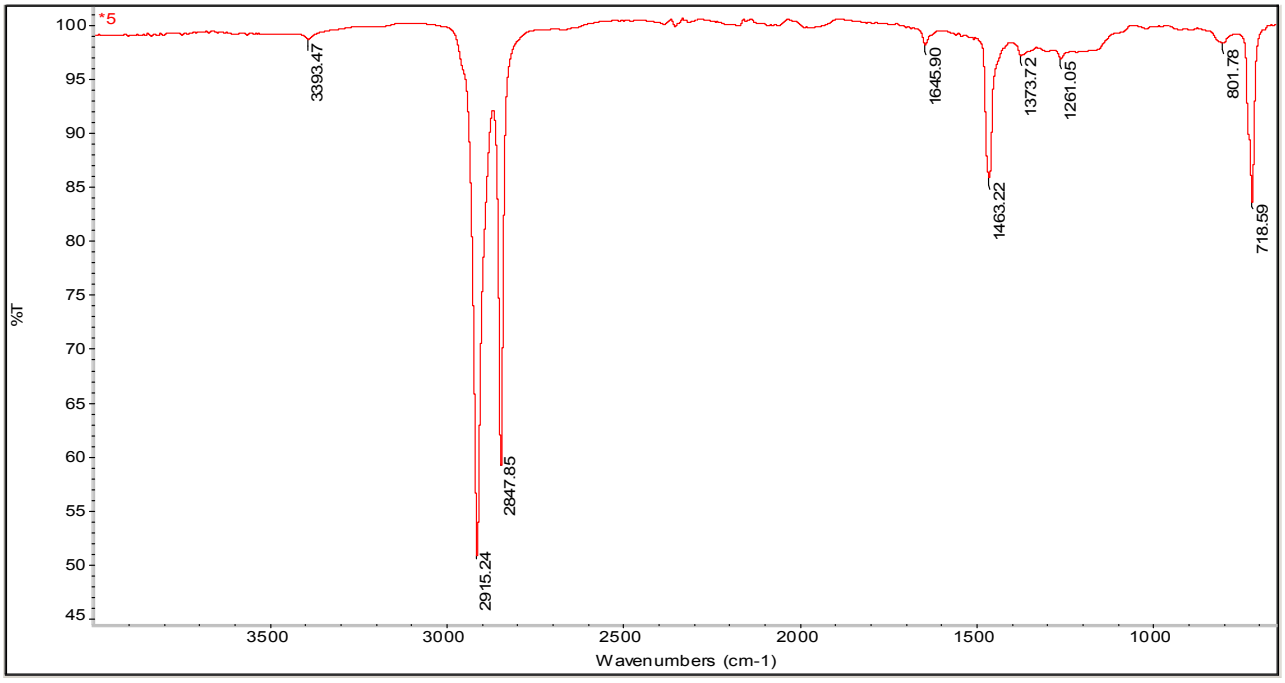


Figure 1(h)LDPE/TPS (60/40) FT-IR spectrum(showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

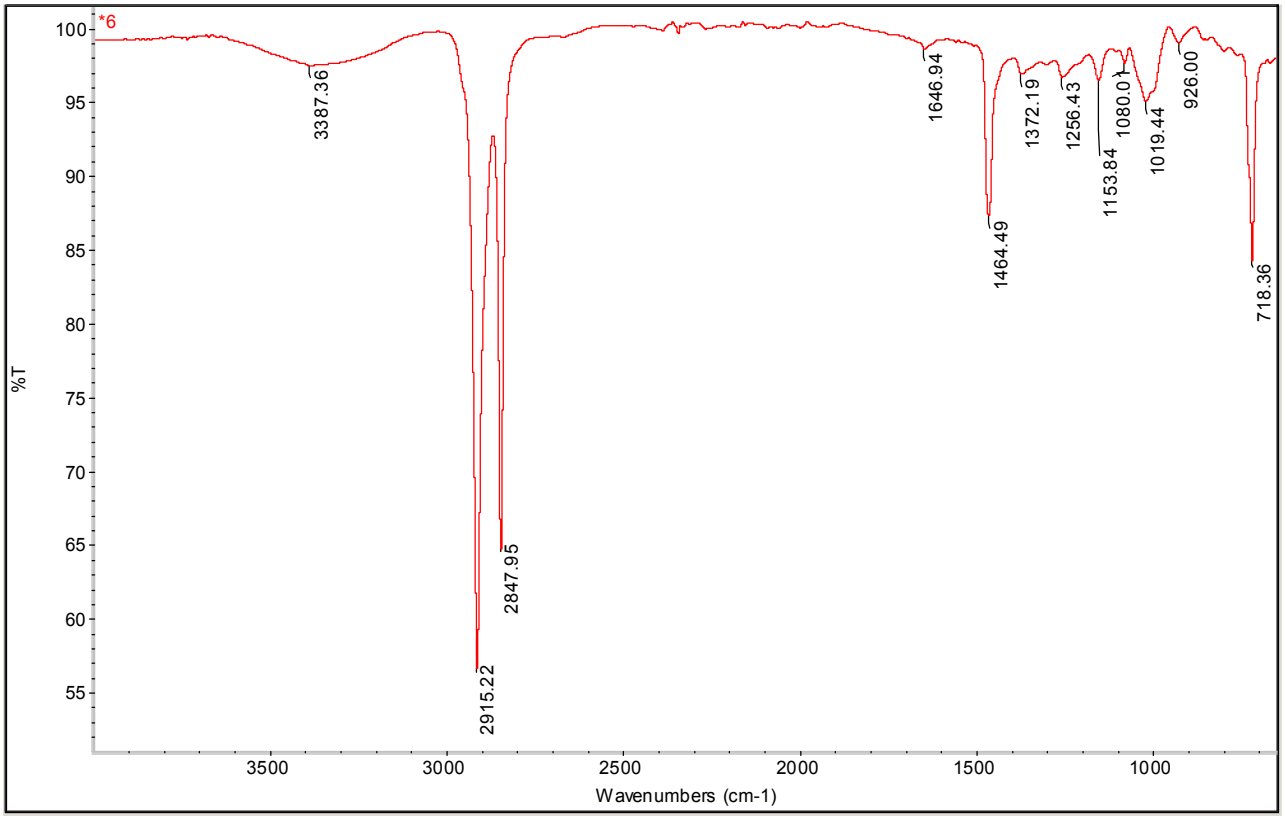


Figure 1(i)LDPE/TPS (50/50) FT- IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

The FT-IR spectra (figure 1j – 1n) characterized the LDPE/SDCA composites. Figure 1(j) exhibited C – H stretches at 2847cm^{-1} and 2915cm^{-1},corresponding to LDPE major C – H stretches, the O –H absorption bands at 3305 cm^{-1} and1080 cm^{-1}, C – O band at 1154 cm^{-1} from the starch dicarboxylic acid, and various other bands associated with bending vibrations.

The O – H wave number increases gradually from 3305 cm^{-1} to 3382 cm^{-1} as the SDCA concentration increases in the composites thus indicating increase in vibrational frequencies at this point with increasing filler content. This could be responsible for high susceptibility of the LDPE/SDCA to water and microbes during the water absorption and soil burial tests respectively.

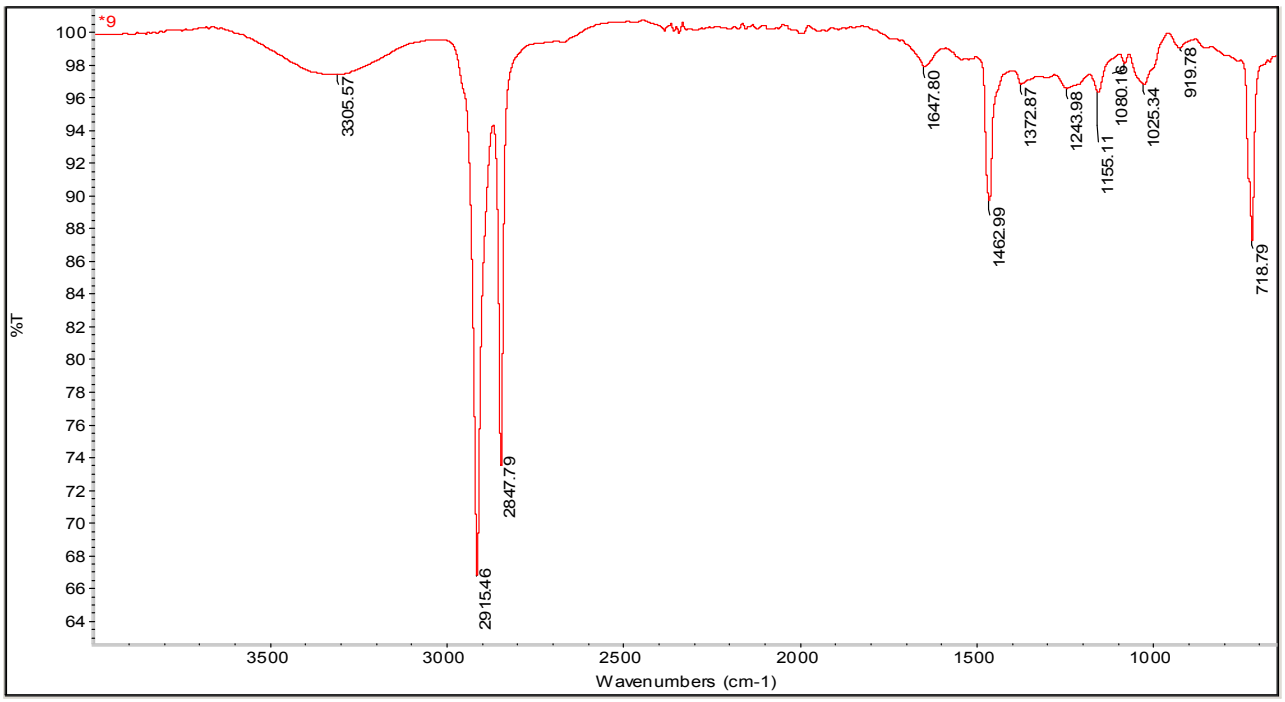


Figure 1(j)LDPE/SDCA (90/10) FT- IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

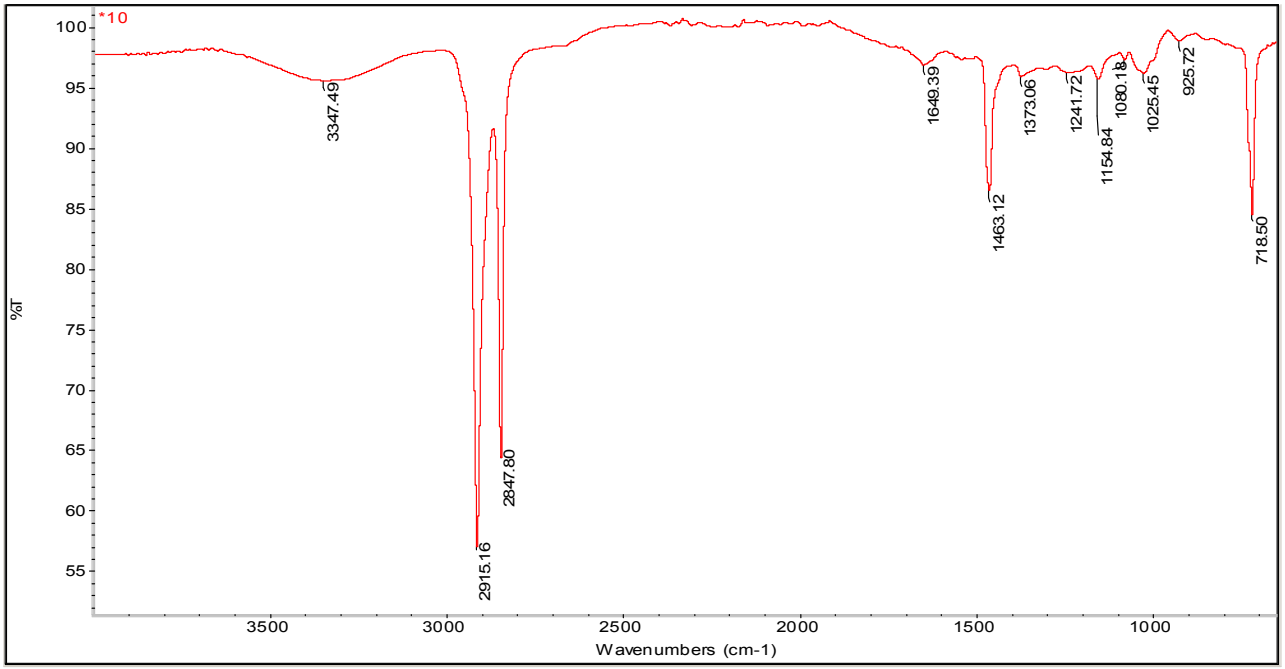


Figure 1(k)LDPE/SDCA (80/20) FT- IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

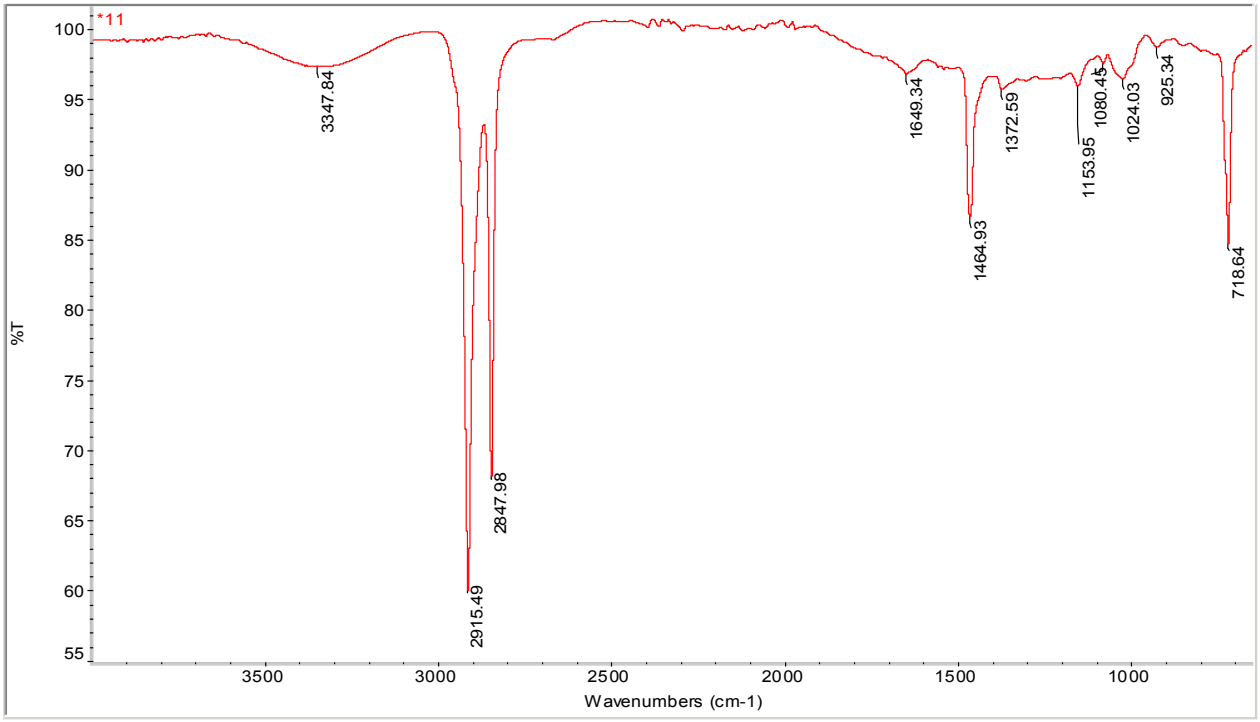


Figure 1(L) LDPE/SDCA (70/30) FT-IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

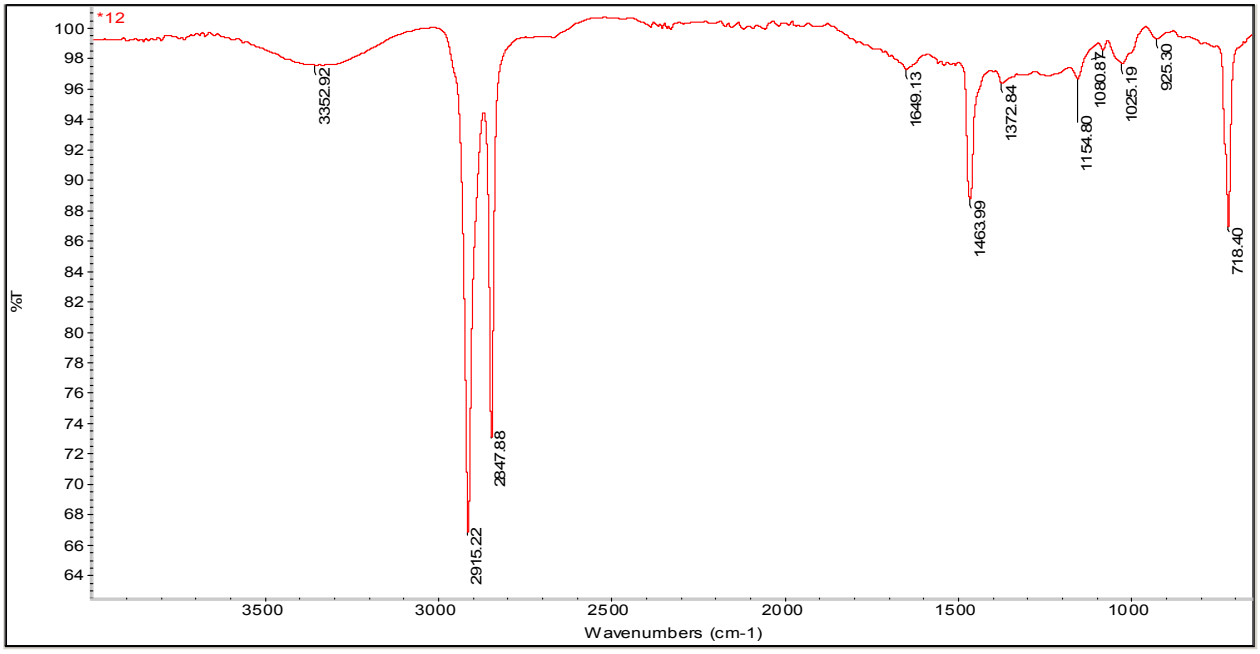


Figure 1(m)LDPE/SDCA (60/40) FT-IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

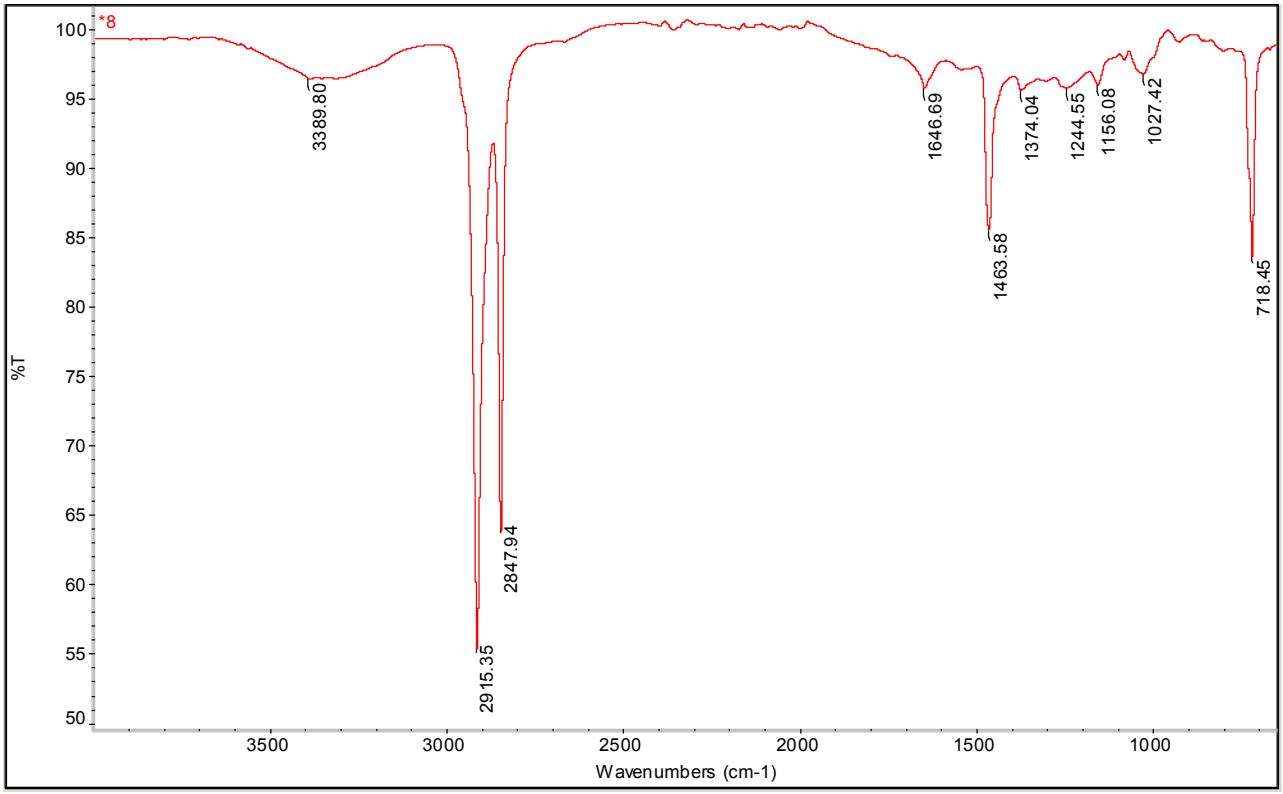


Figure 1(n)LDPE/SDCA (50/50) FT-IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

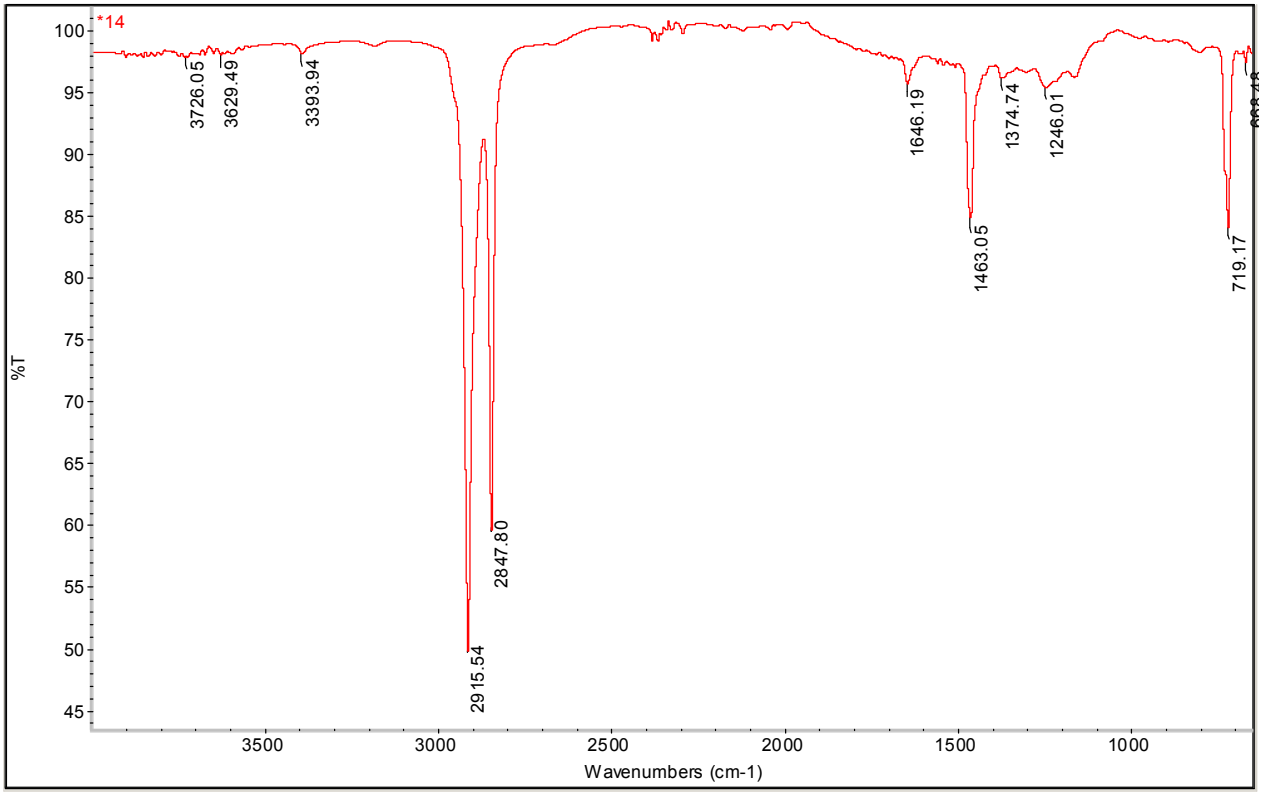


Figure 1(p)LDPE/STA (80/20) FT - IR spectrum (showing the frequencies of IR radiation absorbed and the % of the incident light transmitted)

The FT – IR spectrum of the LDPE/STA figure 1p shows a new C – O stretch band introduced by the starch at 1246 cm^{-1}. Comparing with figure 1a it will be observed that the complexation of the starch with the LDPE causes a shift to the left of C – O band from 1150 cm^{-1} to 1246 cm^{-1}.

However, the major C – H bands for the LDPE are not tempered. Weak bands indicating some activities appeared on the region between 3620 cm^{-1} to 3720 cm^{-1} which could be associated with both O – H stretch band and hydrogen bonding between the starch molecules.

4.2 Scanning Electron Microscopy (SEM)

The surface morphology of the samples were observed using Scanning Electron Microscope Jeol JSM 7600F.

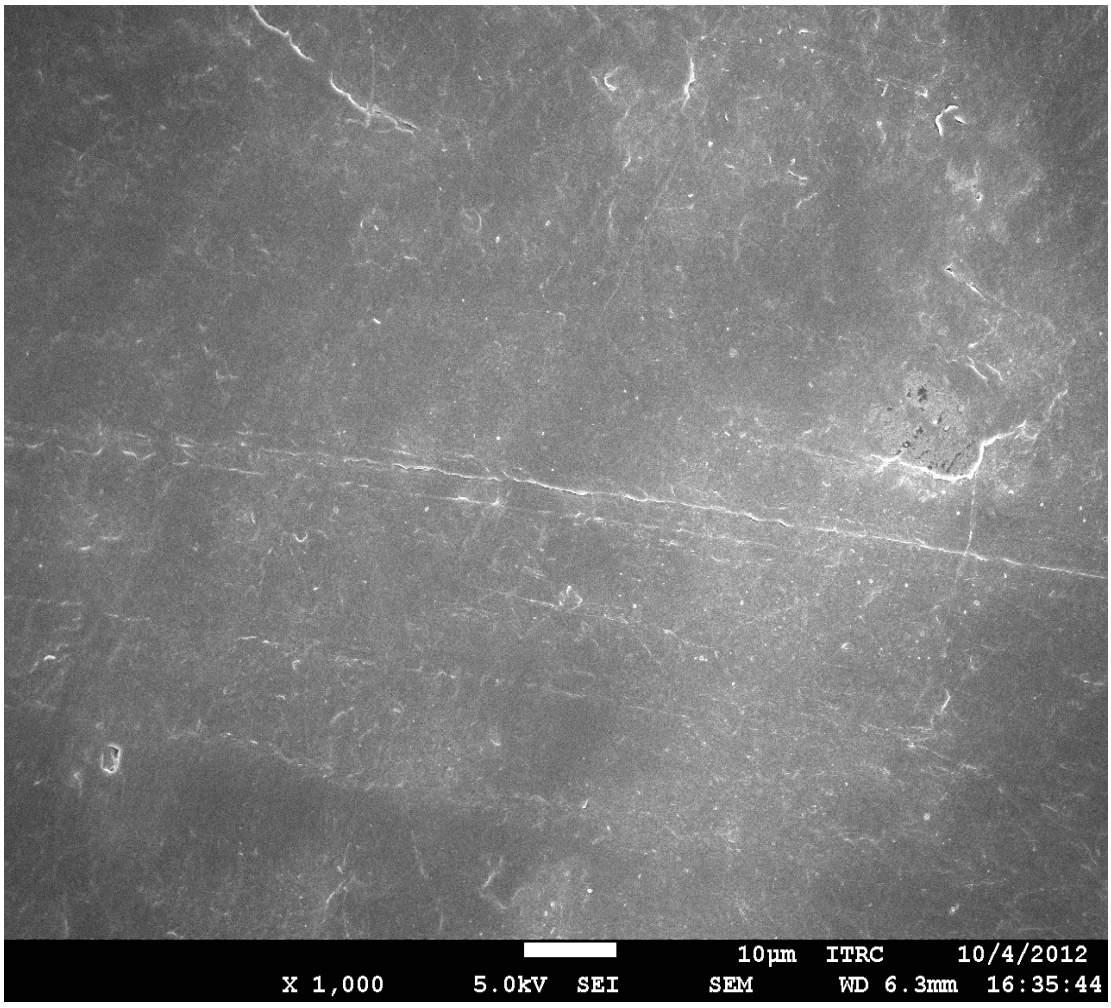


Plate II (a) Scanning electron micrograph of 100% Low density polyethylene (LDPE)

The LDPE (Plate IIa) shows a flat continuous surface

Plate IIb shows the mophological structure of starch granules, the structure indicates oval shaped granules of various sizes. The TPS micrograph (Plate IIc) indicated a rough surface with patches dispersed all over the surface. During plasticization, as the starch and the plasticizer passes through the shearing process of the extruder, the starch granular crystalline structure is disrupted, and fragmented, the bonds between the starch polymer chains (1 → 6 linkages) are broken so that hydrogen bonds are formed between the plasticizer and the starch molecule, thus resulting in the breaking down of the distinct oval shaped granules of the starch to patches of various sizes as shown in Plate IIc.

Plate IId shows the morphology of the starch – ester (SDCA) which is characterized by granular structure of various shapes and sizes dispersed all over the surface. These granules appear swollen which could be attributed to the action of the dicarboxylic acid on the starch granules, there by gelatinizing the starch and partially forming an ester. The micrograph shows line domains all over the surface indicating cracks resulting from weak intermolecular forces, which may be mainly responsible for the poor mechanical properties.

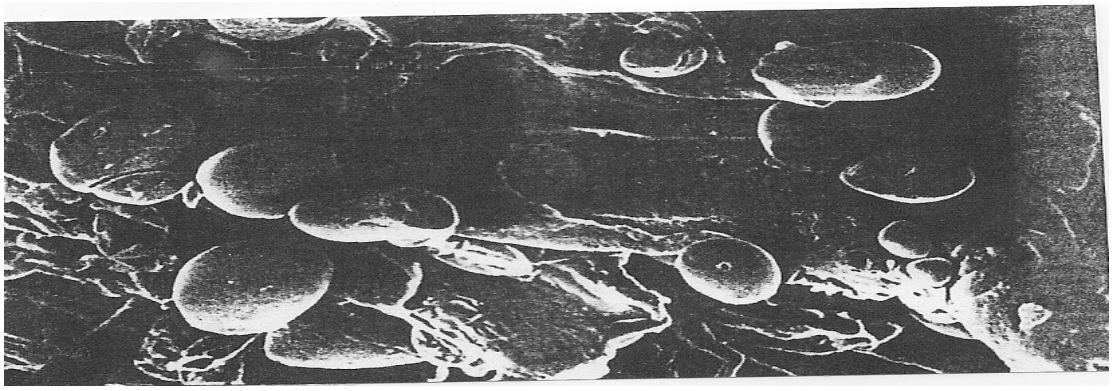


Plate IIb Scanning electron micrograph of fractured surface of sago starch (15 wt %) – LDPE composite (Nawang et al, 2001)

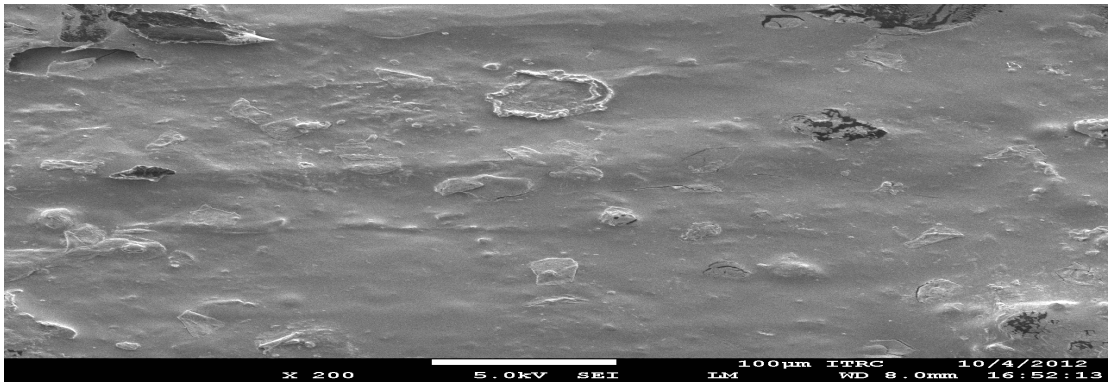


Plate II(c) Scanning electron micrograph of 100% Thermoplastic starch(TPS)

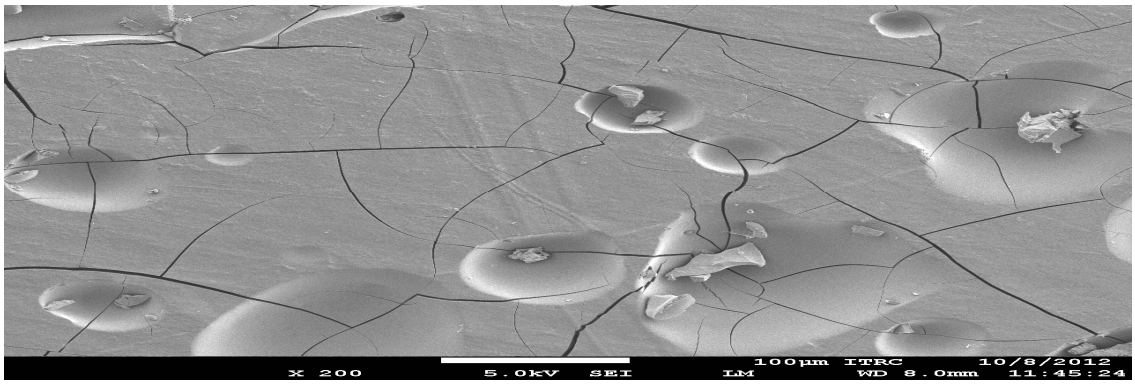


Plate II(d) Scanning electron micrograph of 100% Starch dicarboxylic Acid compound (SDCA)

Plates IIe, f, g, h and i, shows the micrographs of LDPE/TPS composites. In each case the LDPE was melt blended with TPS, such that the LDPE formed the matrix filled with the TPS as the disperse phase. The composites shows relatively fair homogeneous flat surface. The thermoplastic starch may be observed as a whitish dispersion on the LDPE surface that tends to form some domains which may be indicating phase separation.

It may be observed that as the TPS concentration increases in the composites more surface area of the LDPE is covered and the line domains becoming clearer. The LDPE/TPS (90/10) (Plate IIe) appeared flat and smooth with some what whitish agglomerates towards the center, this whitish starch appearance are observed to occupy more surface area on LDPE/TPS (80/20) (Plate IIf), The line domains starts to appear on LDPE/TPS (70/30) (Plate IIg) surface showing small patches and small irregular line domains particularly towards the center. These lines become more apparent and prominent on the LDPE/TPS (60/40) (Plate IIh) and LDPE/TPS (50/50) (Plate IIi). The line domain indicates phase separation since the TPS and The LDPE are not miscible.

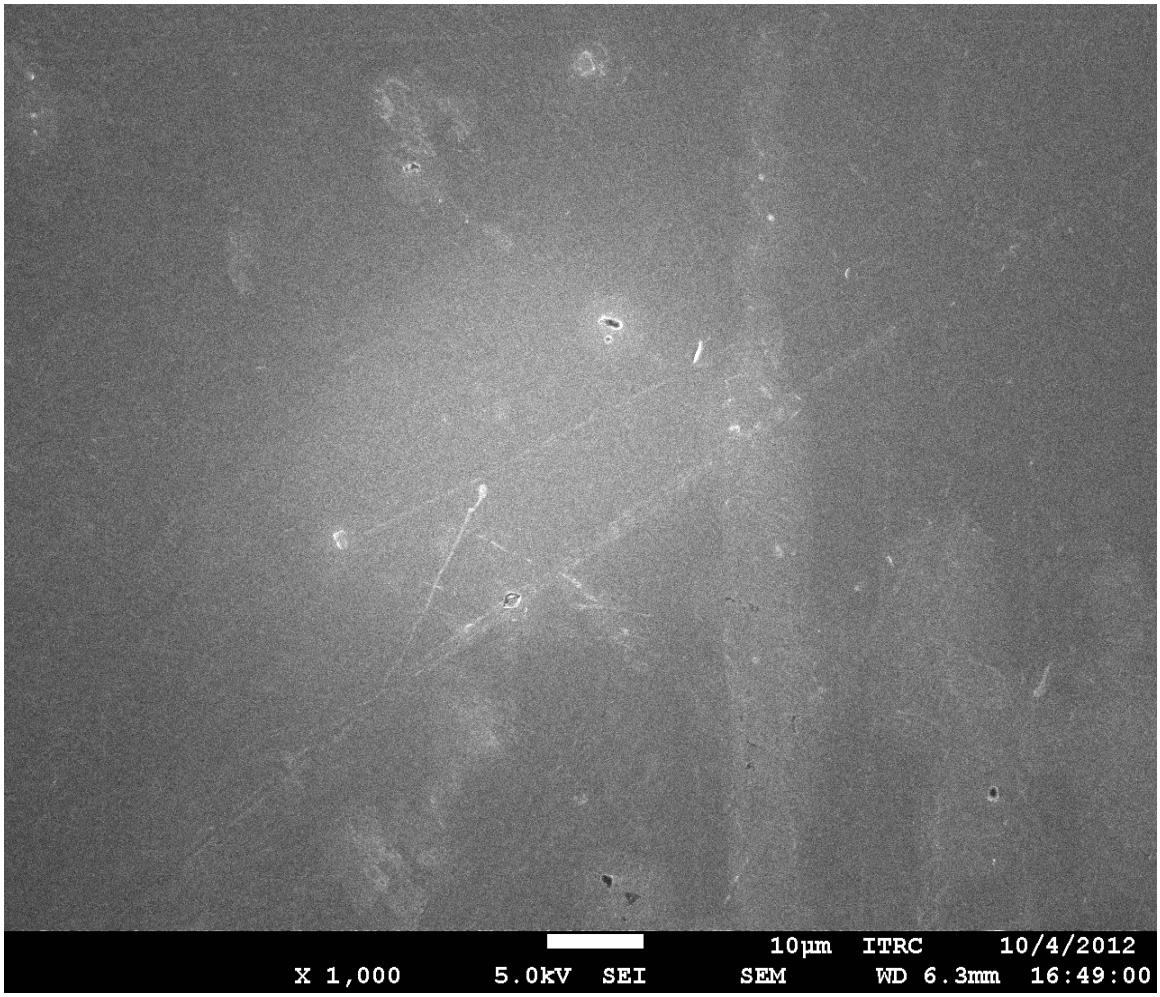


Plate II(e) Scanning electron micrograph of LDPE/TPS (90/10)

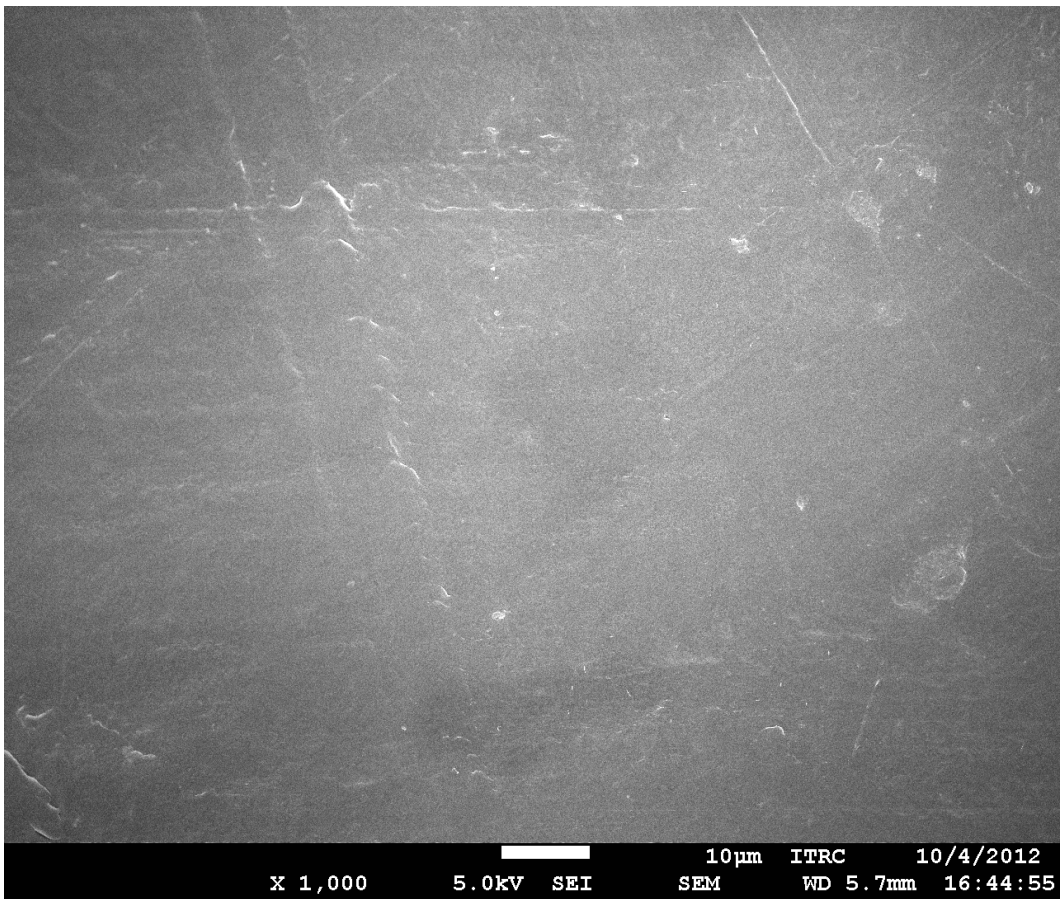


Plate II(f) Scanning electron micrograph of LDPE/TPS (80/20)

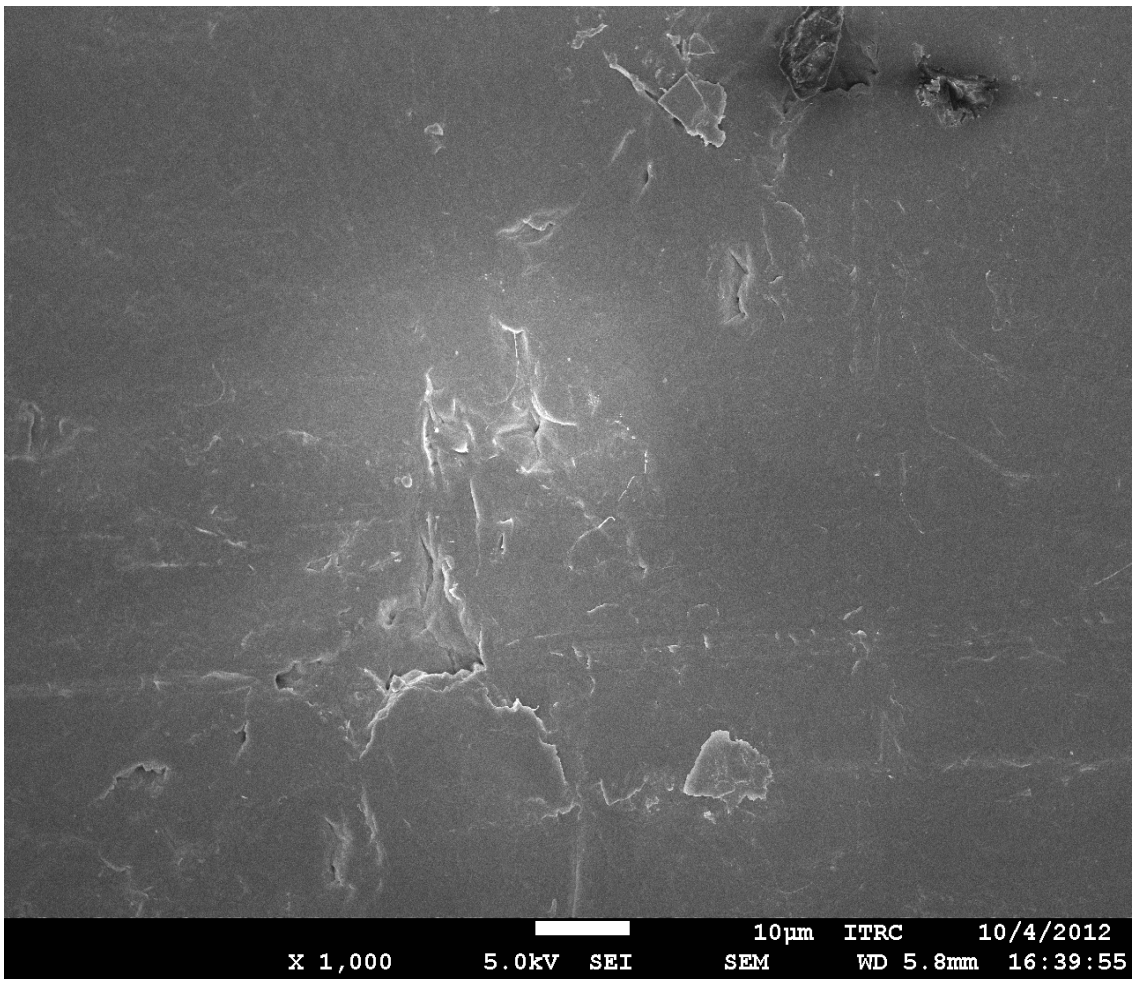


Plate II (g) Scanning electron micrograph of LDPE/TPS (70/30)

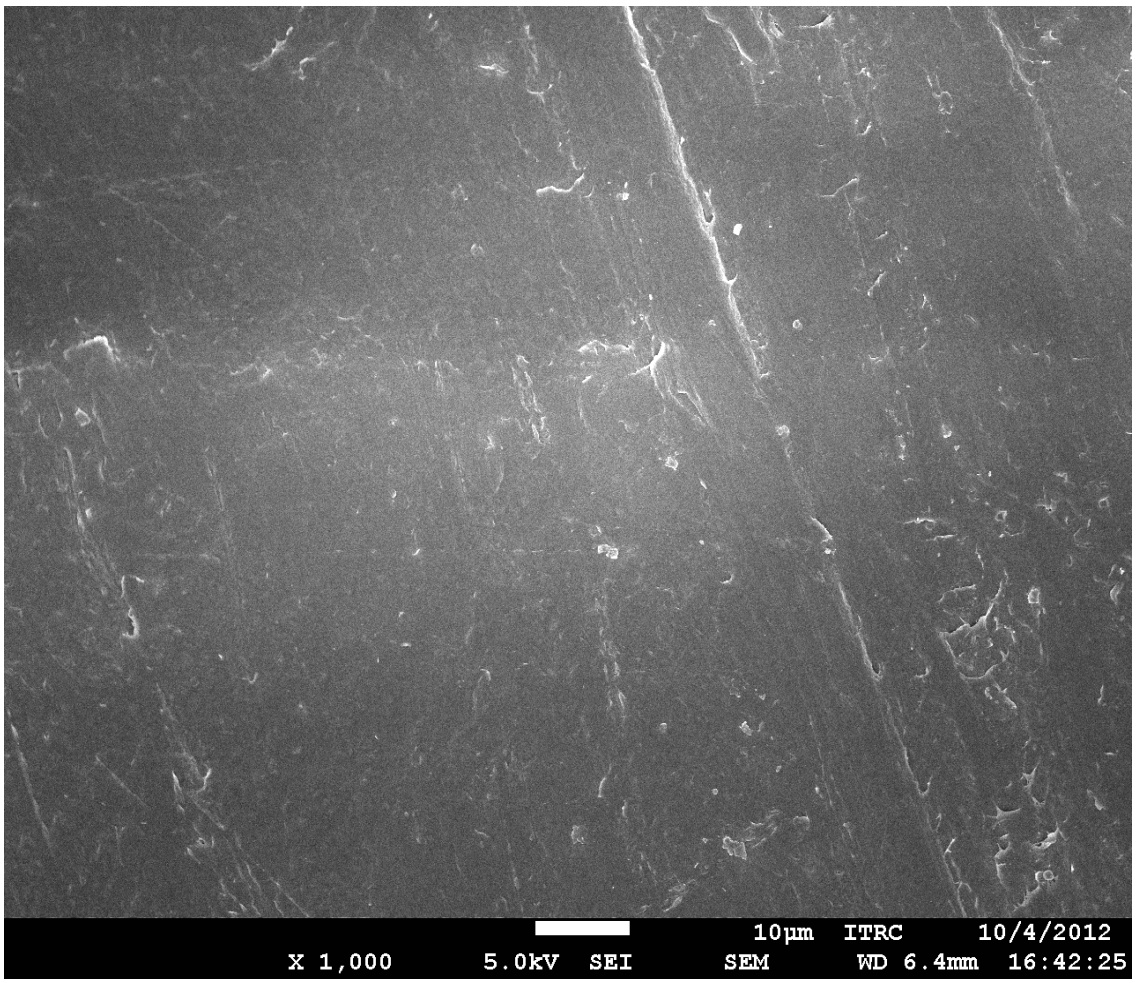


Plate II(h) Scanning electron micrograph of LDPE/TPS (60/40)

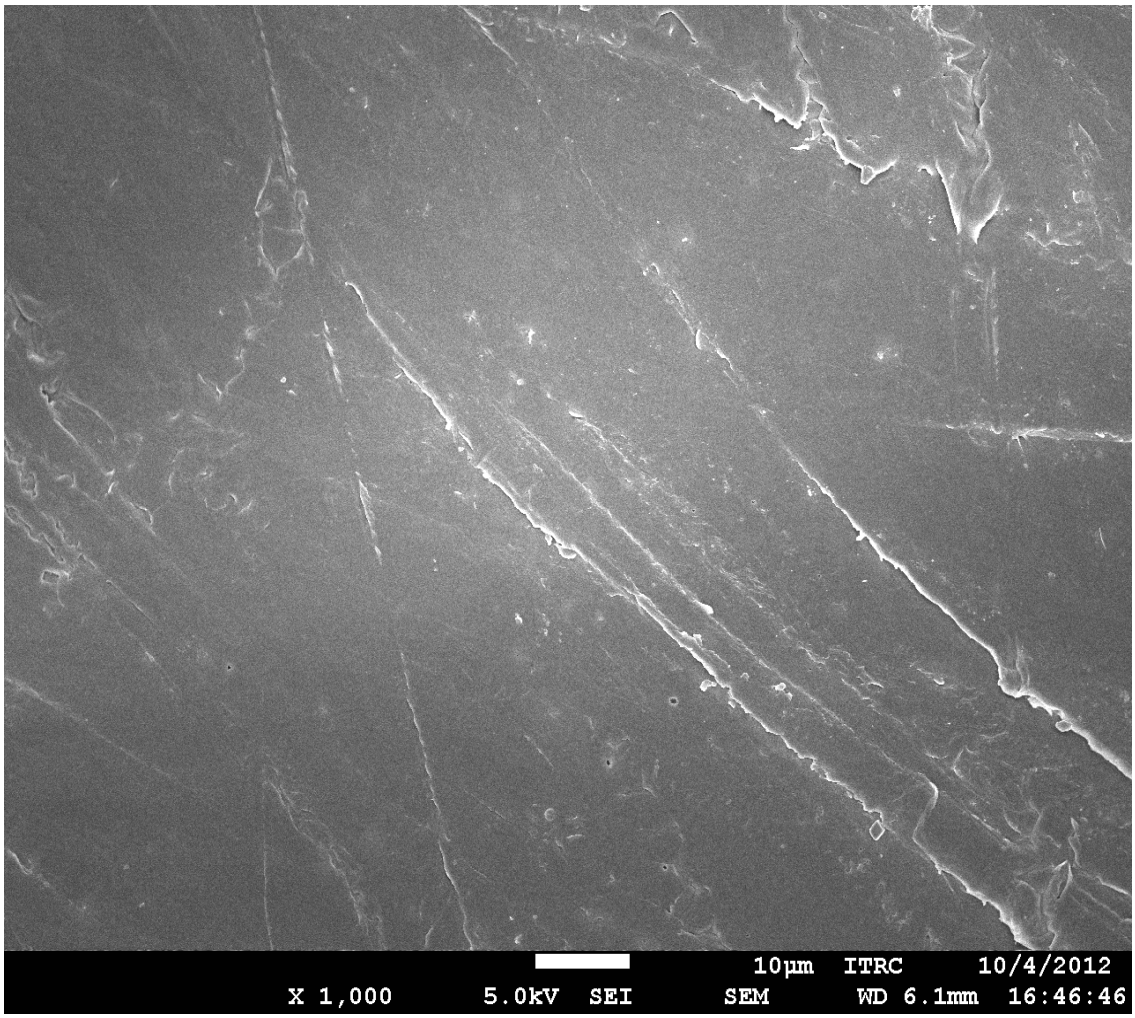


Plate II (i) Scanning electron micrograph of LDPE/TPS (50/50)

Plates IIj, k, L, m and n shows the micrographs of LDPE/SDCA composites. Here also the LDPE is the continuous phase and the SDCA the disperse phase. The composites shows more or less even distribution of the filler on the matrix as the molten SDCA is not

so viscous but tacky, as it spreads within the LDPE it tends to stick. The physical appearance of the composite is whitish and brittle. The brittleness properties increases with increase in the filler content, It may be suggested that as the SDCA is being spread by the action of the two roll mill, i.e heat and pressure, it goes in between the LDPE molecular chains and branches and stuck, thereby destructing the hydrogen bonding between the intermolecular chains/branches of the LDPE. This phenomenon is more prominent as filler load increases.

Physical examination of the composites and close comparism of the SEM micrographs of corresponding composites of the LDPE i.e LDPE/TPS (90/10) with LDPE/SDCA (90/10) etc, it will be observed that the LDPE/SDCA has a better physical and morphological appearance in terms of surface flatness and homogeneity than LDPE/TPS for 90/10 and 80/20 ratios, while the reverse is the case for higher ratios, thus it will be expected that the mechanical properties will have a similar effect. This is due to the fact that the SDCA is more hydrophilic as compared to TPS. The hydrolyzing action of the acid on starch make SDCA more susceptible to moisture as compared to TPS which tends towards hydrophobicity due to plasticization of the starch.

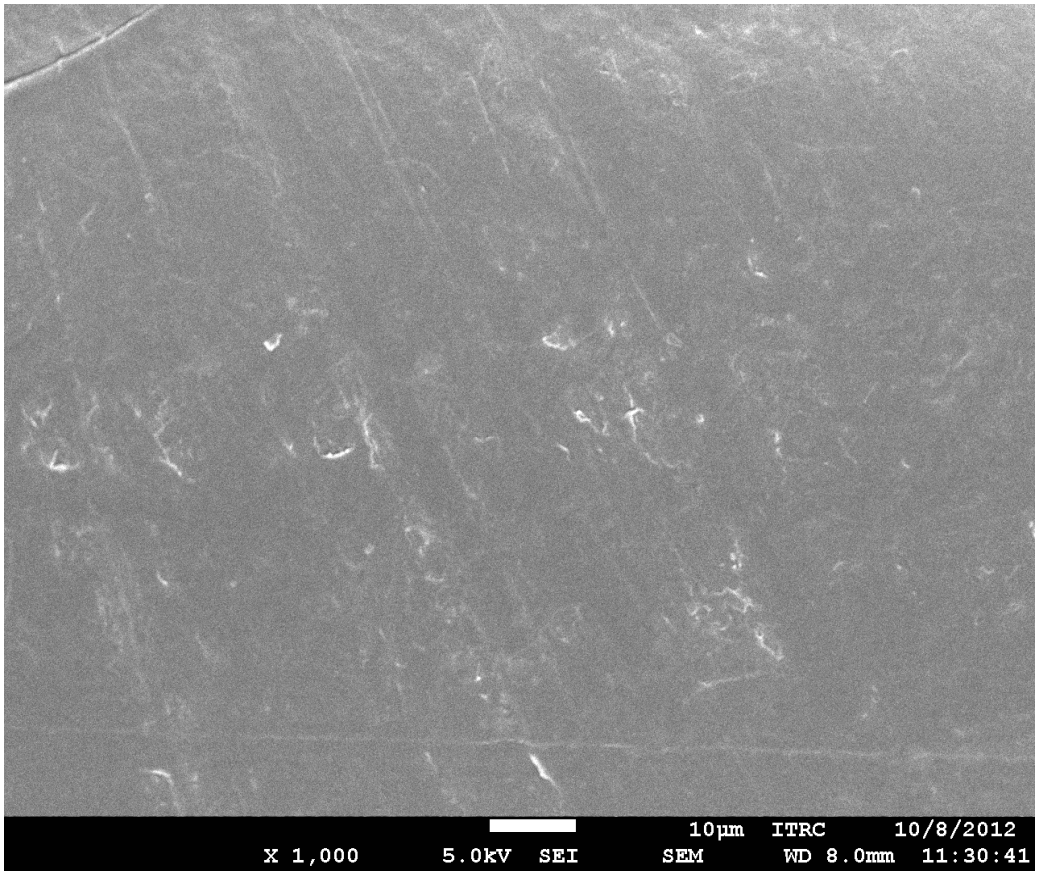


Plate II(j) Scanning electron micrograph of LDPE/SDCA(90/10)

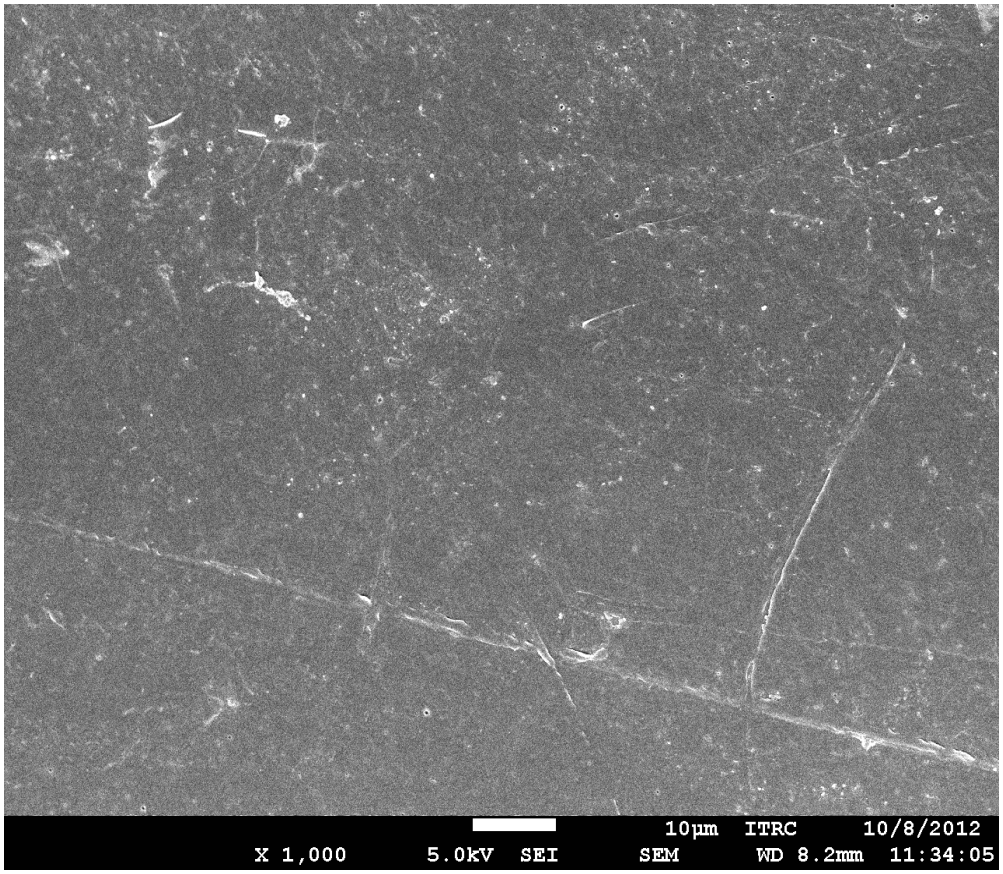


Plate II(k) Scanning electron micrograph of LDPE/SDCA(80/20)

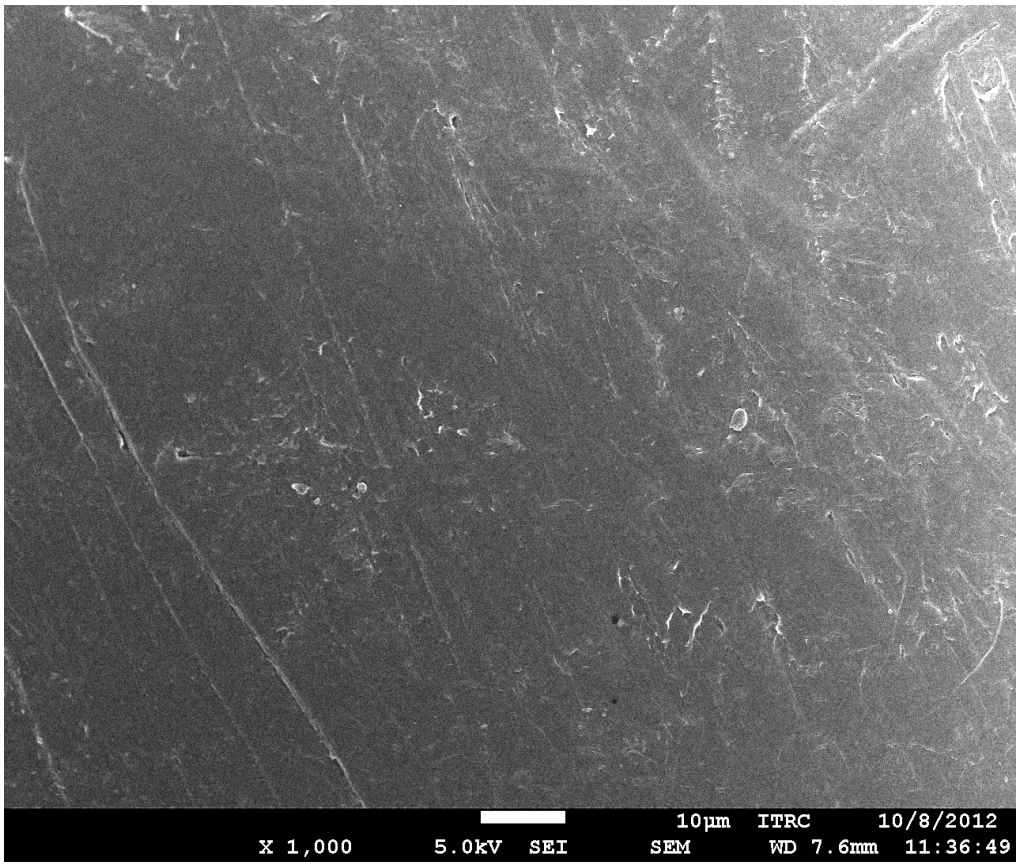


Plate II (L) Scanning electron micrograph of LDPE/SDCA(70/30)

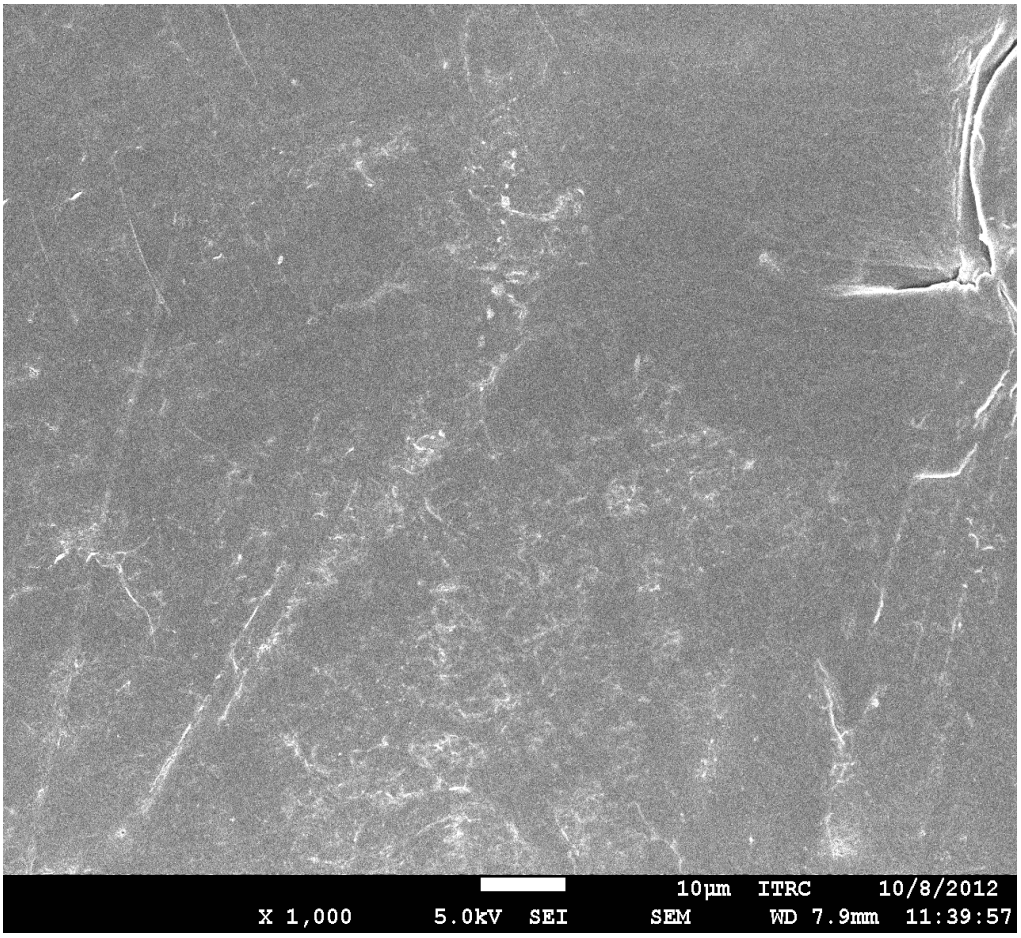


Plate II (m) Scanning electron micrograph of LDPE/SDCA(60/40)

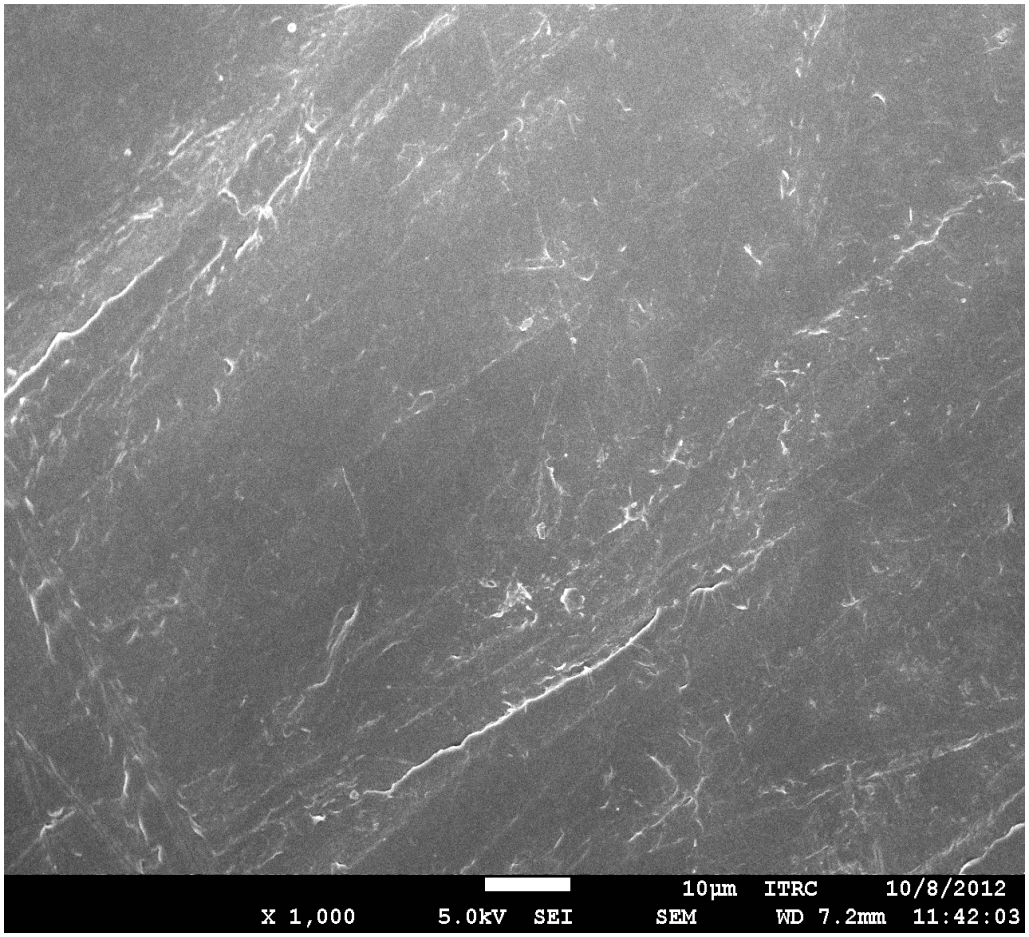


Plate II (n) Scanning electron micrograph of LDPE/SDCA(50/50)

4.3 Wide Angle X- Ray Diffraction

The degree of crystallinity of the samples were studied using a Bruker AXS X-ray diffractometer with nickel – filtered CuKα rays (λ = 1.542 A^o), employing Bragg's

equation, $\lambda = 2d\sin\theta$, where λ is the wavelength of the X – ray radiation used, d is the spacing between diffractional lattice planes, and θ is the measured diffraction angle, the crystallographs of the samples were obtained and shown in figure(s) 2a – p, from which the degree of crystallinity of the composite samples were estimated using the following equation.

Percentage of crystallinity ($\mathbf{X_C}$ %) is measured as ratio of crystalline area to Total area.

$$X_C = \frac{A_C}{A_a + A_C} x100\%$$

Where

A_C= Area of crystalline region

A_a = Area of amorphous region

X_C = Percentage of crystallinity

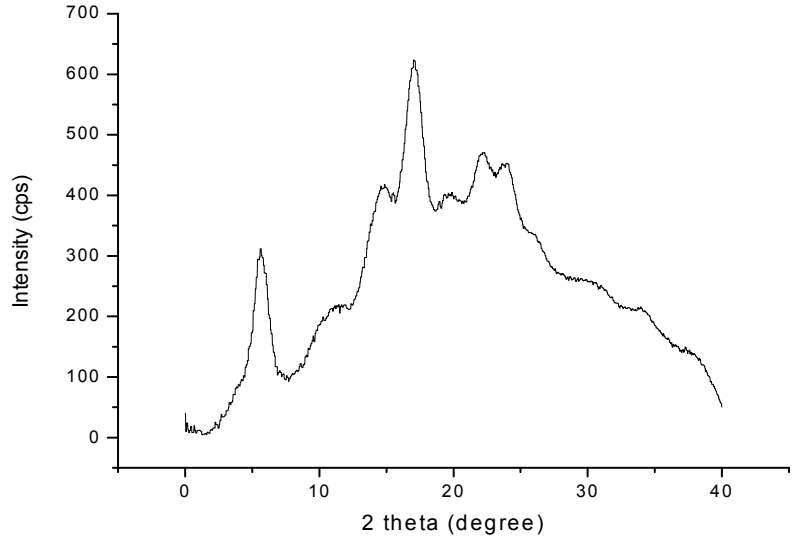


Figure 2a: Wide angle X-ray diffraction crystallograph of 100% Starch (STA)

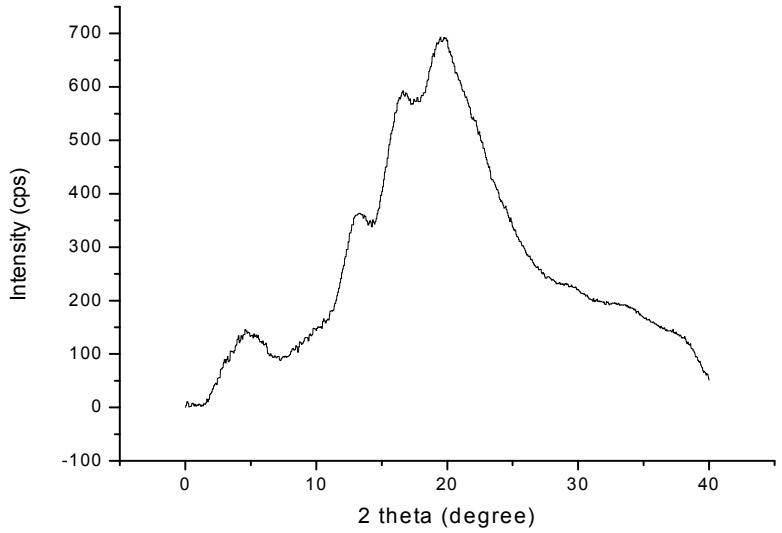


Figure 2b: Wide angle X-ray diffraction crystallograph of 100% Thermoplastic – starch (TPS)

The starch pattern (Figure 2a) exhibited two major peaks at $2\theta \approx 5^{o}$ and 17^{o} and an unresolved doublet at a $2\theta \approx 22^{o}$ and 24^{o}. This agrees with the work of Zhang et al (2010).

However, when the starch is plasticized, the thermoplastic starch pattern (figure 2b) shows some what modified structure, its major peak is indicated at $2\theta \approx 20^{o}$. This is due to the stretching effect of the polymer resulting from the high shear process of the extruder and the embedment of the plasticizer in between the polymer chains. This new crystalline pattern indicated in figure 2b is due to the plasticization process, the hydrogen bonds are formed between starch and the plasticizer molecules while the stronger hydroxyl bonds between the starch molecules are being broken as suggested earlier by the FTIR results. This phenomenon is observed and confirms the micrograph of the thermoplastic starch plate 1c, which suggested improve in hydrophobicity of the material.

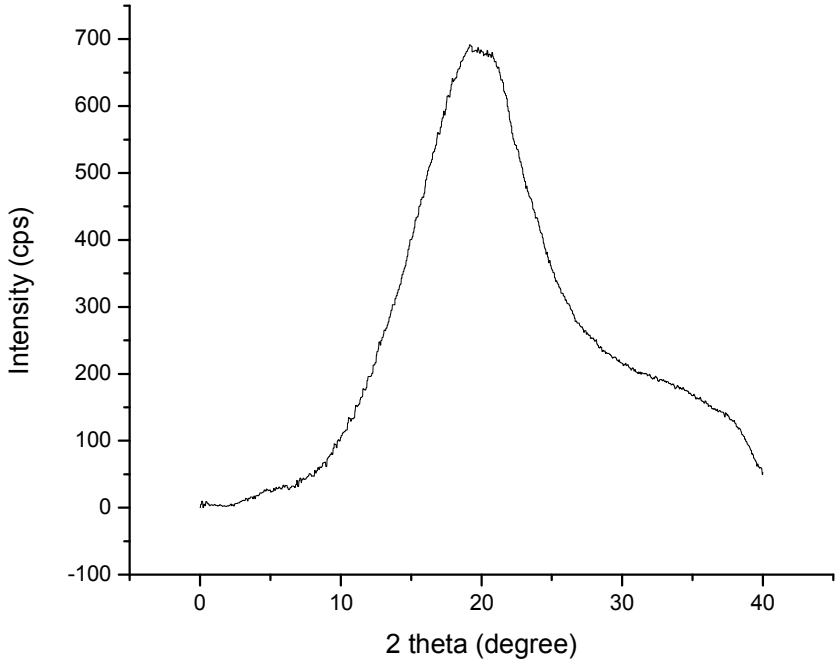


Figure 2c: Wide angle X-ray diffraction crystallograph of 100% Starch dicarboxylic acid compound (SDCA)

Figure 2c is the X – ray pattern of starch treated with dicarboxylic (Oxalic) acid. The SDCA displayed a completely different crystalline structure as compared to figure 2a, showing a broad flat X –ray pattern with a peak at $2\theta \approx 20^{o}$, the broadness of the pattern could indicate a material with an amorphous structure.

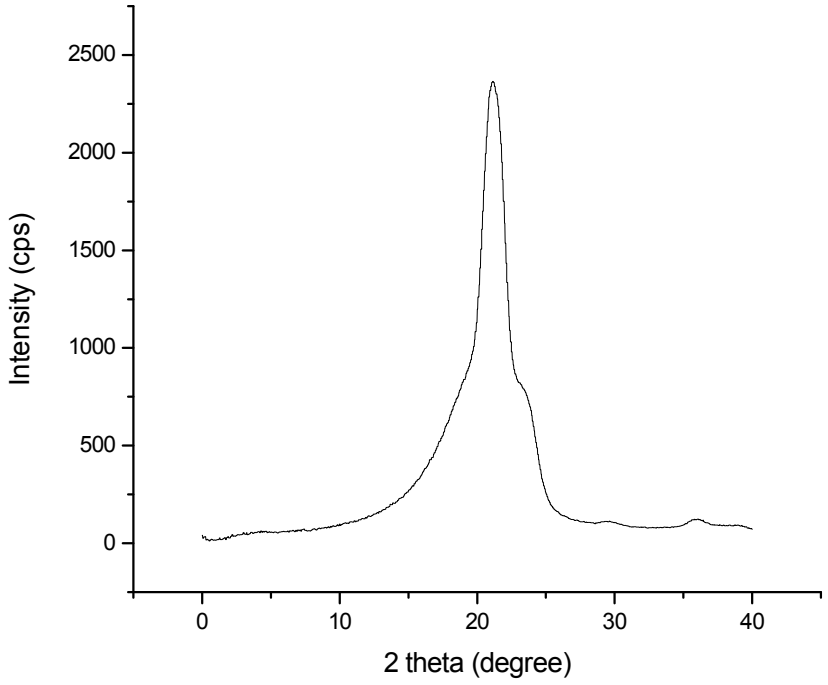


Figure 2d: Wide angle X-ray diffraction crystallograph of 100% Low density polyethylene (LDPE)

The LDPE is characterized with a crystallographic pattern (Figure 2d) with a peak at $2\theta \approx 20^{o}$.

It is interesting to note that the X – ray patterns (Figure 2e-2p) of the various LDPE composites in which the LDPE acts as the matrix with either TPS or SDCA as fillers showed strikingly similar structure with the 100% LDPE pattern. This indeed indicated that the complexation have taken place on the amorphous region and therefore the crystalline region is not affected.

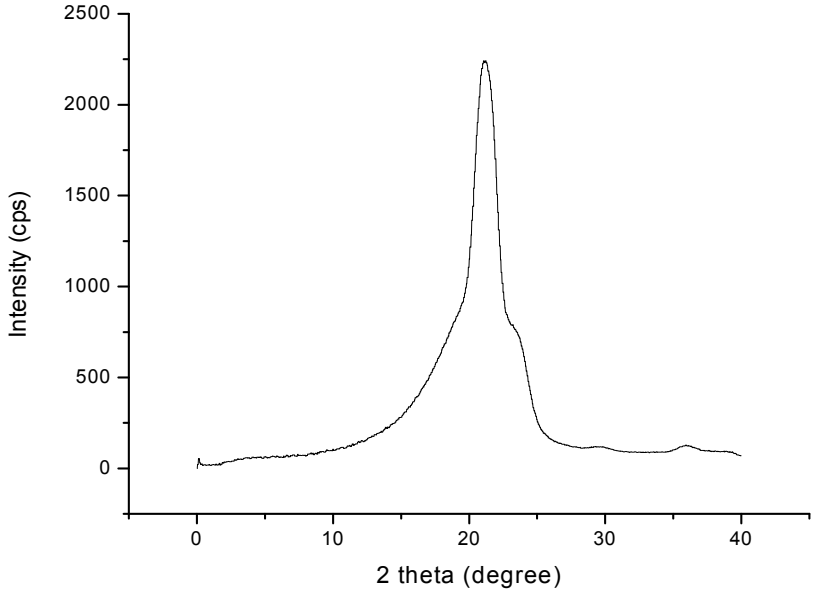


Figure 2e: Wide angle X-ray diffraction crystallograph of LDPE/TPS (90/10).

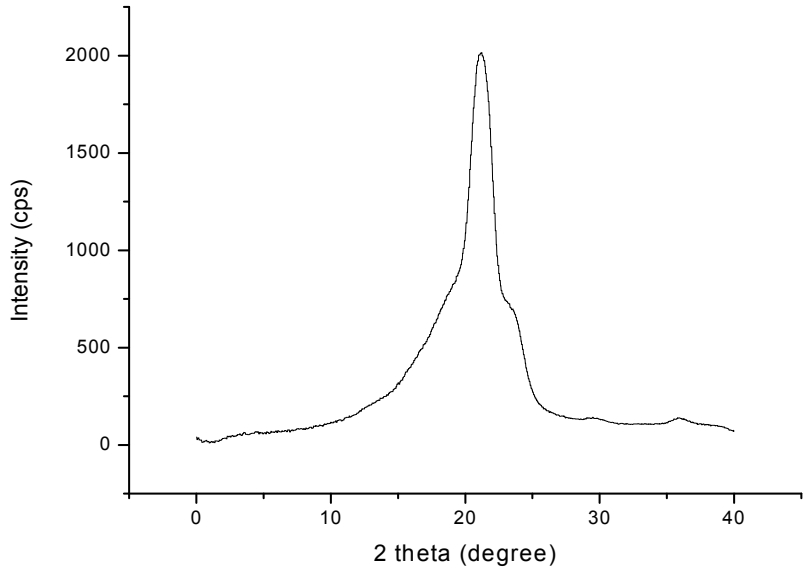


Figure 2f: Wide angle X-ray diffraction crystallograph of LDPE/TPS (80/20).

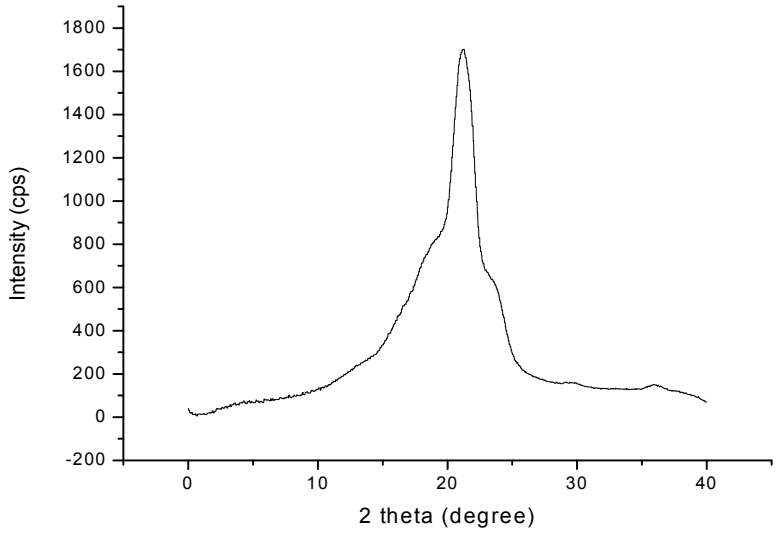


Figure 2g: Wide angle X-ray diffraction crystallograph of LDPE/TPS (70/30)

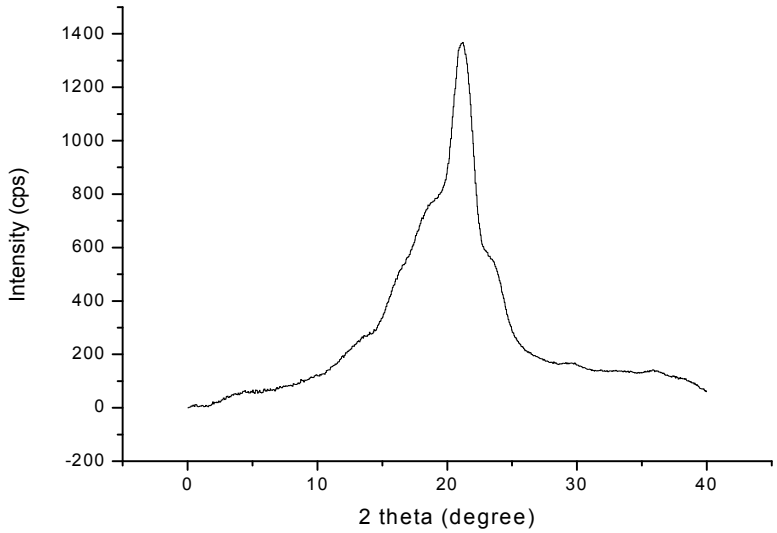


Figure 2h: Wide angle X-ray diffraction crystallograph of LDPE/TPS (60/40).

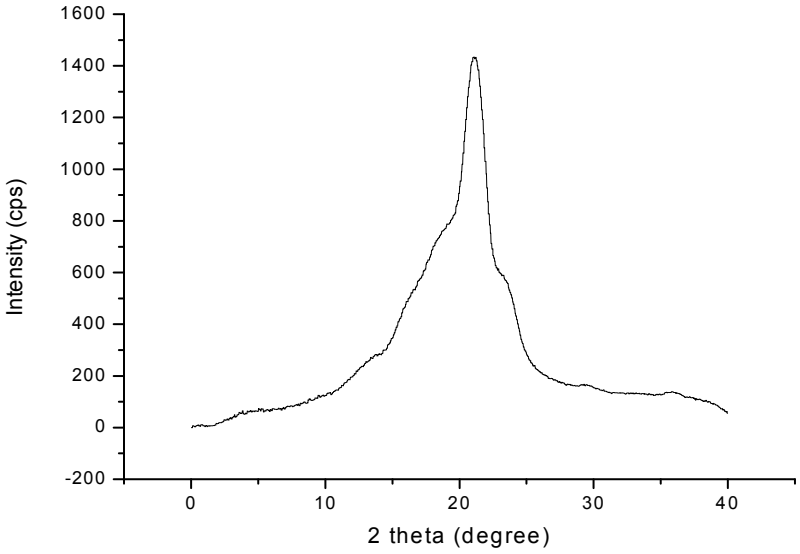


Figure 2i: Wide angle X-ray diffraction crystallograph of LDPE/TPS (50/50).

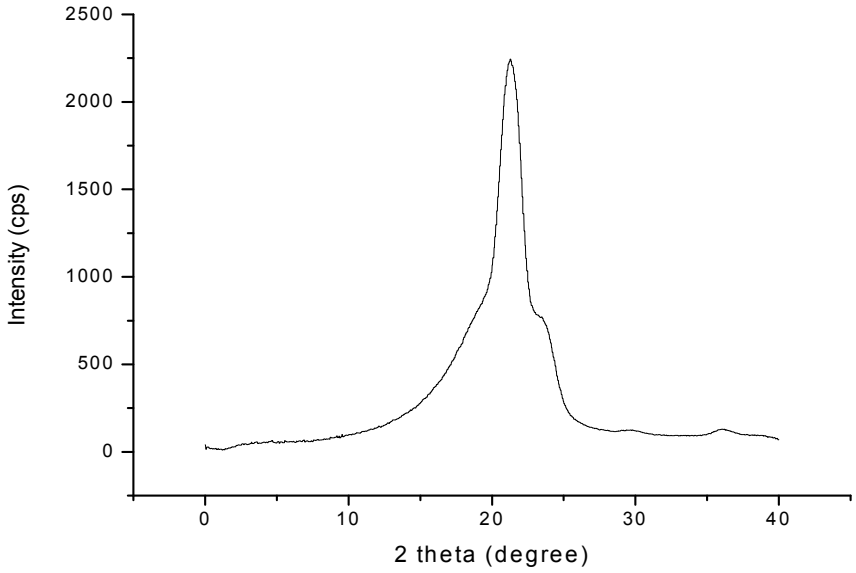


Figure 2j: Wide angle X-ray diffraction crystallograph of LDPE/SDCA (90/10).

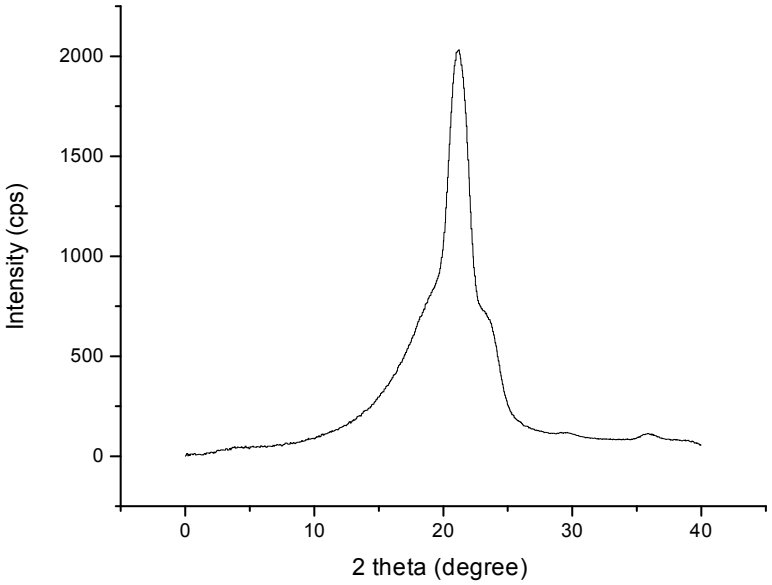


Figure 2k: Wide angle X-ray diffraction crystallograph of LDPE/SDCA (80/20).

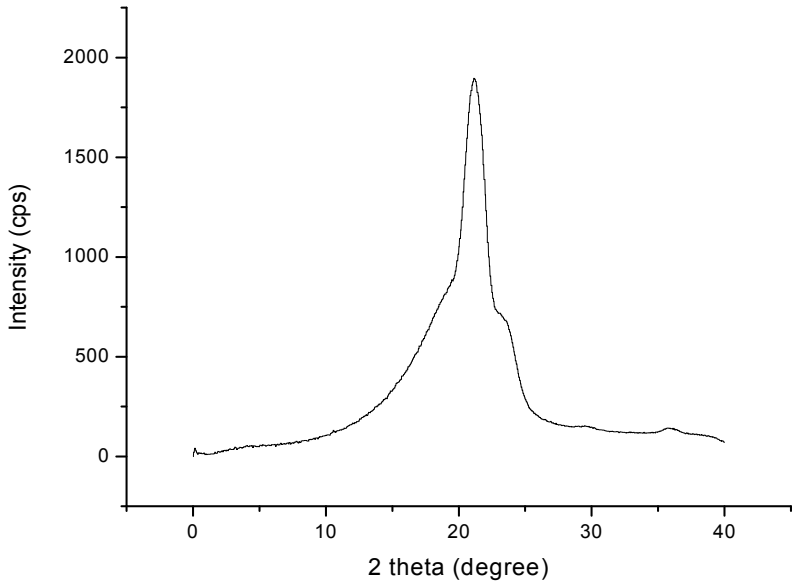


Figure 2L: Wide angle X-ray diffraction crystallograph of LDPE/SDCA (70/30).

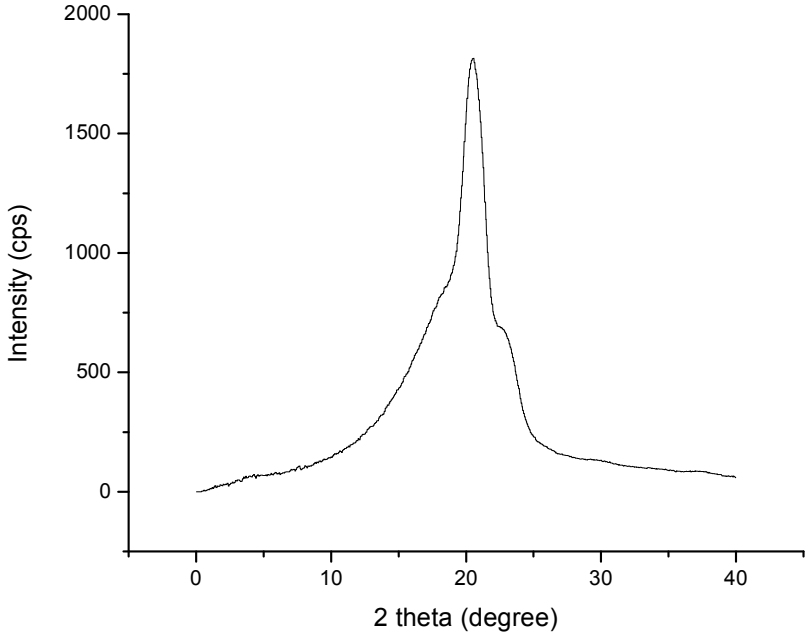


Figure 2m: Wide angle X-ray diffraction crystallograph of LDPE/SDCA (60/40).

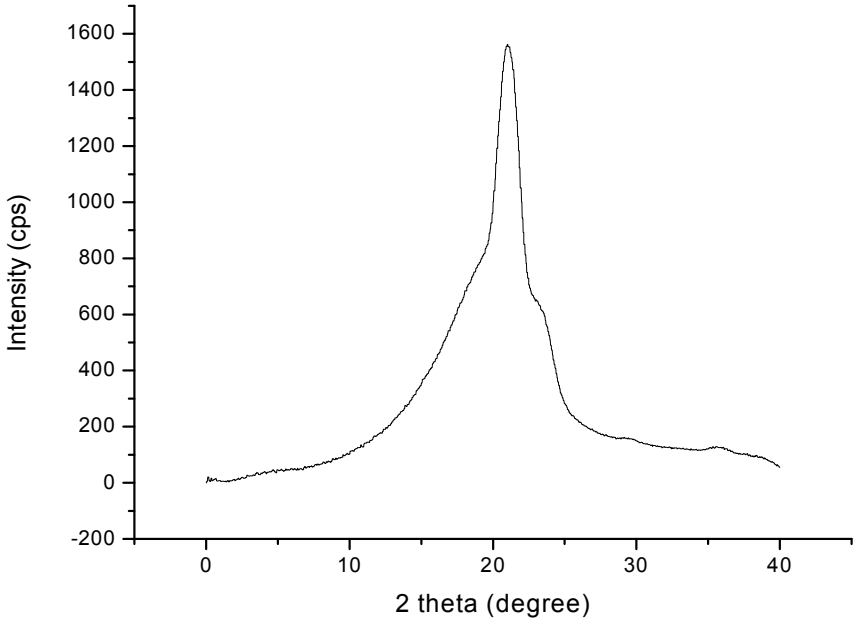


Figure 2n: Wide angle X-ray diffraction crystallograph of LDPE/SDCA (50/50).

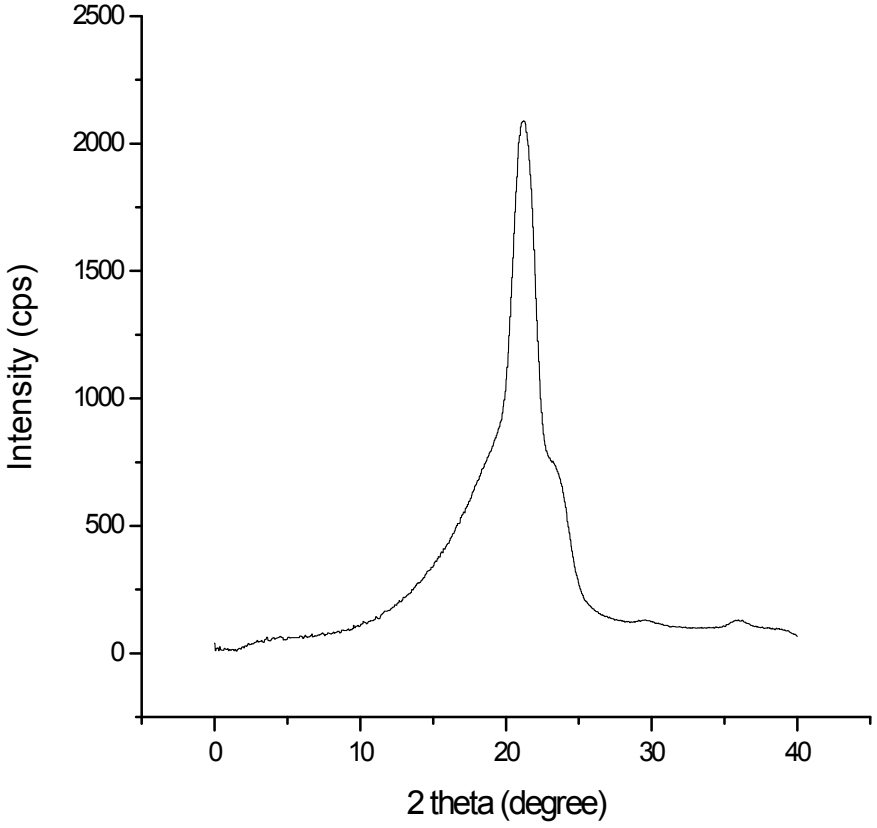


Figure 2p: Wide angle X-ray diffraction crystallograph of LDPE/STA (80/20).

The percentage crystallinity of the sample were estimated and the results shown in figures 2q and 2r. It may be observed from figure 2q, that LDPE exhibited the highest degree of crystallinity with about 42.6% and the SDCA the list with 18%. The starch crystallinity was shown to be 36.8%, as the starch was modified, the crystal structure was destructed and new crystalline structure formed as stated earlier due to the stretching effect of the polymer resulting from the high shear process of the extruder which brings about the replacement of stronger hydroxyl bonds between the starch molecular chains with weaker hydrogen bonds. This is in agreement with the work of other researchers such as Yang et al., (2006) who reported as follows; "This thermoplastification 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."

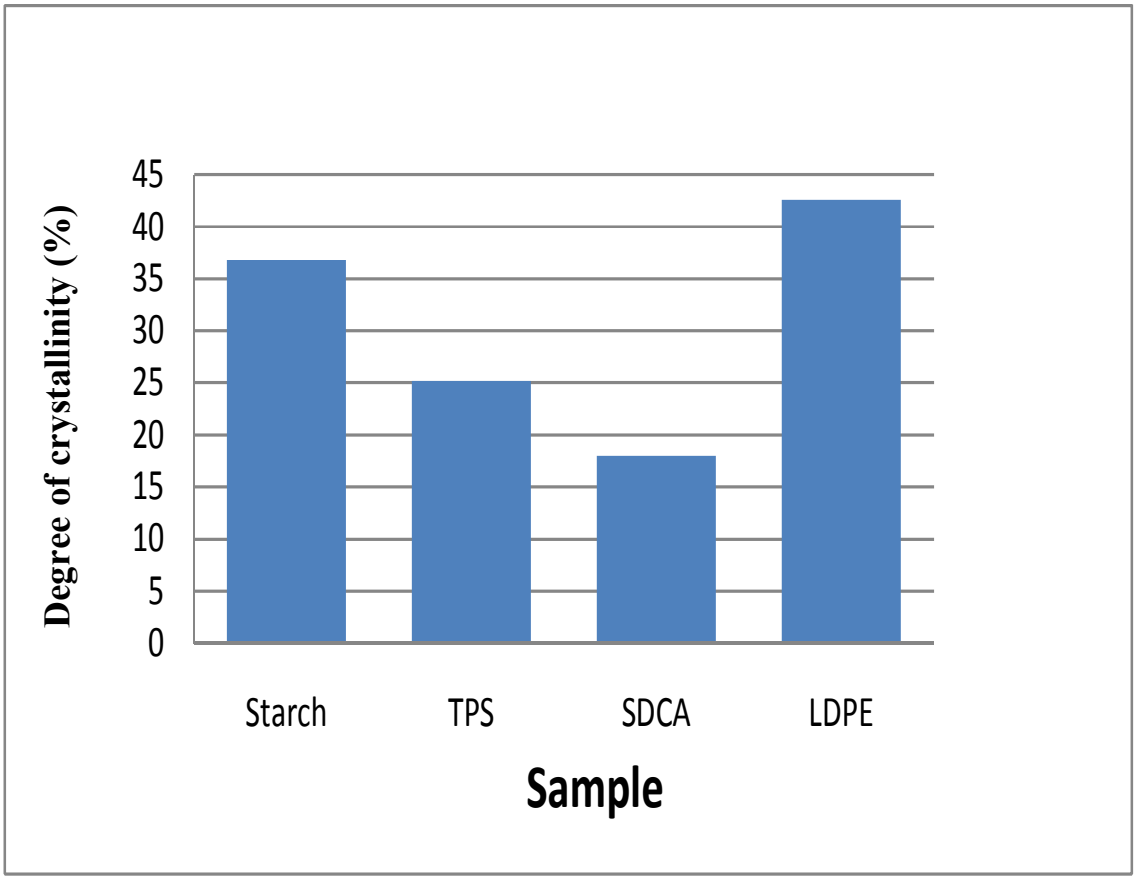


Figure 2q: Percentage crystallinity of Native starch, thermoplastic starch (TPS), Starch dicarboxylic acid (SDCA) and low density polyethylene (LDPE)

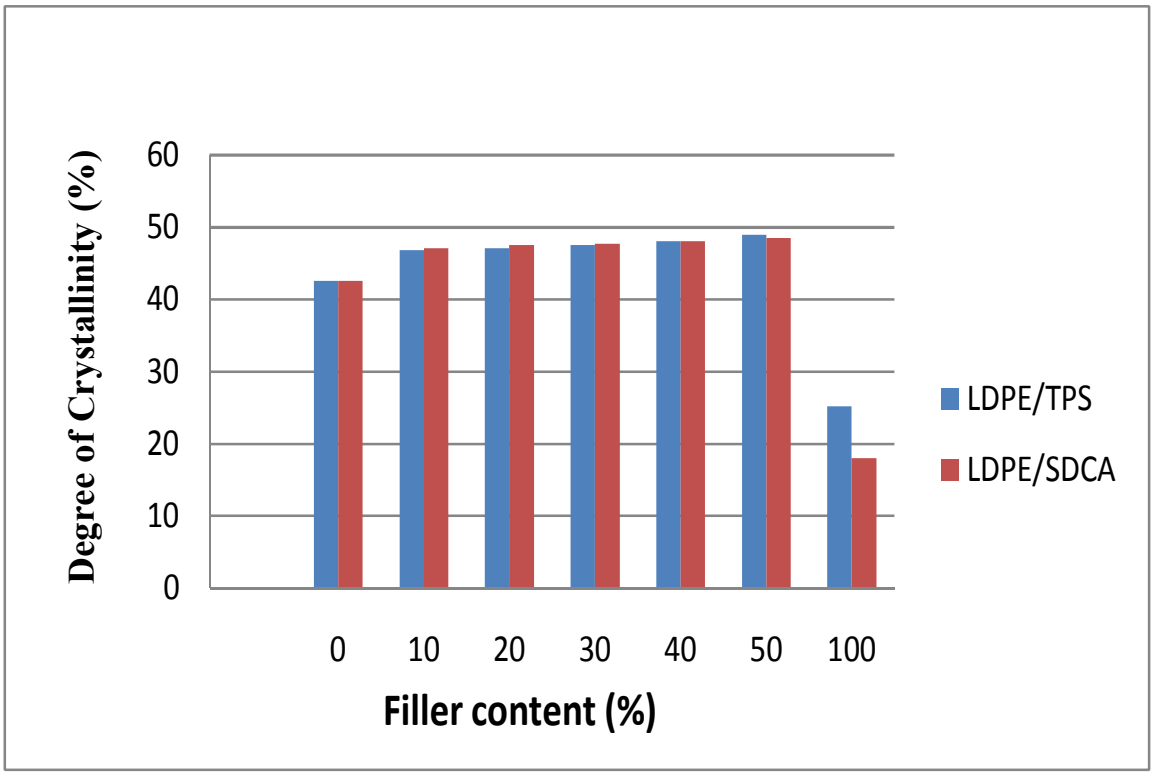


Figure 2r: Percentage crystallinity of LDPE/TPS and LDPE/SDCA

Figure 2r exhibited that the degree of crystallinity of the composites samples for both the LDPE/TPS and LDPE/SDCA increases with increase in filler content. This may be due the fact that the empty spaces in the amorphous region of the LDPE is being occupied by the filler which tends to create a new 'pseudo' crystalline structure, thus as the filler content increases more space is being occupied.

Generally there is no significant difference on the effect of the TPS and the SDCA on the composites crystallinity even though there is a significant difference in their crystallinity, TPS 25.2% and SDCA 18%.

4.4 Mechanical properties

The mechanical properties of a polymer i.e the response to applied forces and deformation are probably their most important properties, contributing to the behavior of polymer in processing. The mechanical properties cover a large number of effects, all of which combine to determine the particular character of the polymer.

Figures 3a, b and c showed that 100% LDPE has the highest tensile stress and very high elongation even at maximum stress, this is attributed to toughness of polyethylene and it's good elastic properties, while starch is a brittle material. The maximum stress was observed to decrease with increasing filler content, which is as a result of incorporation of embrittlement properties of starch to the LDPE matrix. Similar observations were reported by Oromiehie et al (2012).

When the maximum load is applied, there is a reasonable extension before breakage incase of LDPE/TPS composites and 100% TPS (Figure 3a) suggesting that TPS tends to acquire some ductile behaviour due to the effect of plasticization and therefore have better compatibility with the matrix as compared to SDCA , while the LDPE/SDCA composites and 100% SDCA immediately breaks on reaching the maximum load (Figure 3b) as does the LDPE/STA (Figure 3c) due to their brittle nature.

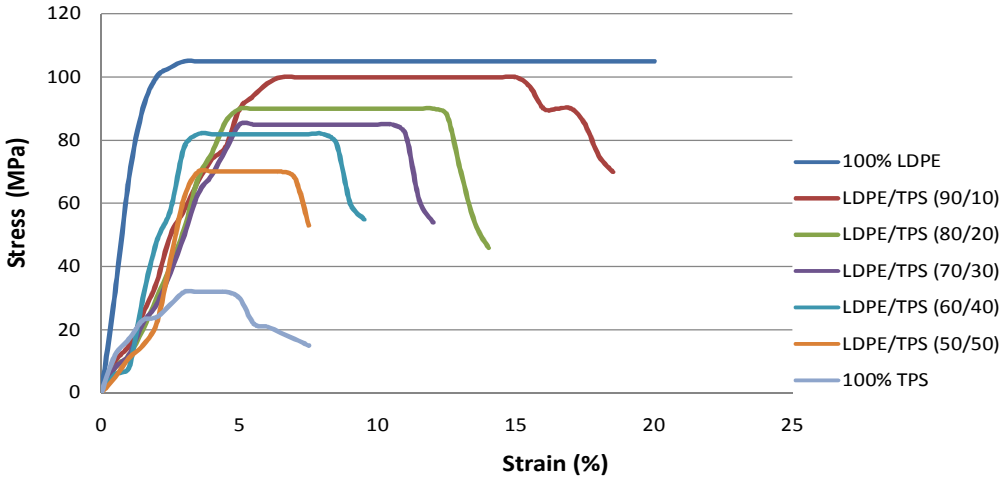


Figure 3a Tensile Stress/Strain curves for (LDPE/TPS)

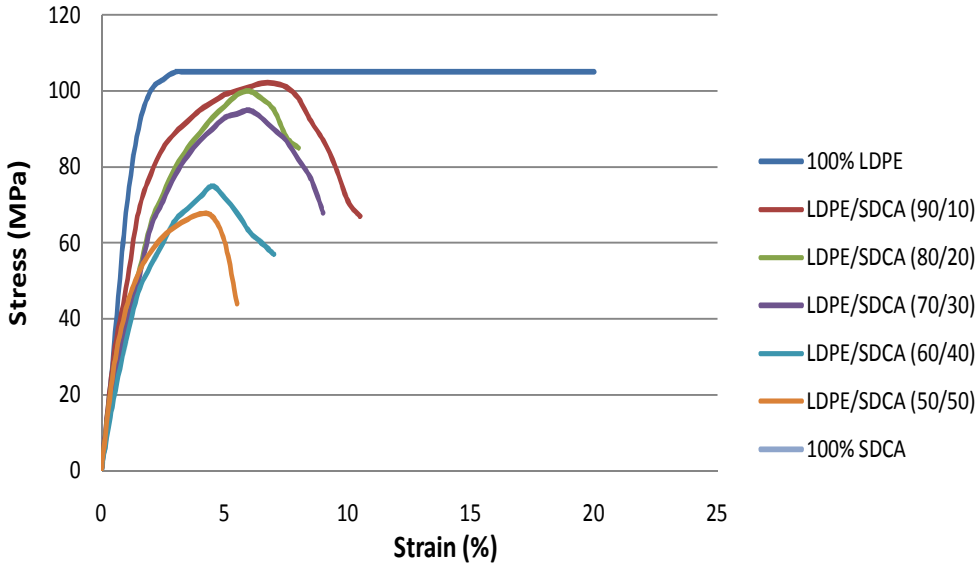


Figure 3b Tensile Stress/Strain curves for (LDPE/SDCA)

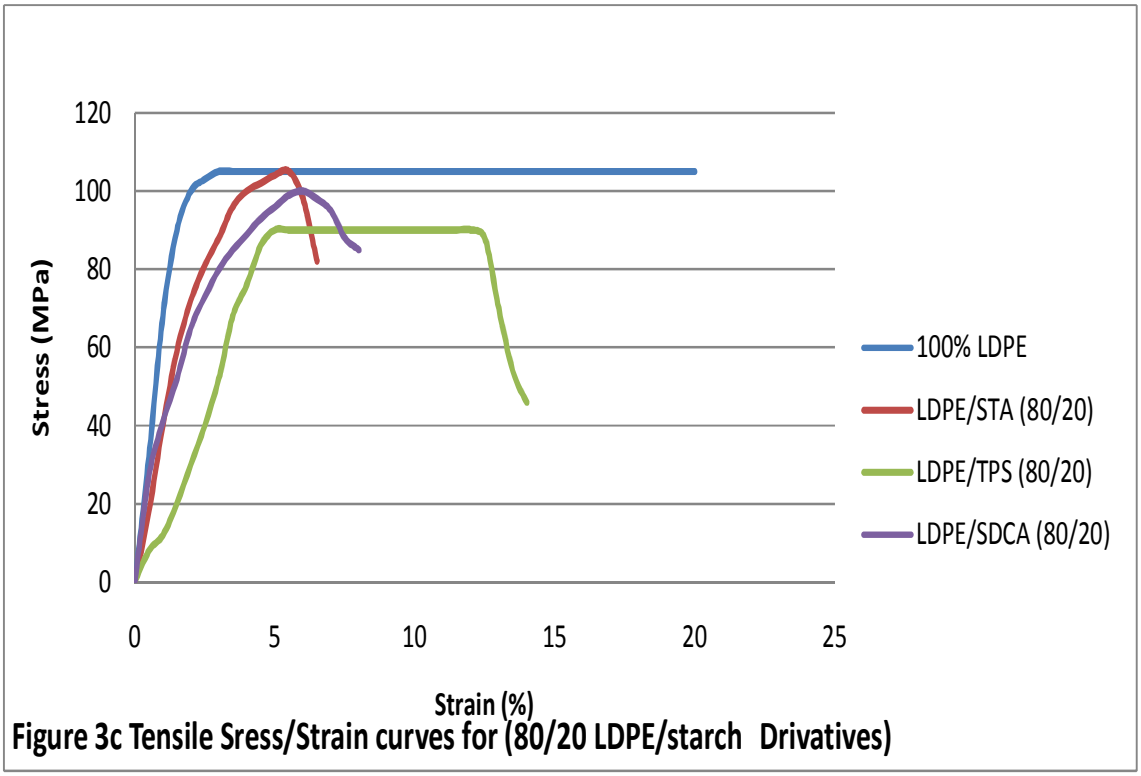


Figure 3c Tensile Sress/Strain curves for (80/20 LDPE/starch Drivatives)

Figure 3c compared the tensile properties of LDPE/STA (80/20), LDPE/TPS (80/20) and LDPE/SDCA (80/20), it may be observed that the LDPE/STA has higher maximum stress followed by LDPE/SDCA with LDPE/TPS withstanding the least stress, however, the LDPE/TPS has better elongation properties as it tends to show ductile behaviour, while the other two composites exhibited brittleness properties. It may also be stated that the LDPE/STA and LDPE/SDCA show higher stiffness properties as compared to LDPE/TPS which is attributed to the plasticization of starch in TPS.

Table 6: Mechanical properties

S/No	Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Flexural Modulus (MPa)	Flexural Strength (MPa)	Hardness (Shore) D-type
1	100% LDPE	9.3	9.0	>300	12.27	17.16	45
2	LDPE/TPS (90/10)	10.49	8.87	125.0	12.5	16.20	46
3	LDPE/TPS (80/20)	12.73	8.59	93.3	12.9	15.49	47
4	LDPE/TPS (70/30)	15.4	7.76	81.67	13.25	10.10	48
5	LDPE/TPS (60/40)	17.0	7.16	61.67	13.8	9.89	48
6	LDPE/TPS (50/50)	18.1	6.85	50.0	15.0	9.74	49
7	100 % TPS	2.5	1.71	53.3	3.75	2.59	56
8	LDPE/ SDCA (90/10)	9.8	8.25	70.3	13.39	8.76	48
9	LDPE/ SDCA (80/20)	10.6	6.74	66.67	13.85	8.54	39
10	LDPE/ SDCA (70/30)	13.7	4.94	59.25	16.7	7.35	38
11	LDPE/ SDCA (60/40)	17.1	3.31	46.3	17.4	6.84	37
12	LDPE/ SDCA (50/50)	20.4	2.89	35.19	18.6	6.19	34
13	100 % SDCA	Fail	Fail	Fail	Fail	Fail	Fail
14	LDPE/STA (80/20)	11.2	8.83	43.2	12.7	8.17	50

Table 6 showing the Tensile strength, flexural strength, Young's modulus, flexural modulus, maximum elongation at break and hardness of composites samples.

4.4.1 Tensile Strength

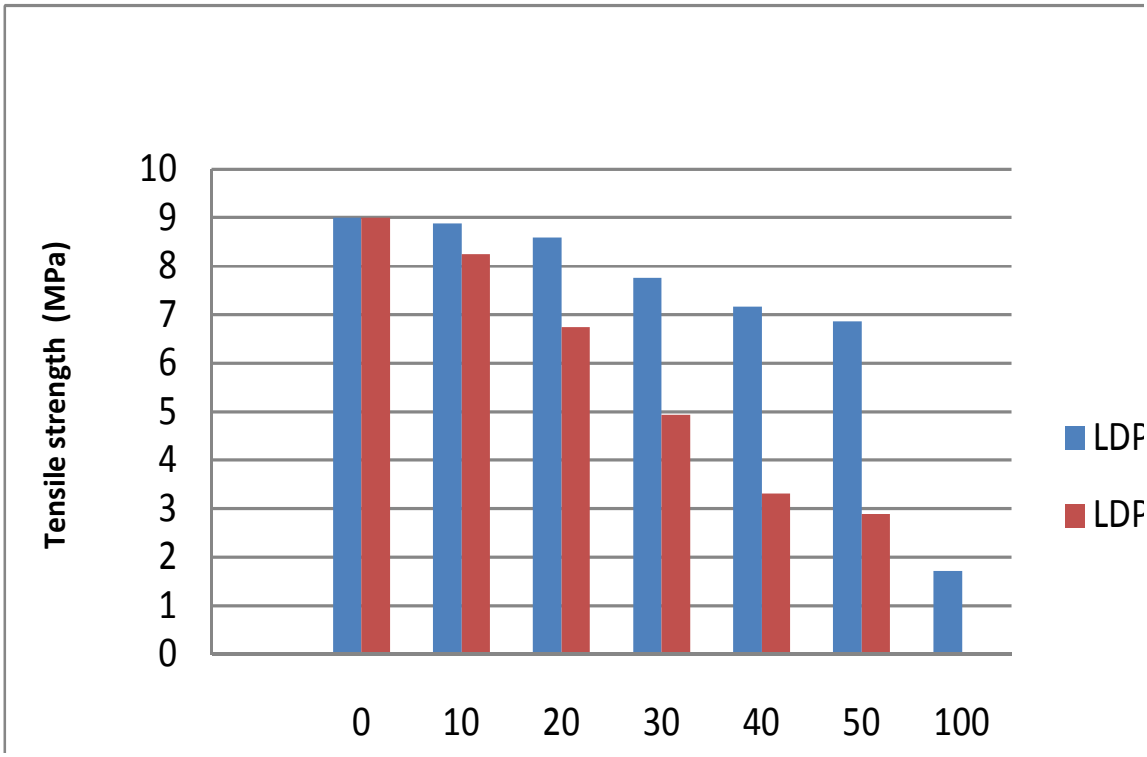


Figure 3d: Tensile strength of LDPE/TPS and LDPE/SDCA composites

It may be observed from Table 6 and figure 3d that the tensile strength decreases with increase in filler concentration in both LDPE/TPS and LDPE/SDCA composites which may be attributed in both cases to poor adhesion between the matrix and the fillers as a result of incompatibility. However, LDPE/TPS exhibited a relatively greater strength as compared to LDPE/SDCA, thus indicating that TPS tends to be more compatible with the LDPE than the SDCA.

Mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and degree of adhesion of the filler to the polymer matrix (Park, et al 2002).

4.4.2Young's Modulus

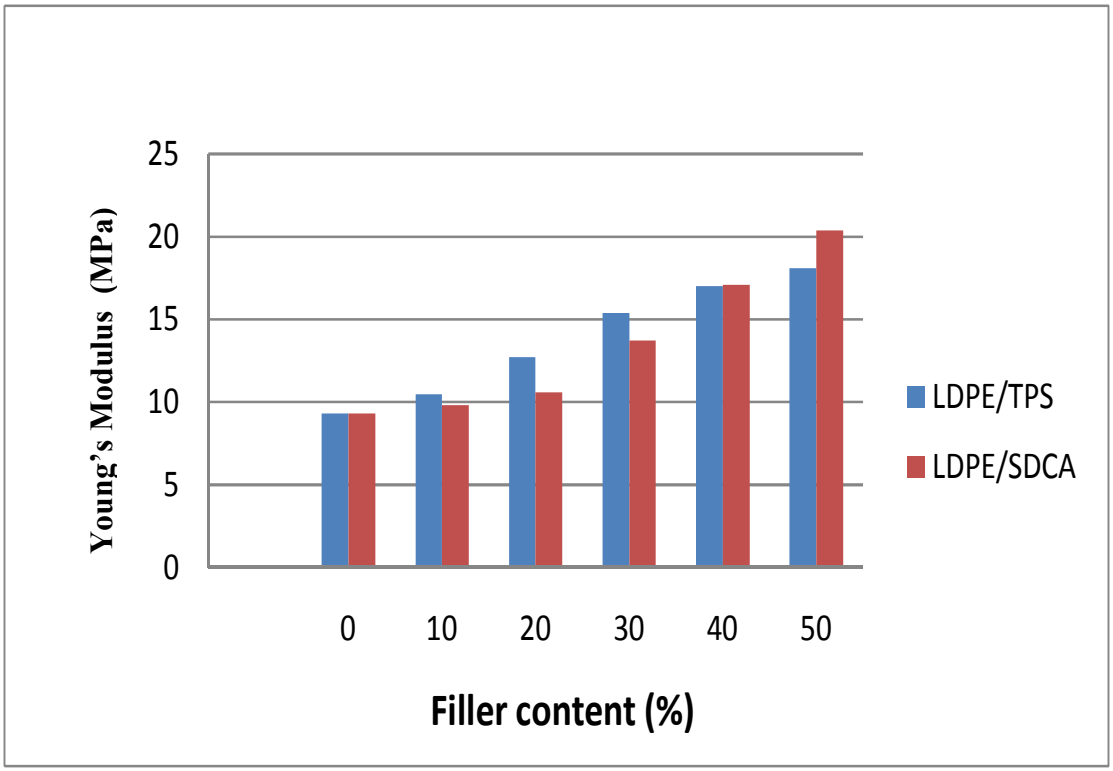


Figure 3e: Tensile Modulus of LDPE/TPS and LDPE/SDCA composites

The measure of the stiffness of a material is given by the value of the modulus. Thus, the higher the modulus of a material, the less it extends for a given force (Booth, 1979). The tensile modulus of the composite samples (Figure 3e) shows an increasing trend as the filler concentrations increases. The increasing modulus with increasing incorporation of the starch in LDPE can be explained by the crystallinity, hydrogen bonding, and stiffening effect of the starch granules (Thakore et al 2001).

4.4.3 Percentage Elongation

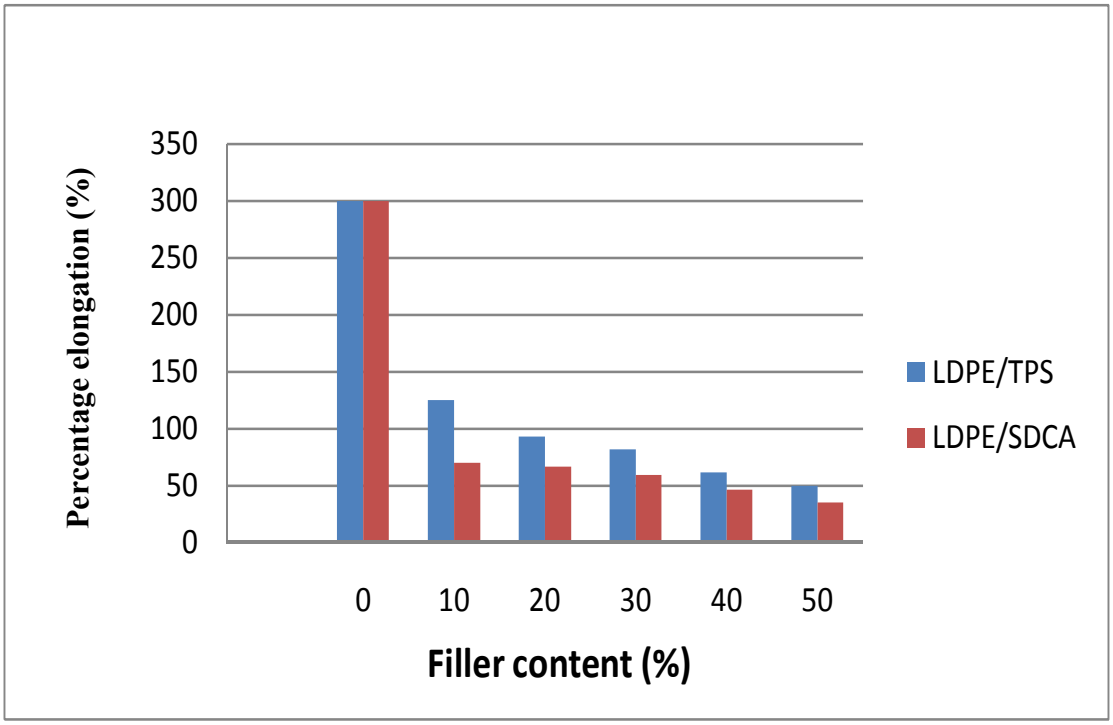


Figure 3f: Percentage elongation of LDPE/TPS and LDPE/SDCA composites

Figure 3f showed that the percentage elongation decreases with increase in filler concentration in both LDPE/TPS and LDPE/SDCA composites, this could be attributed to the discontinuity between the LDPE matrix and the starch fillers due to their incompatibility and poor adhession.

It can be seen that the elongation properties are better for the LDPE/TPS composites as compared to LDPE/SDCA composites, as clearly indicated also in figures 3a and 3b. While the LDPE/TPS composites (Figure 3a) shows a reasonable elongation at the maximum stress, the LDPE/SDCA composite (Figure 3b) immediately breaks on reaching the maximum stress, a phenomenon which resulted from the amorphous nature of the LDPE/SDCA composites and its embrittlement properties.

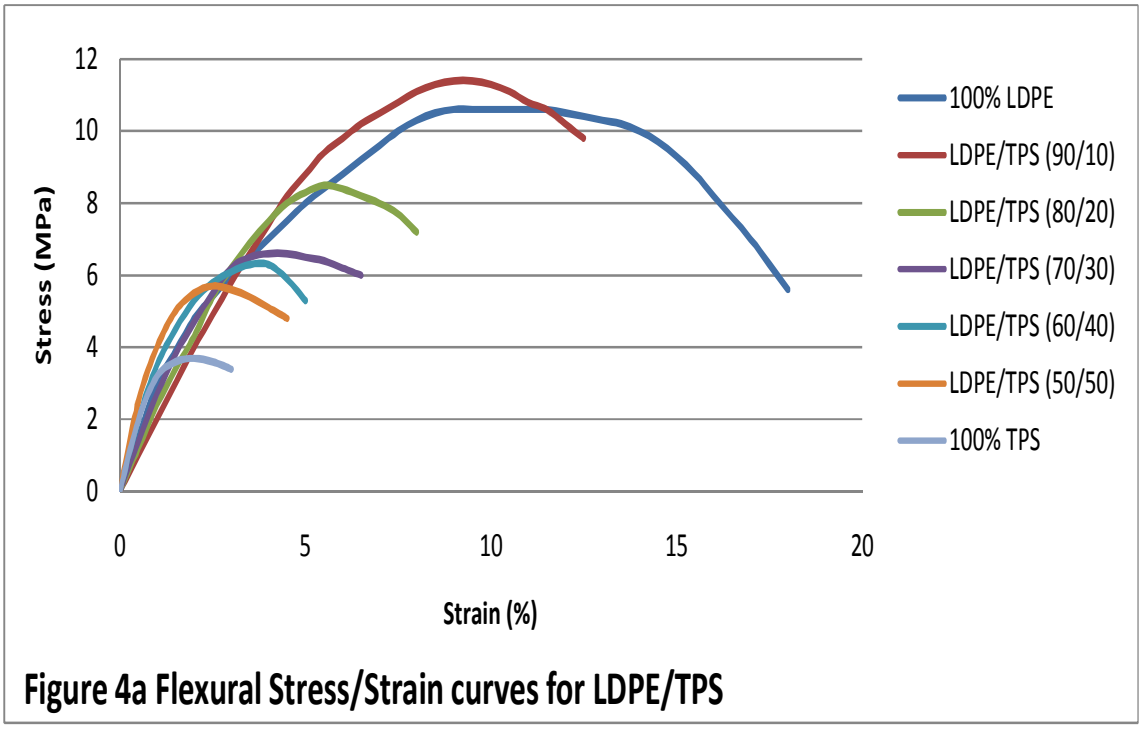


Figure 4a Flexural Stress/Strain curves for LDPE/TPS

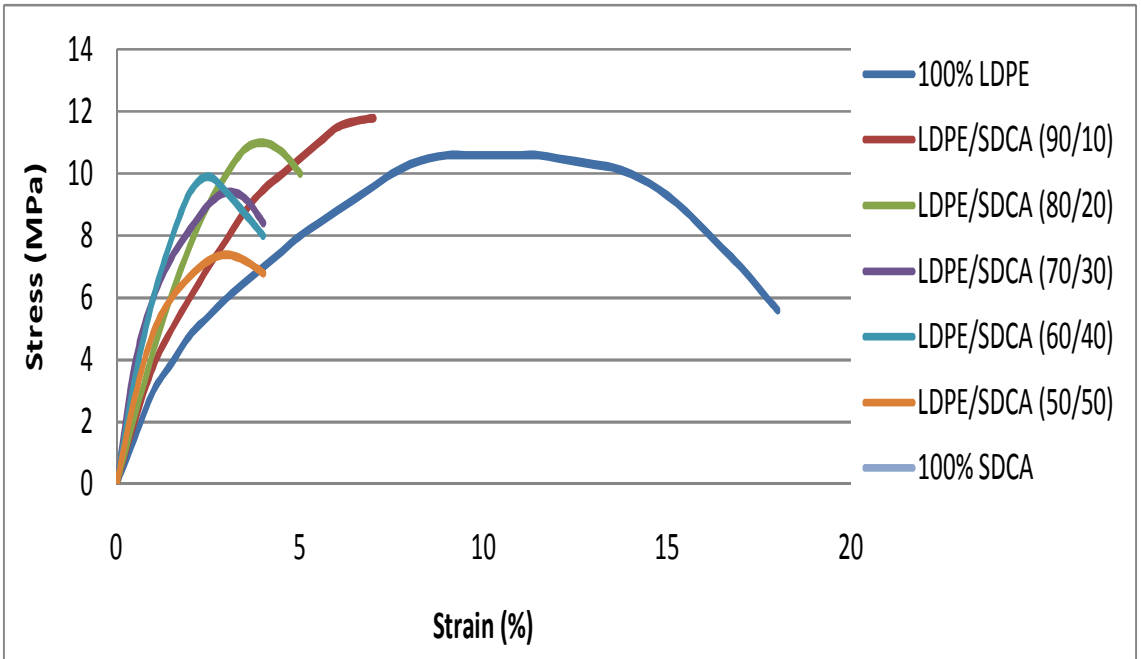


Figure 4b Flexural Stress/Strain curves for LDPE/SDCA

4.4.4 Flexural strength

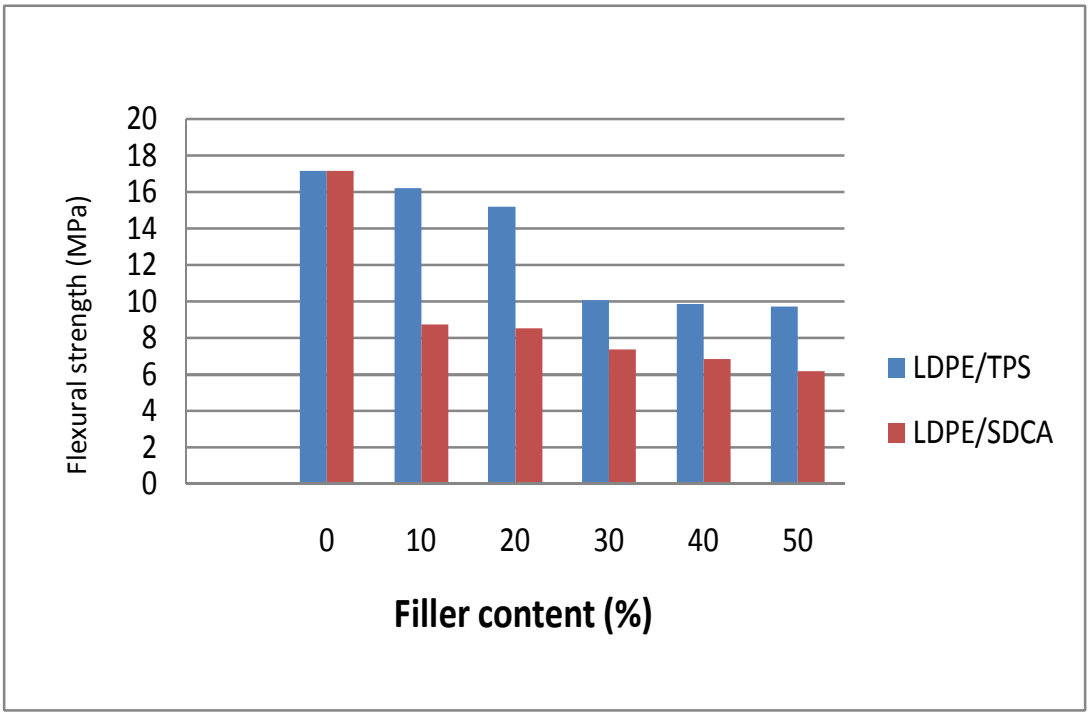


Figure 4c: Flexural strength of LDPE/TPS and LDPE/SDCA composites

Flexural strength of a material measures the flexure or bending properties of plastic materials. For materials like plastic that considerably deform but do not break, the load at output is marked as the flexural strength or flexural yield strength.

Similar to tensile strength, the flexural strength is inversely proportional to filler content (Figure 4c) due to the embrittlement properties of both the TPS and the SDCA incorporated into the LDPE and also poor inter-phase continuity between the filler and matrix.

4.4.5 Flexural Modulus

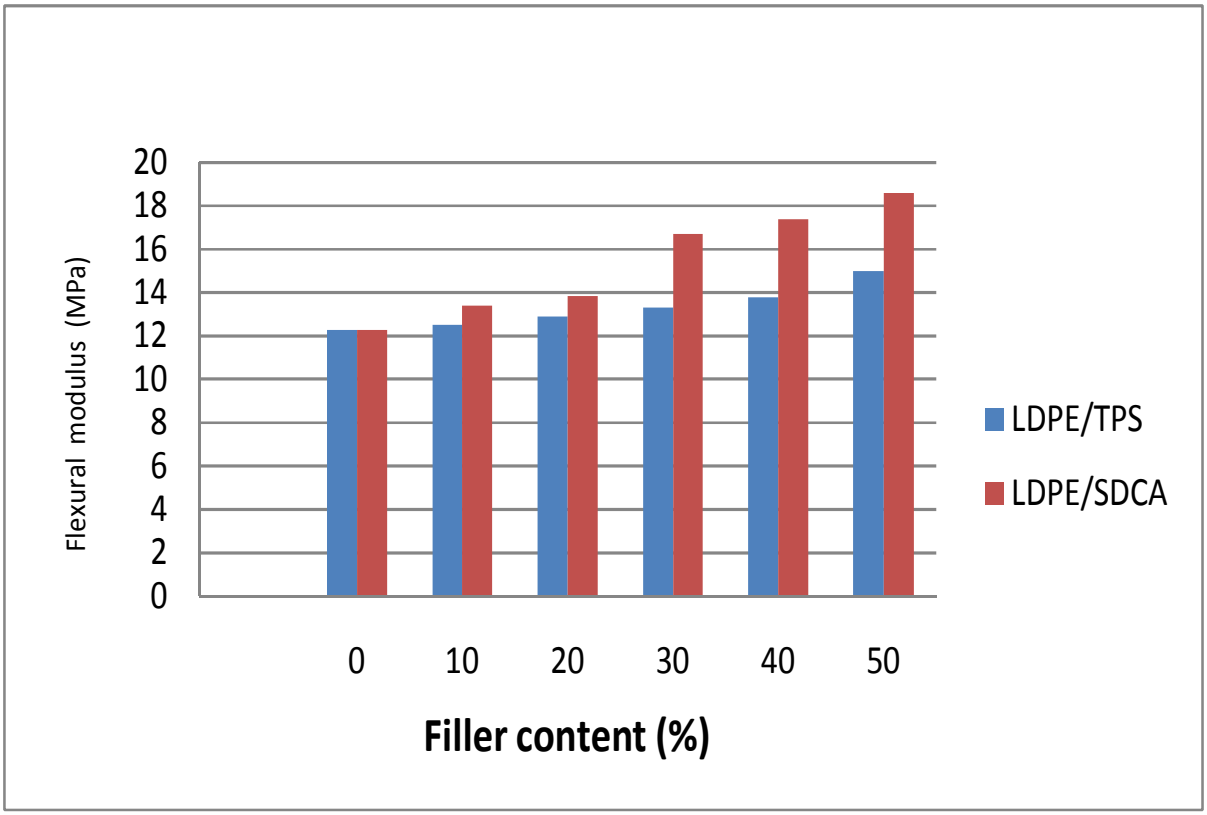


Figure 4d: Flexural Modulus of LDPE/TPS and LDPE/SDCA composites

Figure 4d showed a direct relationship between the flexural modulus and the filler content, this is attributed to the fact that as the LDPE matrix get filled, the filler – filler interaction becomes more pronounced than the filler – matrix interaction (Rasit et al 2012), thus, the composites becomes more rigid and stiffer making bending more difficult to achieve.

The LDPE/SDCA showed higher flexible stiffness as compared to LDPE/TPS due to the plasticization effect of the TPS which gives it some elasticity property.

4.4.6 Hardness properties

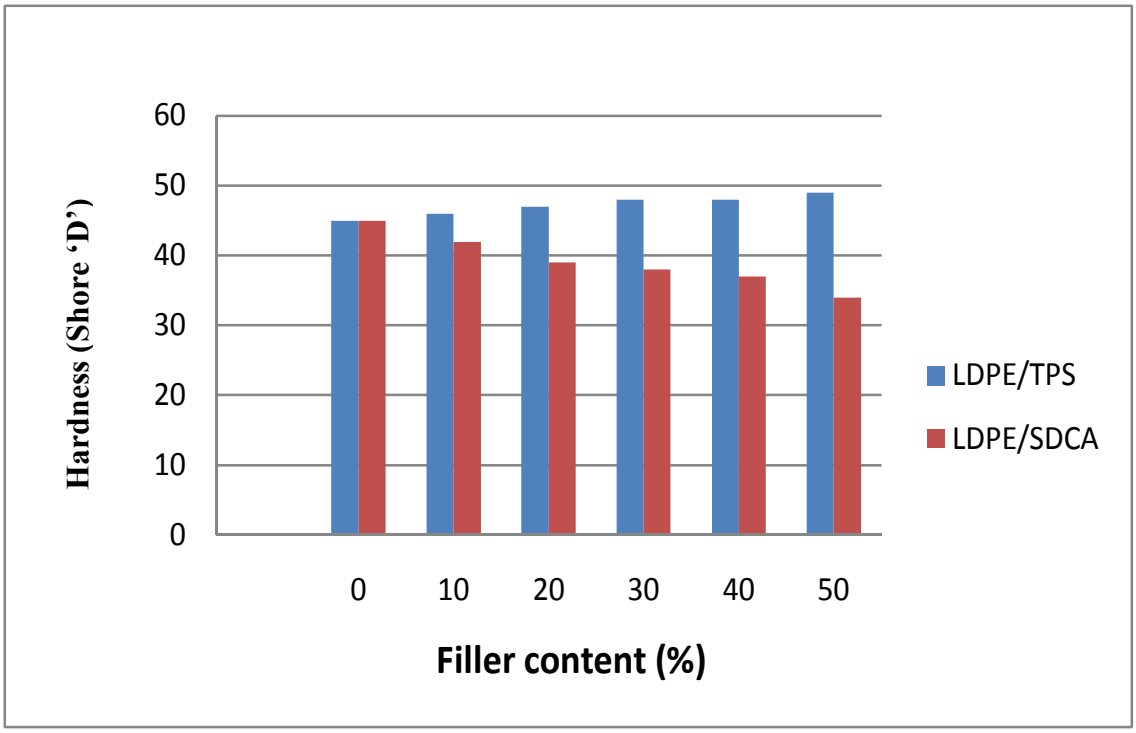


Figure 5: Hardness properties of LDPE/TPS and LDPE/SDCA composites

Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration.

Figure 5 showed that while the hardness property increases with increase in filler content for the LDPE/TPS composites, the inverse is the case for the LDPE/SDCA composites there by the hardness is inversely proportional to the filler content, this phenomenon may not be unconnected to the amorphous nature of the SDCA and the semi crystalline structure of the TPS.

4.4.7 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical thermal analysis (DMTA) over a wide range of temperature provides valuable insight into the structure and viscoelastic behaviour of polymer composites(Murayama, 1978). The damping is a sensitive indicator of all kinds of molecular motions that are going on in a material during the testing. These dynamic parameters have been used to determine the glass transition temperature relation spectra, degree of crystallinity, molecular orientations, crosslinking, phase separation, structural changes resulting from processing and chemical composition of polymeric composites (Tsai and Halpin, 1980).

The results of the dynamic mechanical analysis of the samples under investigation are shown in figures 6a-m. It may be observed that in all the samples tested, the storage moduli (E') decreases with increase in temperature. This indicated that there is loss in stiffness of the material with rise in temperature. The LDPE (figure 6a) shows the highest storage modulus at very low temperature (-140°C), however as the temperature rises the storage modulus rapidly decreases, this could be explain from the molecular orientation of the material. Similarly, the loss modulus decreases with increase in temperature for all the samples.

The LDPE DMA thermograms figure 6(a) indicated that as the temperature increases from (-140°C) the storage modulus decreases slowly, 2 weak peaks appeared from the storage modulus and tanδ curves at ≈ -110°C and -30°C which could be attributed to β and α relaxations respectively, β – transition is related to toughness of the material, and α – transition may be related to T_g.

The TPS DMA thermograms figure 6(g) showed prominent peaks from the storage modulus and tanδ curves at -50°C which may be attributed to T_g due to the plasticizer (Glycerol) 3 other medium peaks were exhibited at between 0 °C – 10 °C, ≈60 °C and ≈85 °C. The peak at ≈60 °C is attributed to starch α – relaxation or T_g. Thermoplastic starch is heterogeneous mixture (Oromiehie 2012), the transition at 0 °C – 10 °C could be indicating phase separation.

Figure 6(b – f) showed the DMA thermograms of the LDPE/TPS and Figure 6(h-L) for LDPE/SDCA, in all these curves, the storage moduli and tanδ curves indicated the relaxation peaks at ≈ -110°C and -30°C which were attributed to LDPE transitions points. It could be observed however, the loss moduli of the composites have higher peak values than the pure LDPE and also the amplitude increases with starch content of the composite indicating that the composite have better ability to dissipate energy due to the alterations in crystallinity. The LDPE/SDCA thermograms exhibited relatively higher loss moduli indicating the ability of these composites to dissipate higher energies due to their amorphous characteristics.

The mechanical loss factor (tanδ) increases with increase in temperature for all the samples, the reverse trend of the moduli.

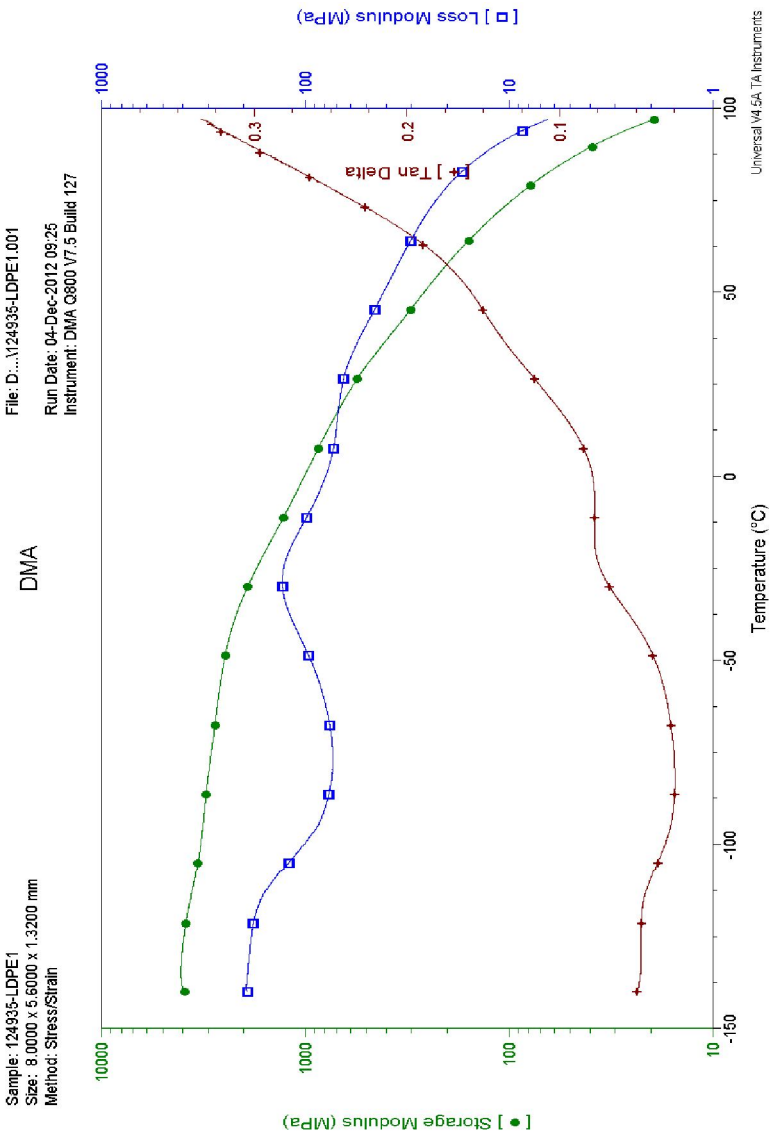


Figure 6a: Dynamic Mechanical Analysis thermogram of low density Polyethylene (LDPE)

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

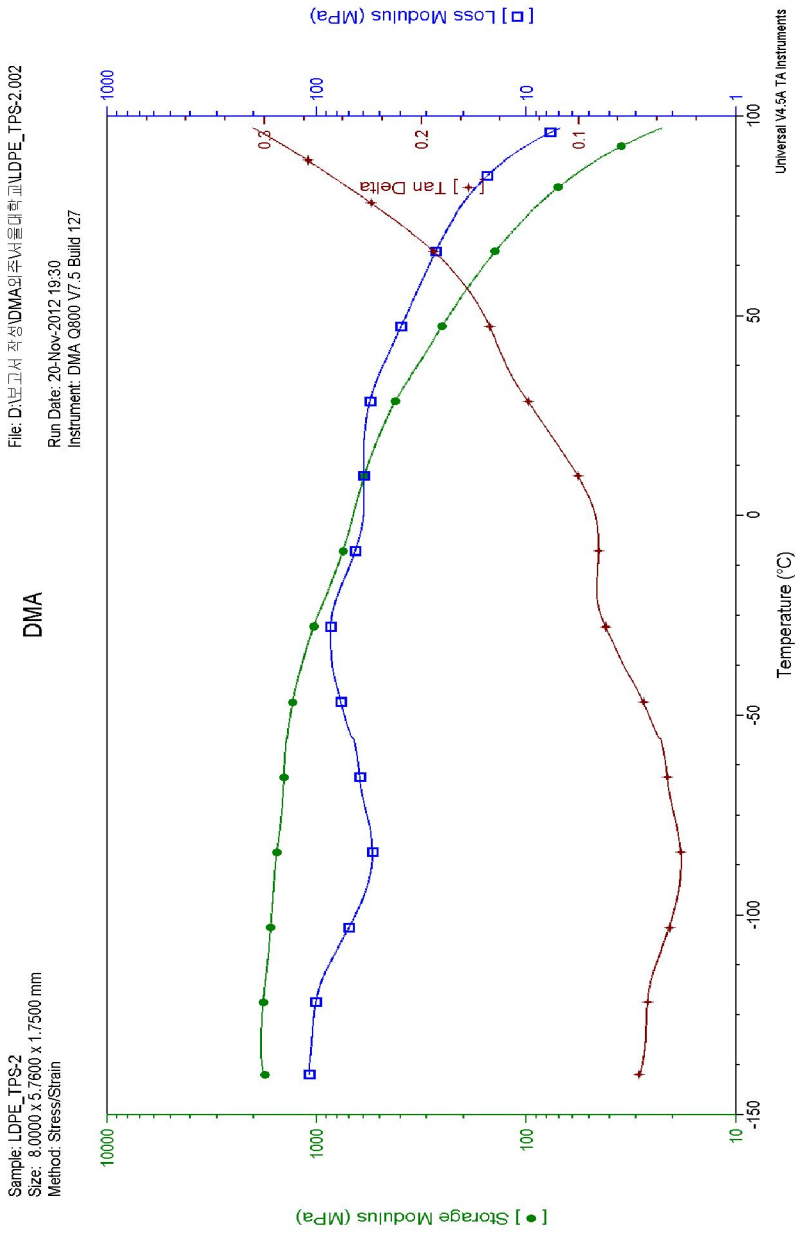


Figure 6(b): Dynamic Mechanical Analysis thermogram of LDPE/TPS (90/10).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

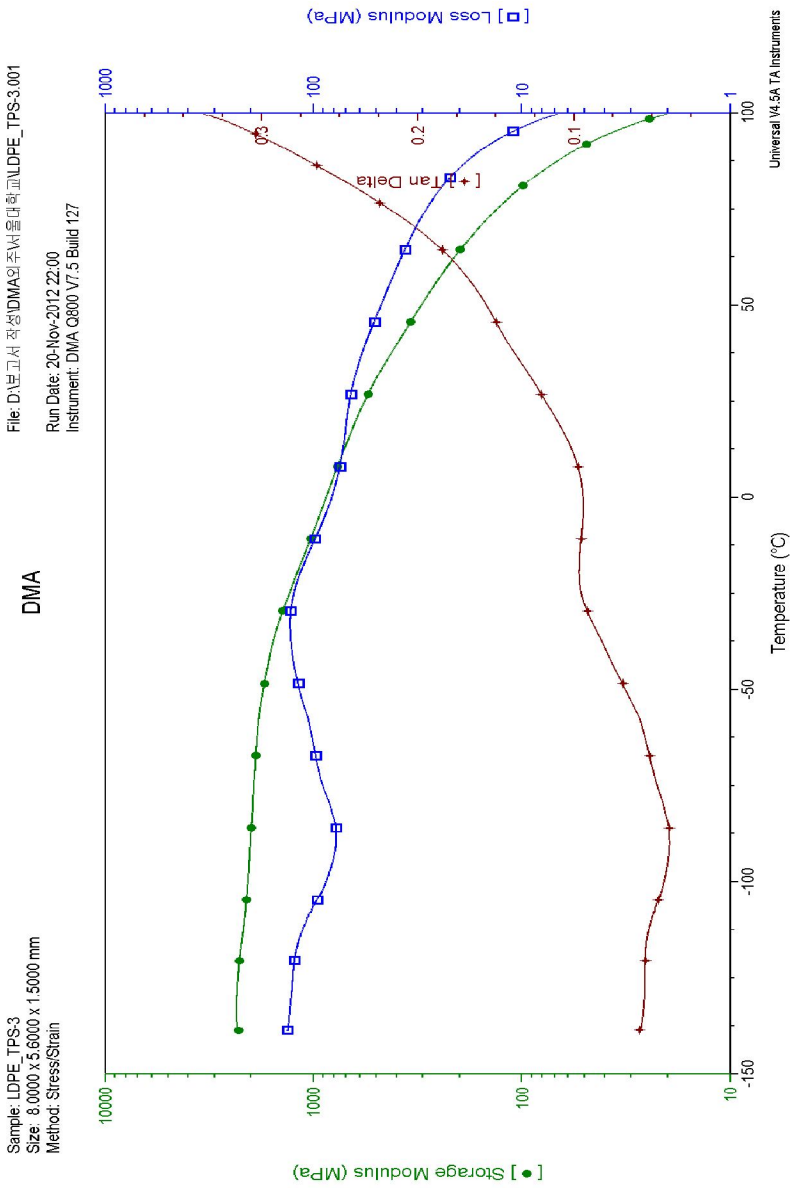


Figure 6(c): Dynamic Mechanical Analysis thermogram of LDPE/TPS (80/20).

Key

Storage modulus

Loss modulus

Tanδ

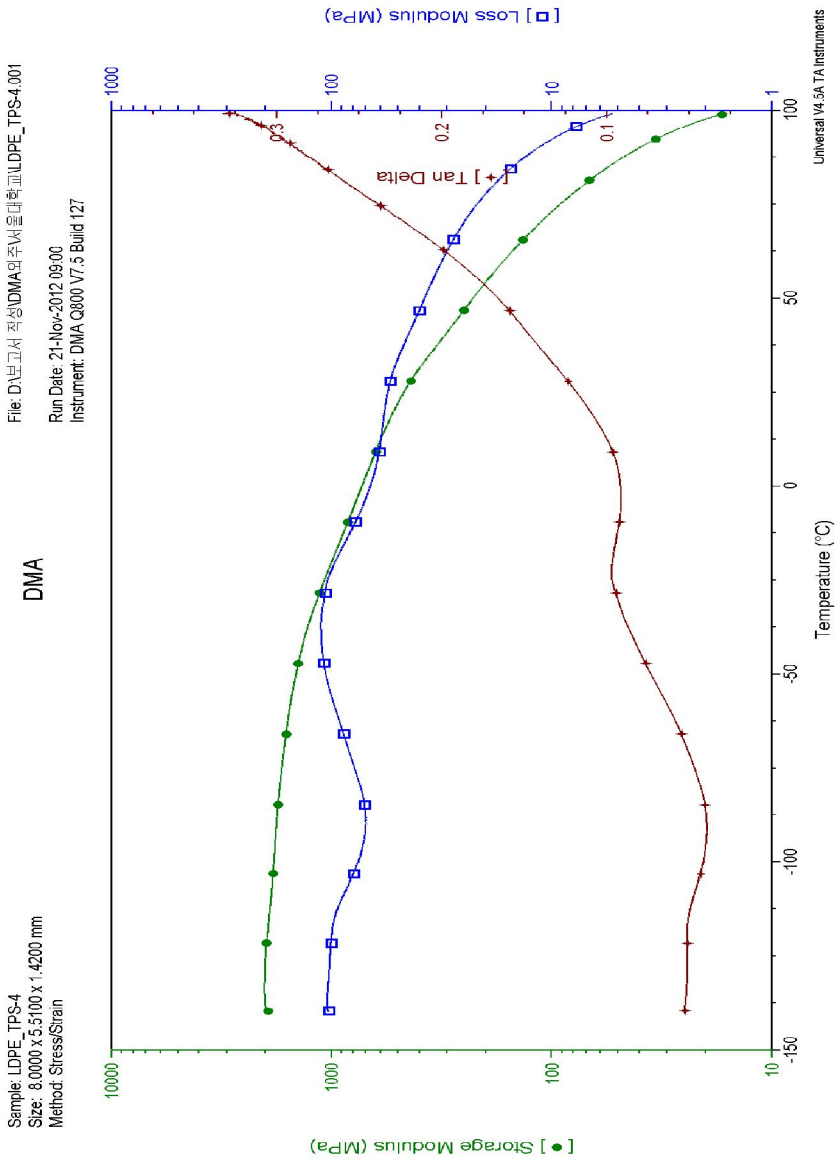


Figure 6(d): Dynamic Mechanical Analysis thermogram of LDPE/TPS (70/30).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

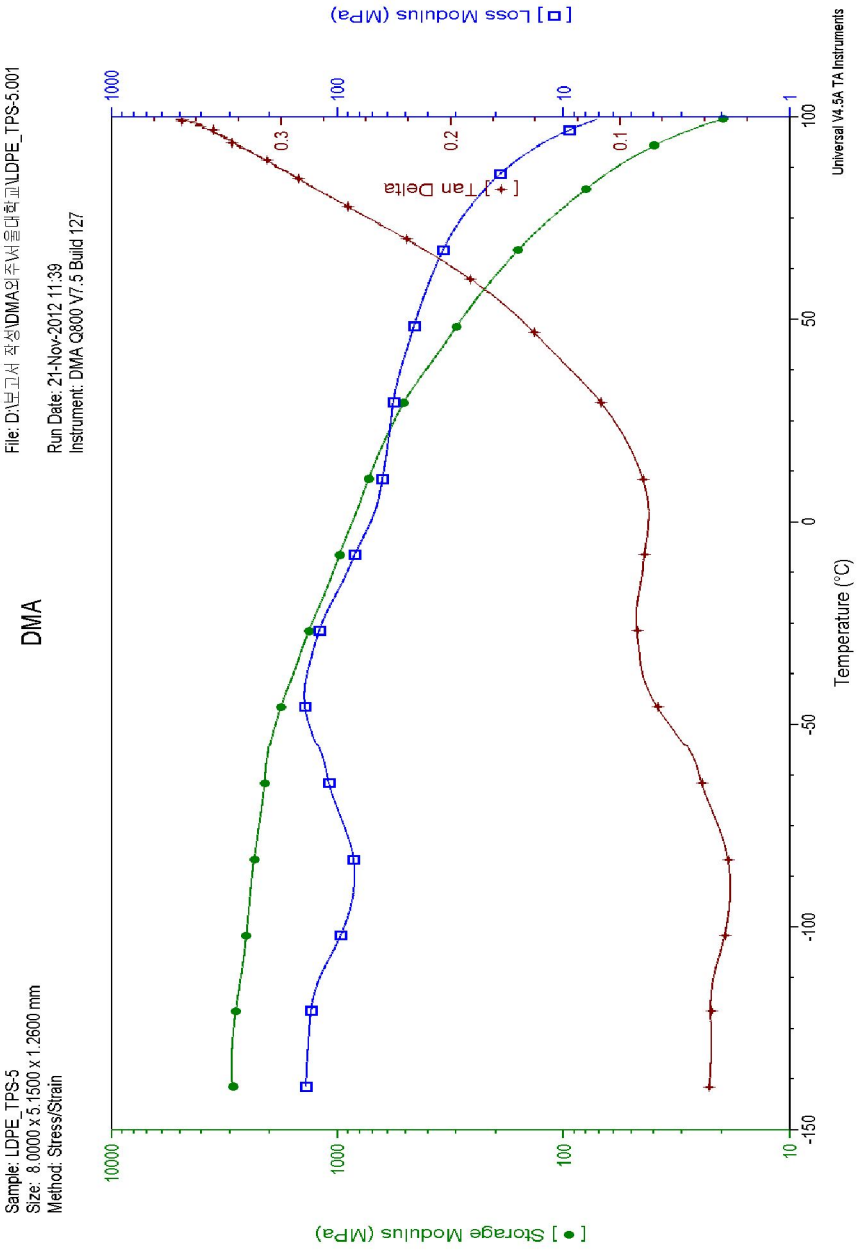


Figure 6(e): Dynamic Mechanical Analysis thermogram of LDPE/TPS (60/40).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

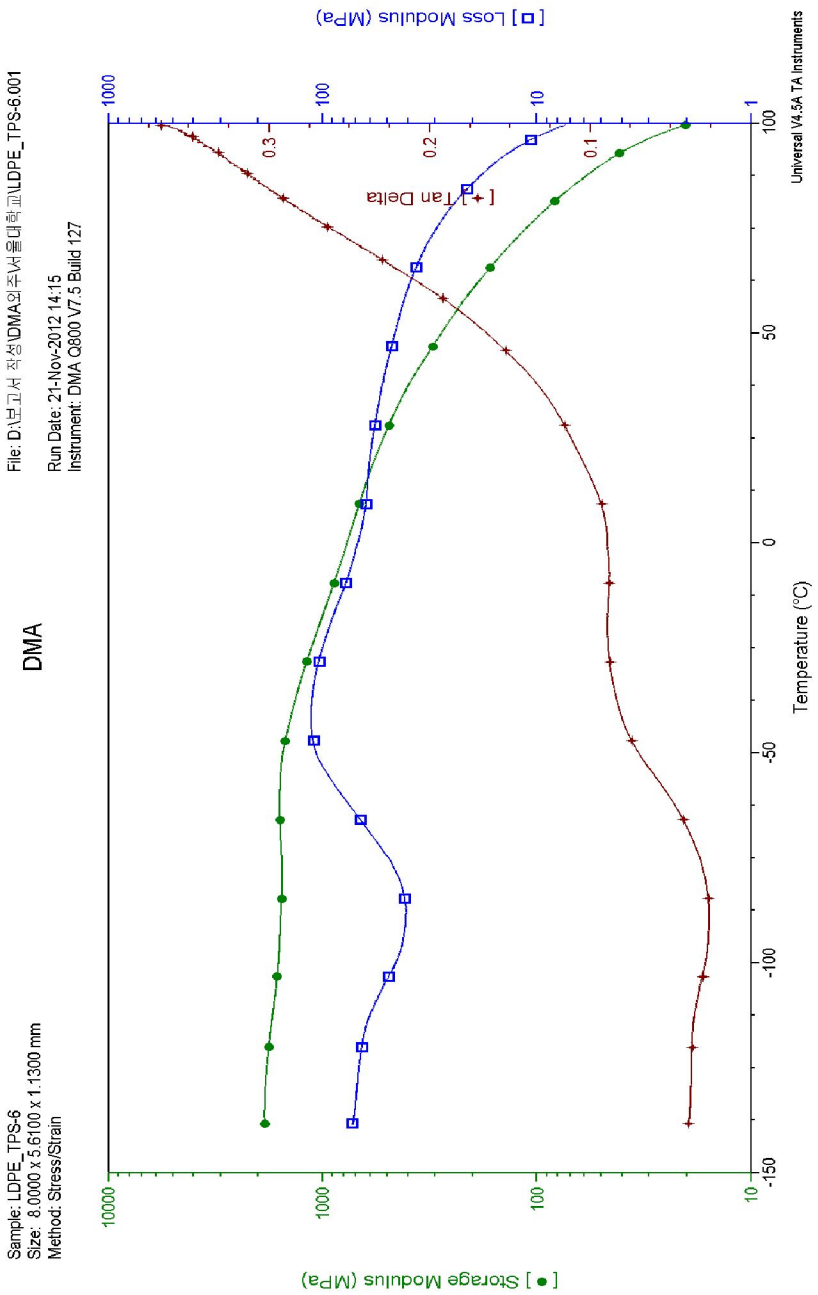


Figure 6(f): Dynamic Mechanical Analysis thermogram of LDPE/TPS (50/50).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

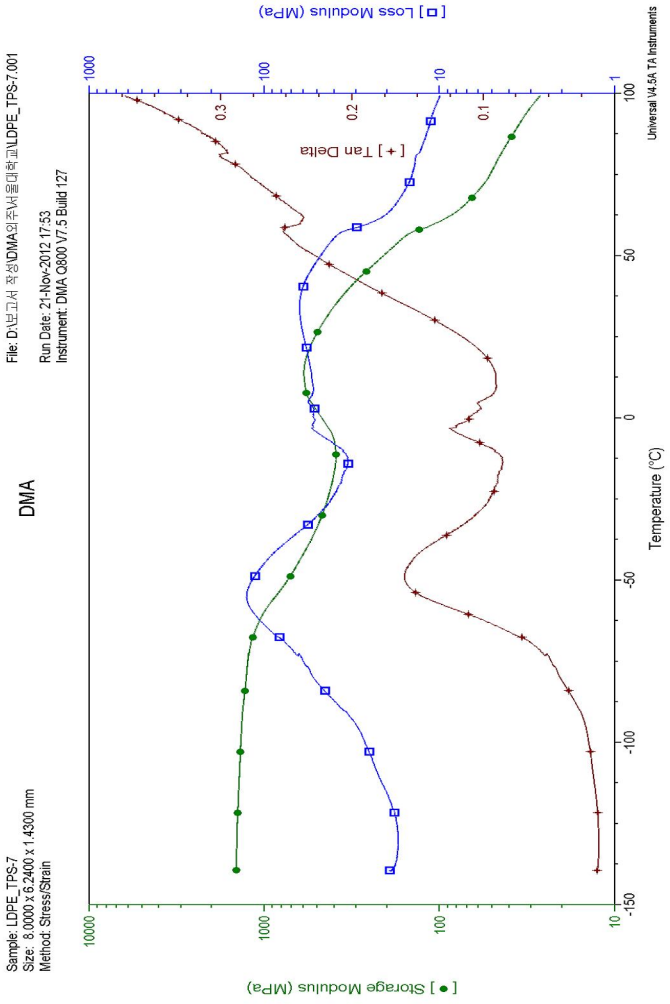


Figure 6(g): Dynamic Mechanical Analysis thermogram of 100% Thermoplastic – Starch (TPS).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

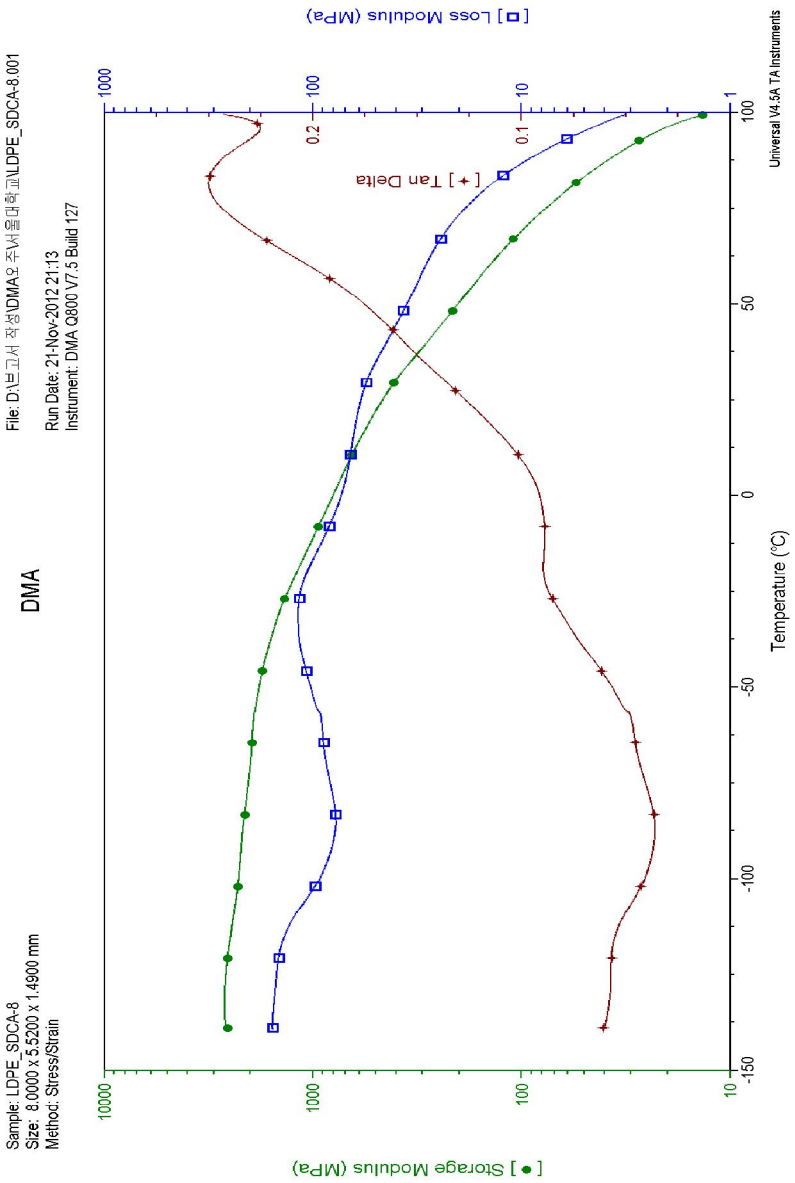


Figure 6(h): Dynamic Mechanical Analysis thermogram of LDPE/SDCA (90/10).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

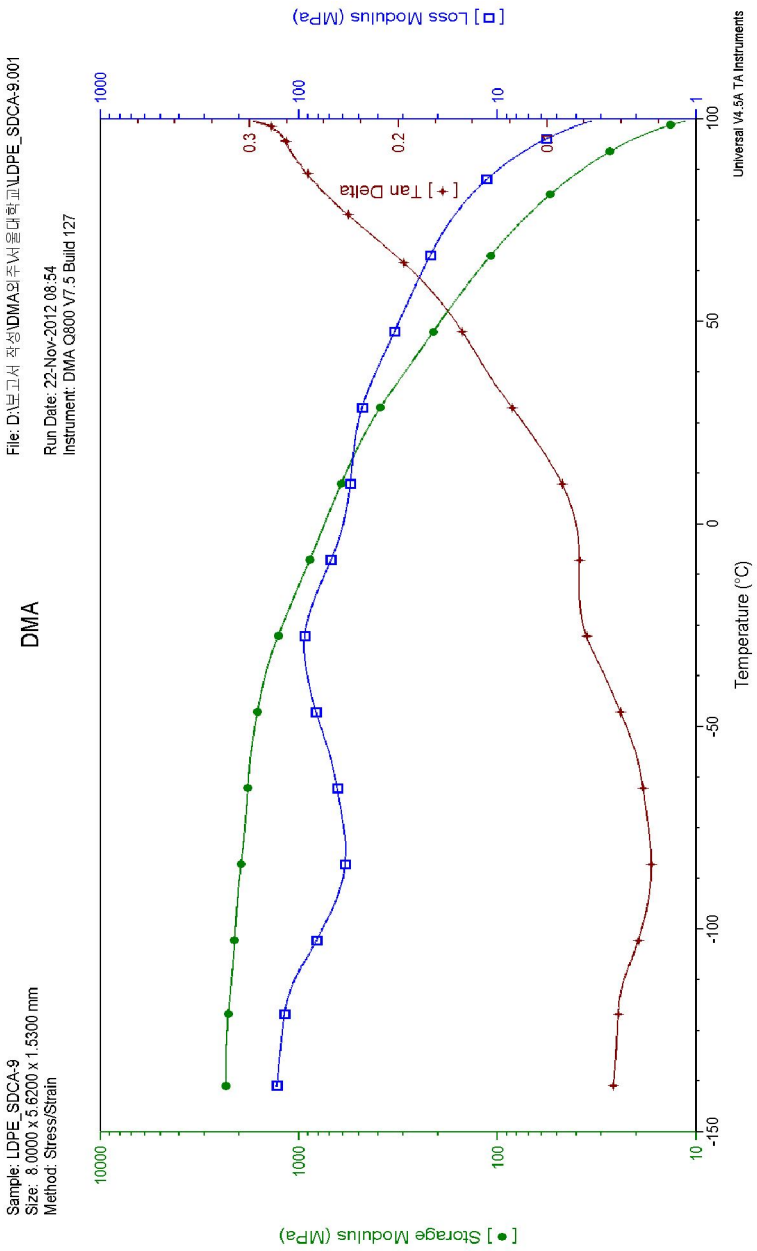


Figure 6(i): Dynamic Mechanical Analysis thermogram of LDPE/SDCA (80/20).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

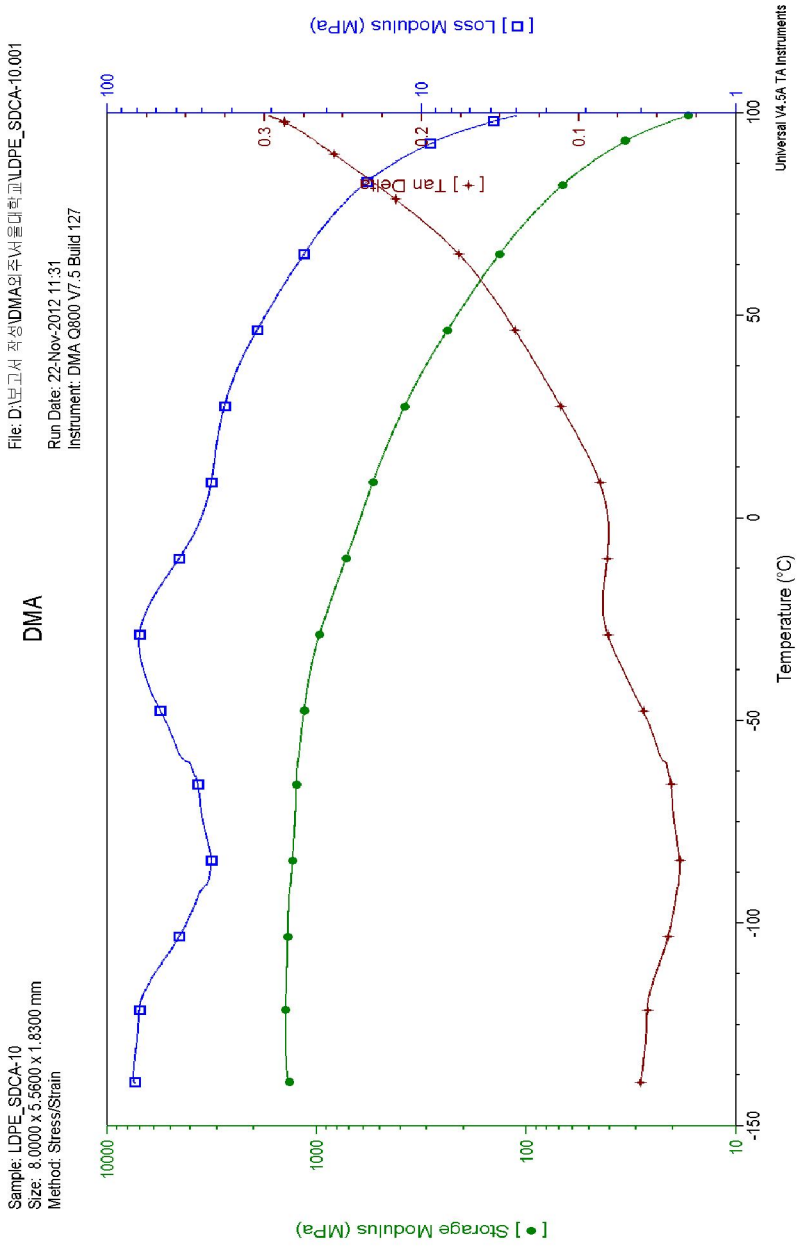


Figure 6(j): Dynamic Mechanical Analysis thermogram of LDPE/SDCA (70/30).

Key ● **Storage modulus**

□ **Loss modulus**

Tanδ

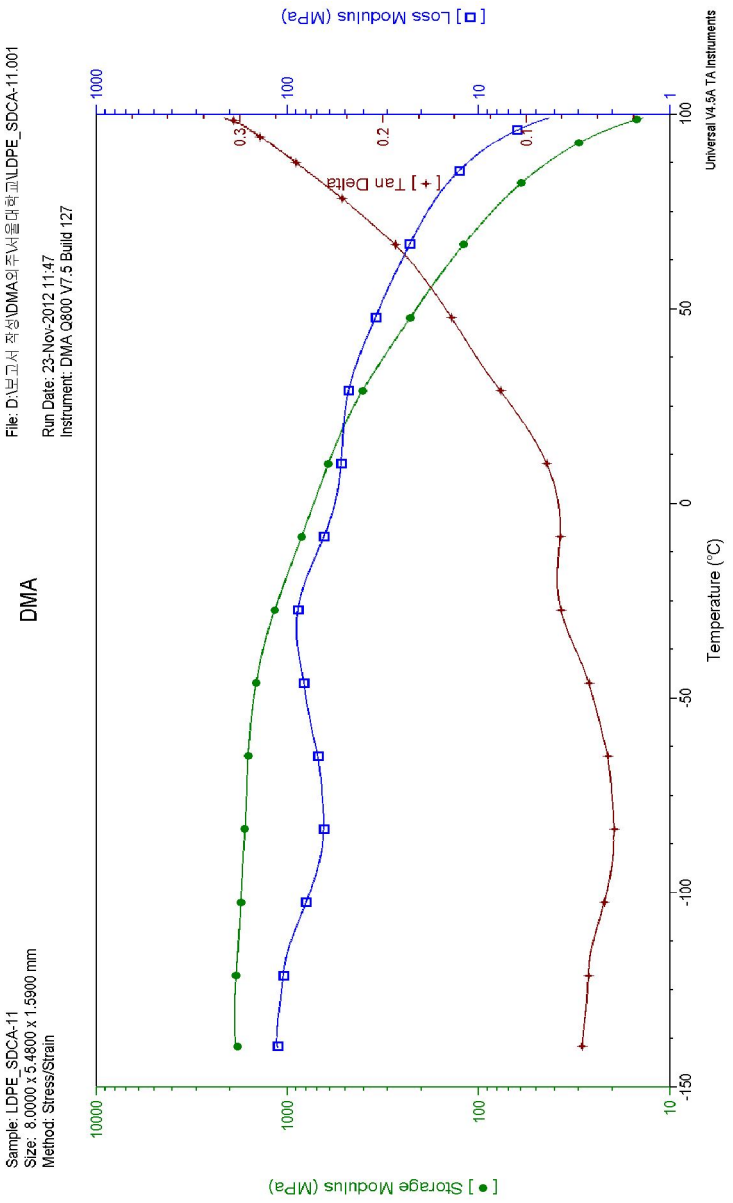


Figure 6(k): Dynamic Mechanical Analysis thermogram of LDPE/SDCA (60/40).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

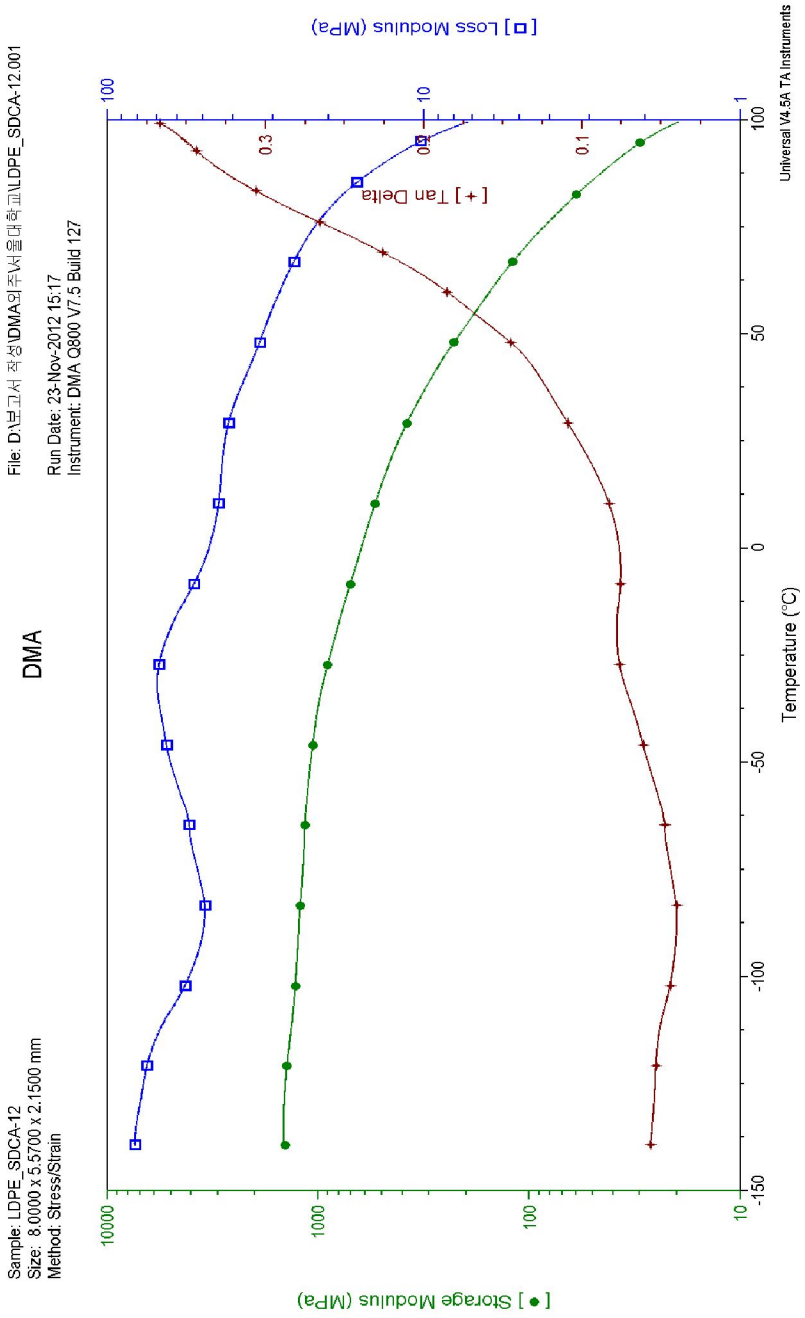


Figure 6(L): Dynamic Mechanical Analysis thermogram of LDPE/SDCA (50/50).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

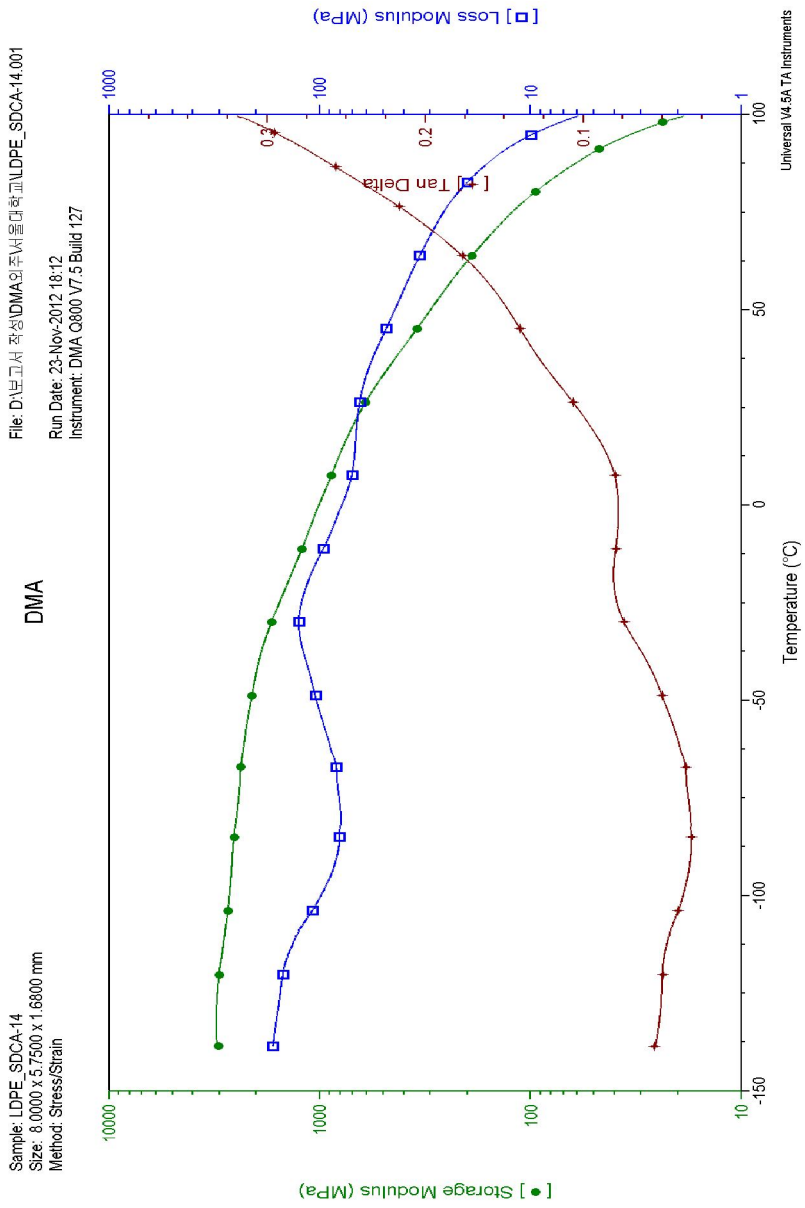


Figure 6(m): Dynamic Mechanical Analysis thermogram of LDPE/STA (80/20).

Key

● **Storage modulus**

□ **Loss modulus**

Tanδ

4.5 Thermal Analysis

Thermal properties (Thermogravimetric analysis and Differential Scanning Calorimetry of the samples were studied using symultanic thermal analyzer SDT Q600 V20.9 Build 20 under Nitrogen atmosphere. The results of the study are shown in figure 7.

4.5.1 Thermogravimetric analysis

The initial weight loss shown from starch thermogravimetric (TGA) curve in figure 7a is attributed to loss of moisture content at temperature of ≈ 70 ^{o}C – 100 ^{o}C . Which corresponds to DTGA peak at ≈ 70 ^{o}C. The TGA curve indicated that the actual starch decomposition started at ≈ 250 ^{o}C and most of the starch was decomposed at ≈ 300 ^{o}C. About 83% of the starch is completely decomposed at ≈ 600 ^{o}C. The remaining 27% might be inorganic impurities or organic matters that could stand high temperatures. Studies on the thermal degradation of starch reported that thermal reactions for starch start around 300 ^{o}C. with thermal condensation between hydroxyl groups of starch chains to form ether segments and liberation of water molecules and other small molecules species. Dehydration of neighbouring hydroxyl groups in the glucose ring also occurred, resulting in the formation of C = C bonds or break down of the glucose ring. Aldehyde groups were formed at the same time possibly as end - groups when the glucose ring was fractured.(Pielichowski and Njuguna 2005)

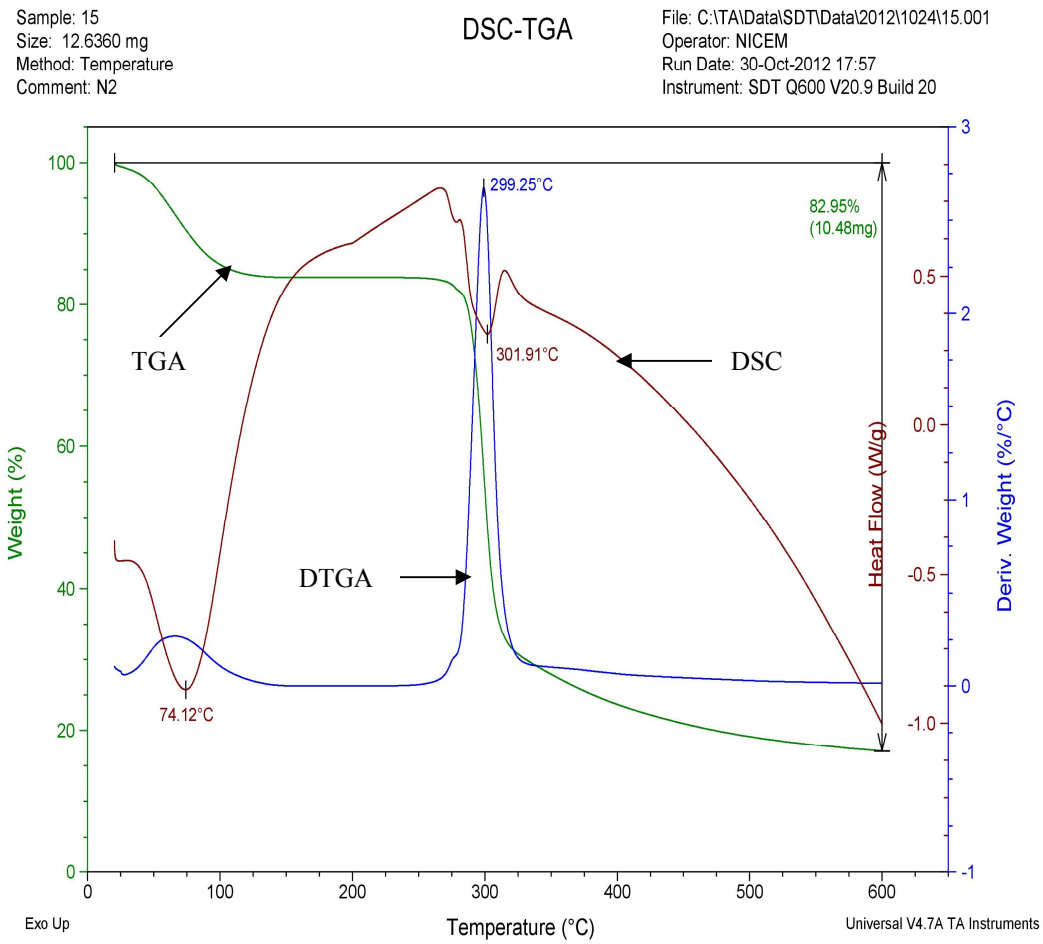


Figure 7a: 100% Starch (STA) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

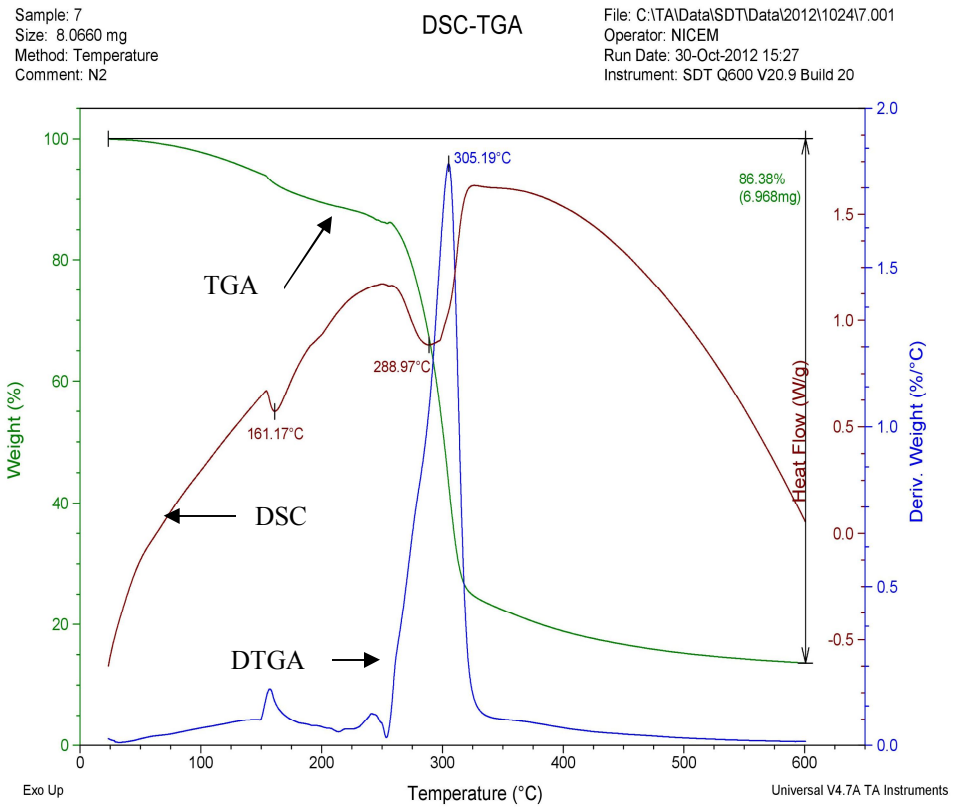


Figure 7b: 100% Thermoplastic – starch (TPS) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

The thermoplastic starch decomposition commenced at ≈ 250 ^{o}C and most of the TPS content was decomposed at ≈ 320 ^{o}C which indicates that it has a better thermal stability though slightly as compared to native starch. The TGA curve figure 7(b) showed that at ≈ 600 ^{o}C about 86.3% of the TPS was decomposed.

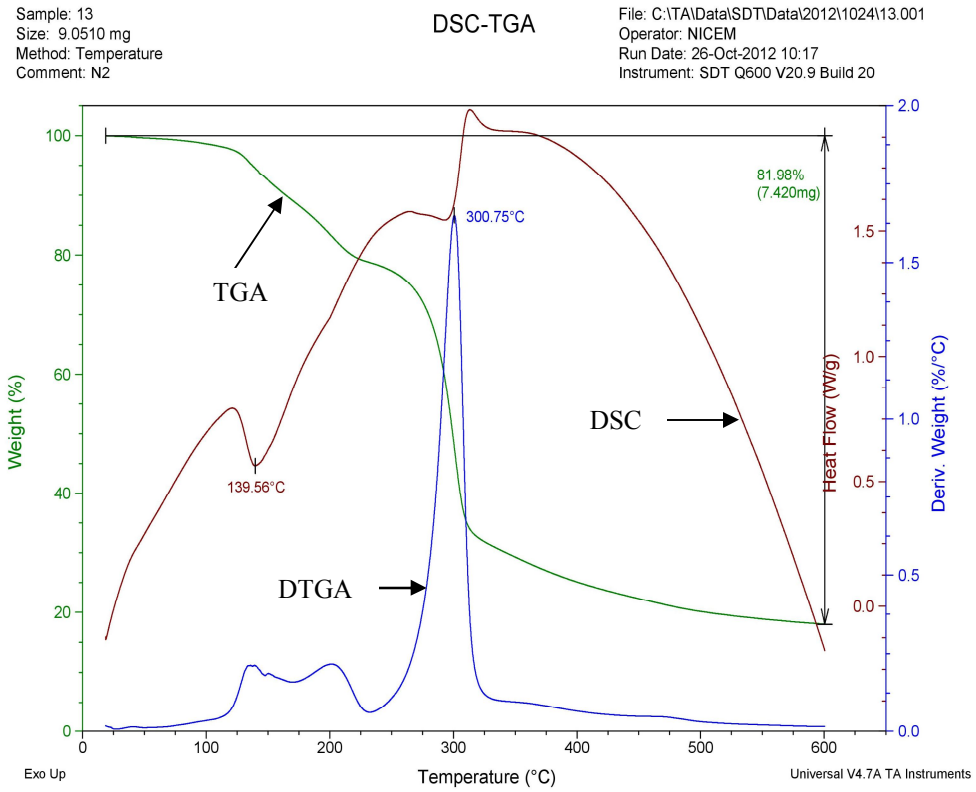


Figure 7c: 100% Starch – dicarboxylic acid compound (SDCA) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

The DTGA curve (from Figure 7c) of the Starch –dicarboxylic acid compound (SDCA) indicated an activity between 120 ^{o}C - 230 ^{o}C which may be attributed to the activities due to the C = C and C = O of partial ester in the molecule. However, the decomposition temperature range of most of the material remains at between 250 ^{o}C and 300 ^{o}C as for the native starch as indicated by the TGA curve. 82% of the material decomposed at 600^{o}C.

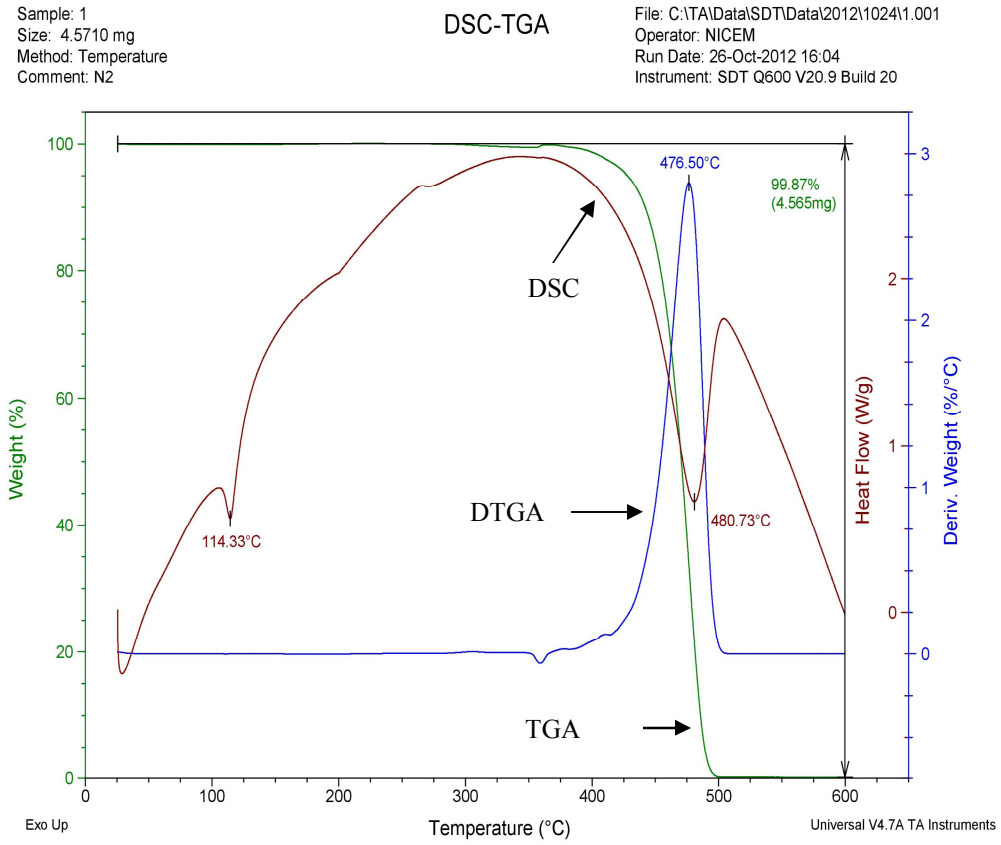


Figure 7d: 100% Low density polyethylene (LDPE) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

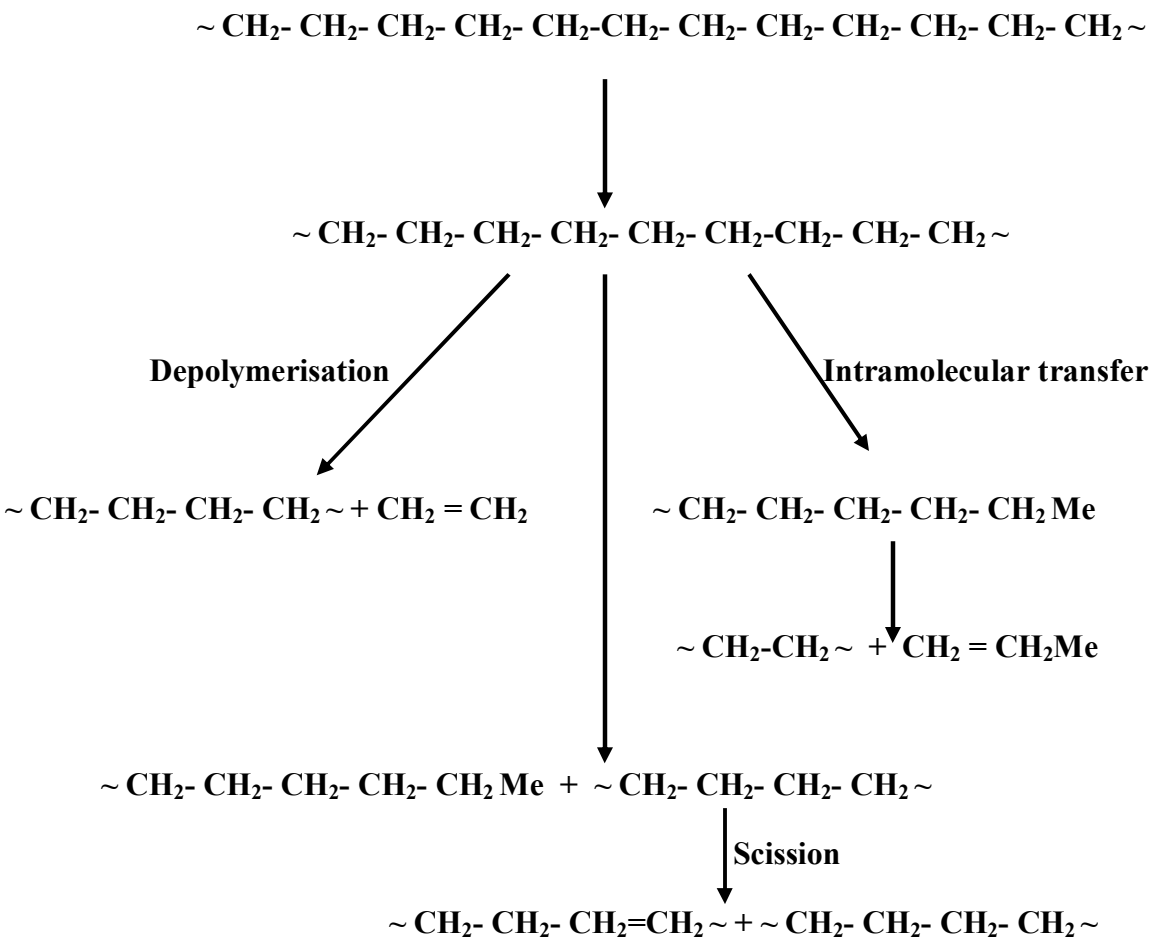
Key — **TGA**

DSC

DTGA

Decomposition of LDPE (from the TGA curve figure 7d) commenced at ≈ 380 ^{o}C, and complete decomposition was at ≈ 500 ^{o}C. The DTGA peak may be observed at ≈ 476 ^{o}C. which is attributed to the complete degradation of both saturated and unsaturated carbon atoms in the Polyethylene.

The degradation mechanism of the polyethylene may be represented as follows (Kalaprasad , 2010);



Polyethylene undergoes random degradation leading to the formation of fragments with active free radical ends. These may either undergo depolymerisation to form daughter free radicals and unsaturated compounds or undergo intramolecular transfer to form secondary free radical which again results in products similar to the earlier case. In the degradation pathway, further scission also can occur (Kalaprasad , 2010).

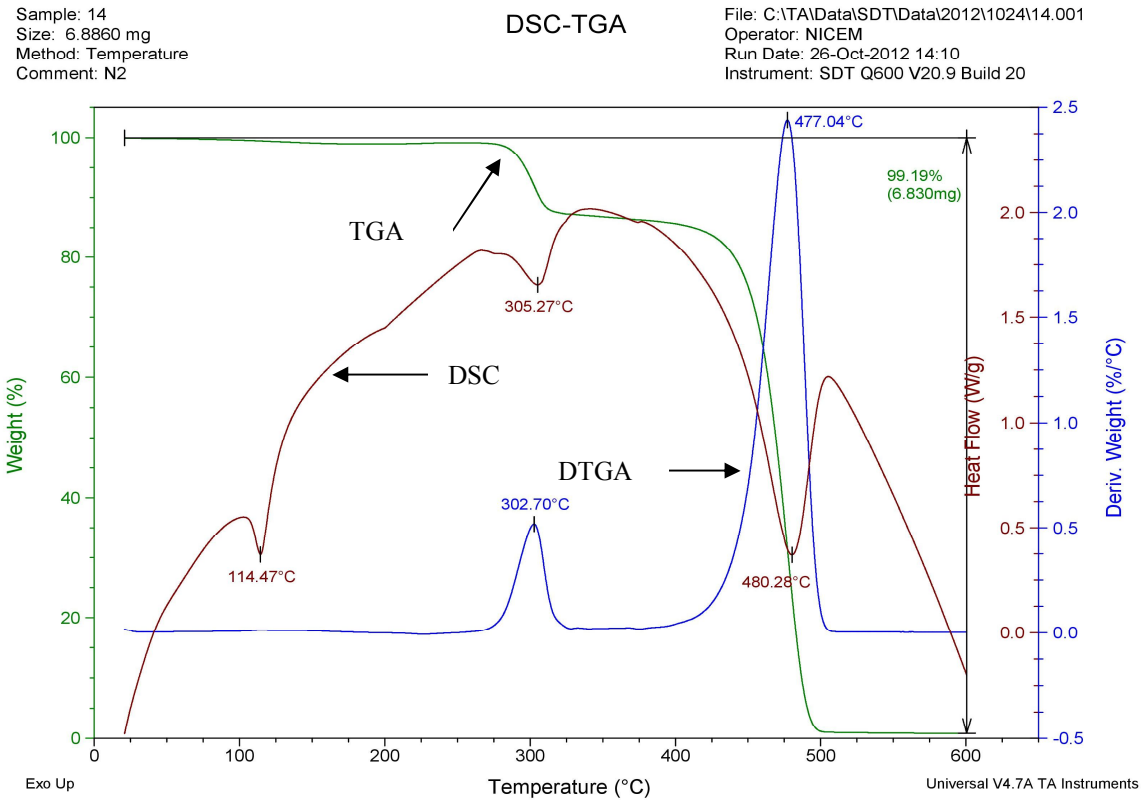


Figure 7e: LDPE/STA (80/20) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

Figures 7f –7p showed the TGA/DSC curves of various composites each of which LDPE is the matrix and either TPS or SDCA is a filler component.

The observed initial weight loss from the TGA curves of the composites is attributed to the filler components of the composites. The decomposition temperature range of both TPS and SDCA is shown to be between 250 ^{o}C - 320 ^{o}C and 250 ^{o}C - 310 ^{o}C respectively when in isolation (not in the composite), that of LDPE is 380 ^{o}C - 500 ^{o}C, however, in the composites there are slight shift upwards in both cases showing a little improvement in thermal stability of these components when in the composites. The starch derivatives (TPS and SDCA) are shown to decompose between 300 ^{o}C – 330 ^{o}C while in the composites and the LDPE may only starts to decompose above 430 ^{o}C after the decomposition of the starch component.

The DTGA curves at about 300 ^{o}C indicate the relative amount of starch decomposed, as it can be seen that the amplitude of the peak increases as the filler content of the composite.

Table 7 showed the step weight loss of the samples at different temperatures. It could be observed that generally LDPE/TPS composites have better thermal stability as compared to LDPE/SDCA. It can also be said that both the LDPE and it's starch derivative composites completely decomposed at 500 ^{o}C..

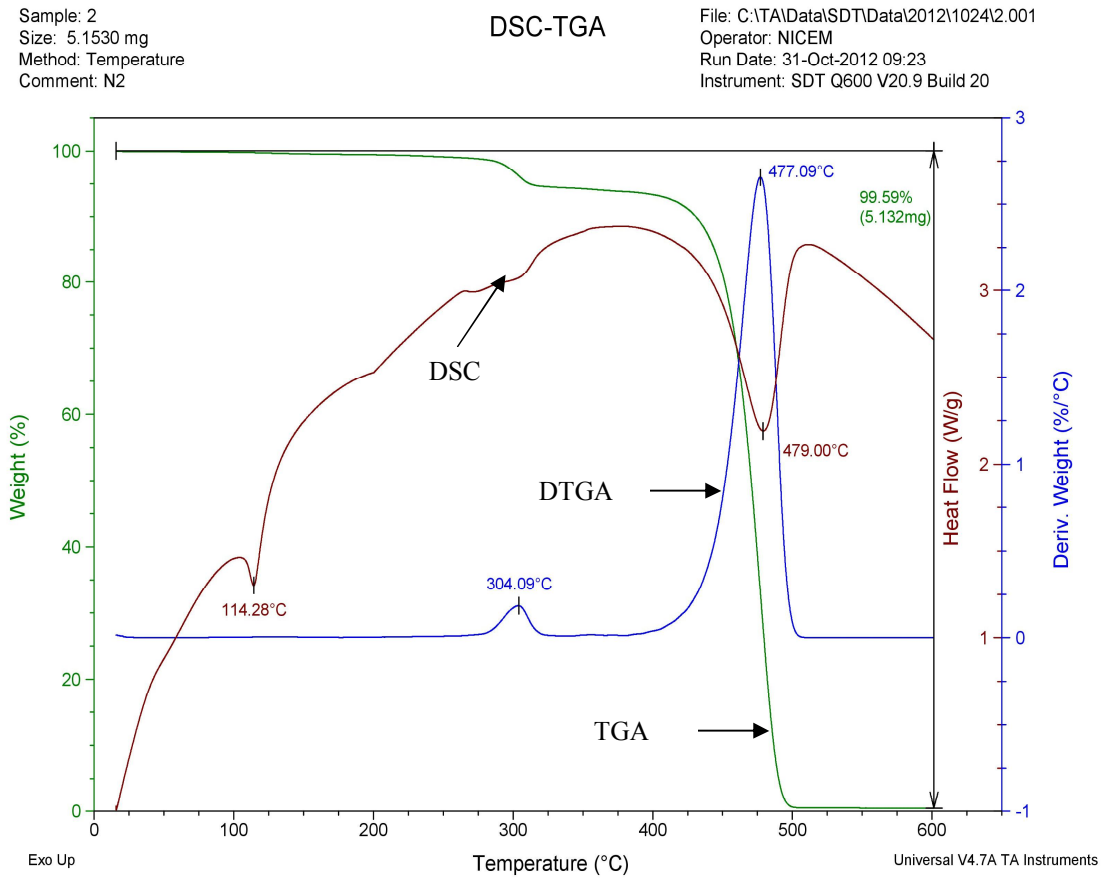


Figure 7f: LDPE/TPS (90/10) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

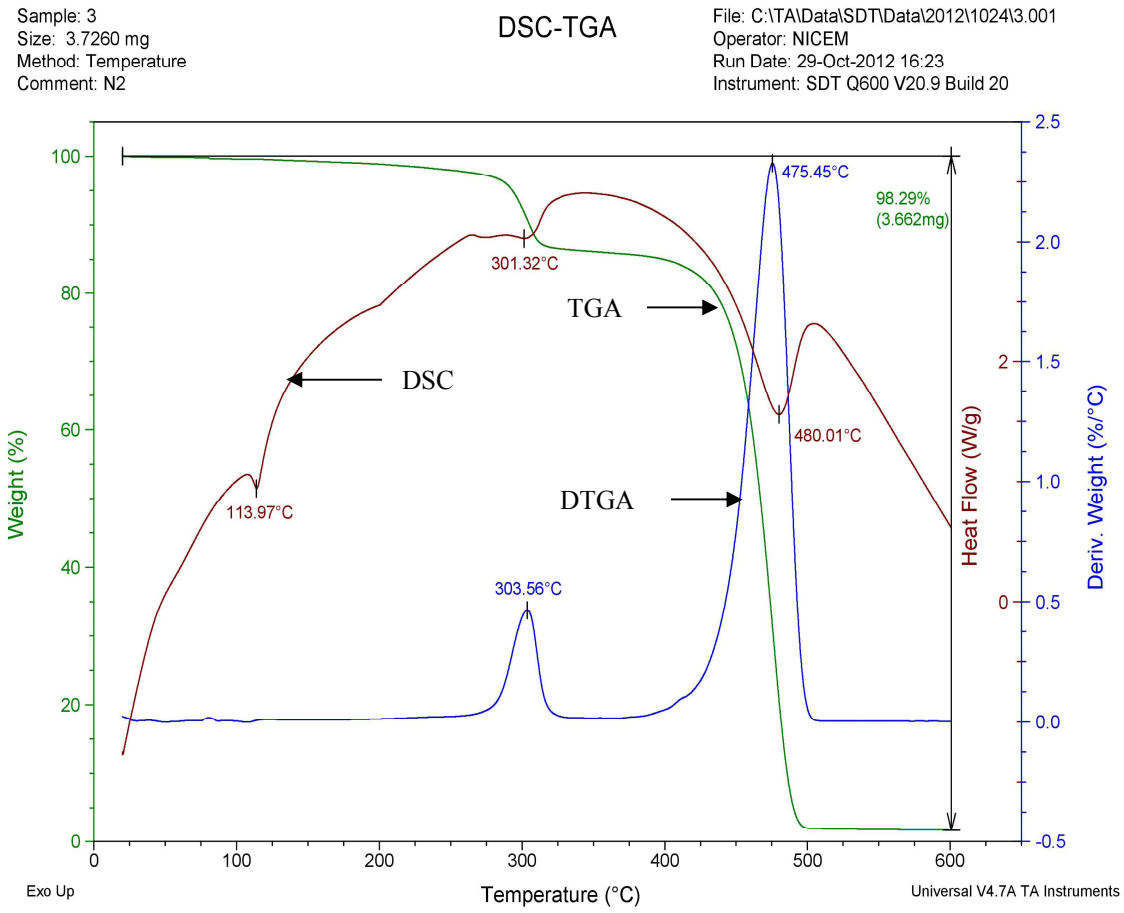


Figure 7g: LDPE/TPS (80/20) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

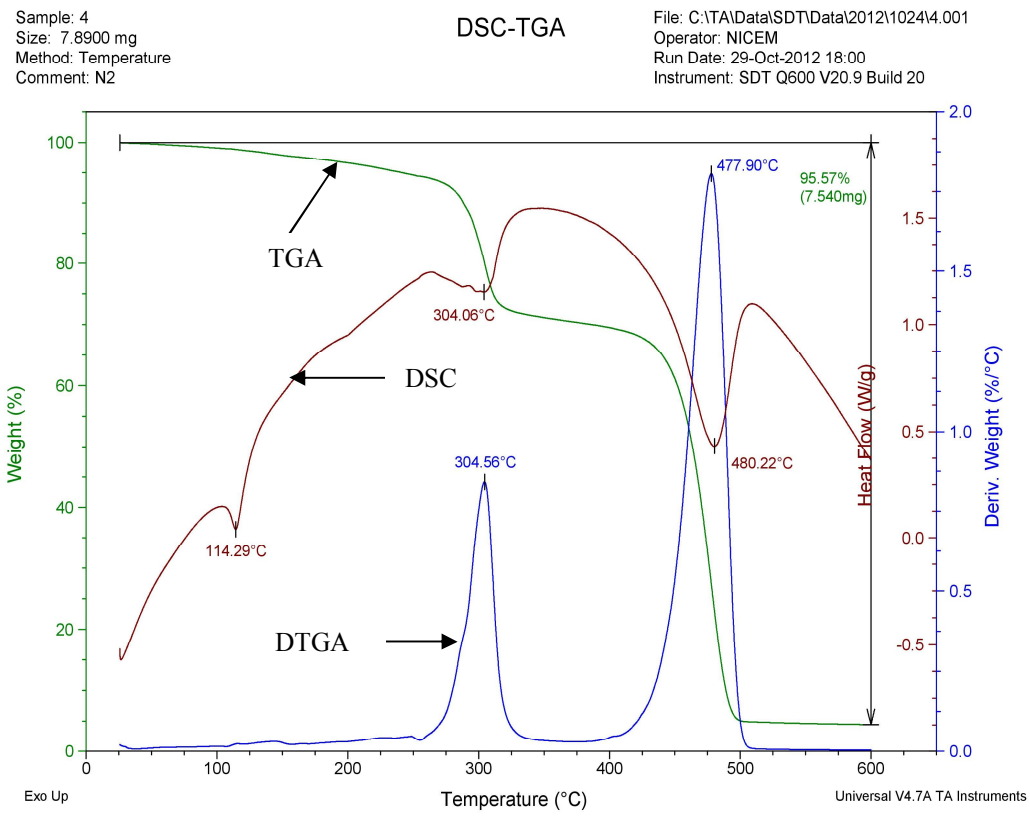


Figure 7h: LDPE/TPS (70/30) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

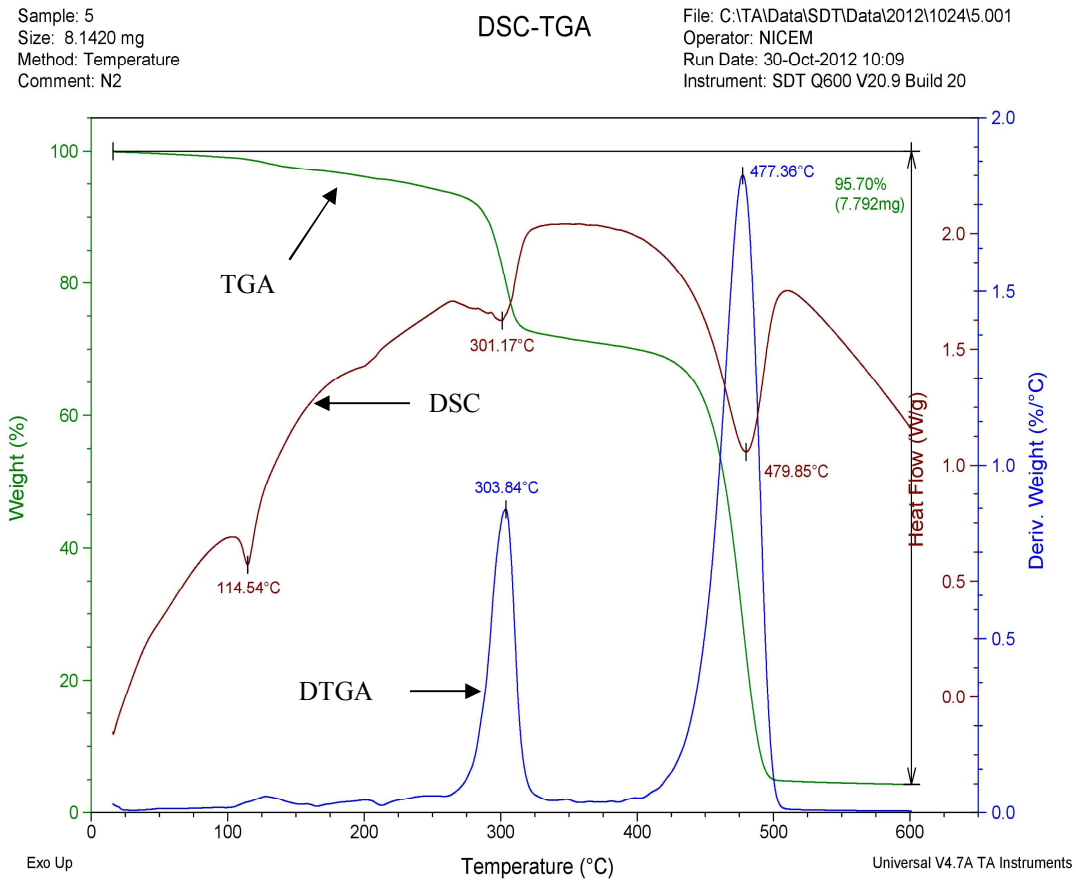


Figure 7i: LDPE/TPS (60/40) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

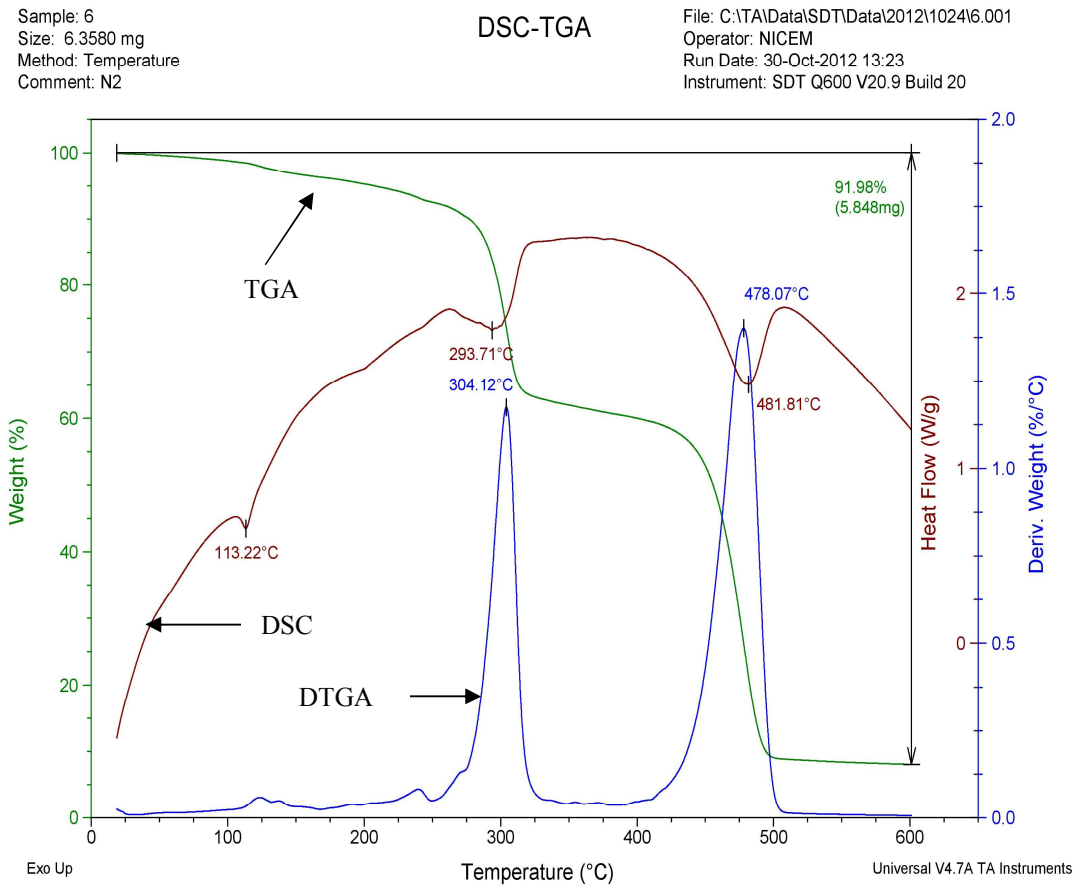


Figure 7j: LDPE/TPS (50/50) DSC/TGA Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

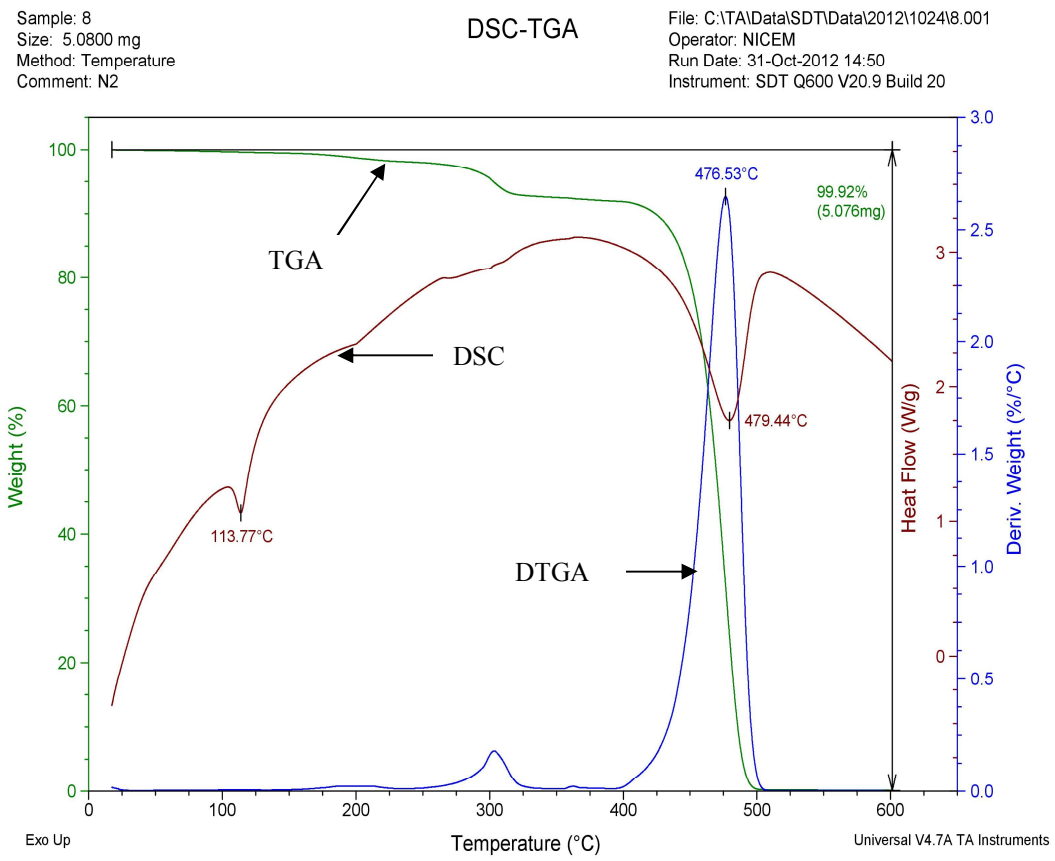


Figure 7k: LDPE/SDCA (90/10) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key — **TGA**

DSC

DTGA

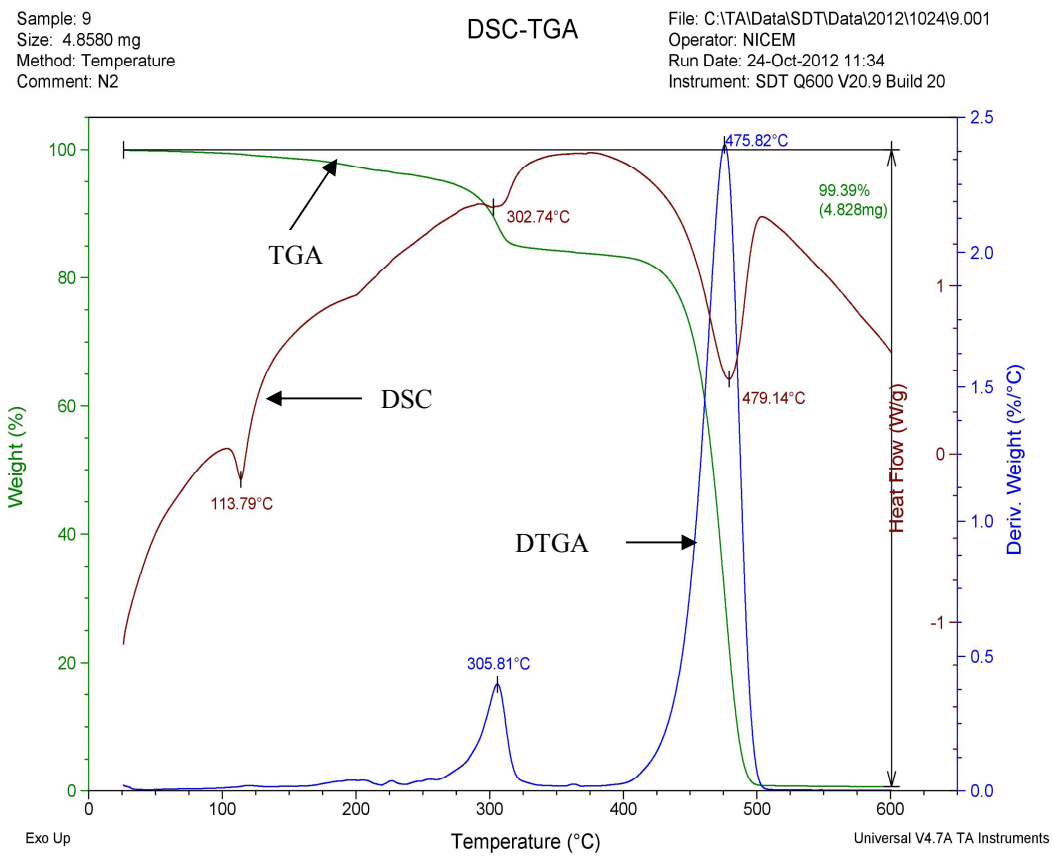


Figure 7L: LDPE/SDCA (80/20) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

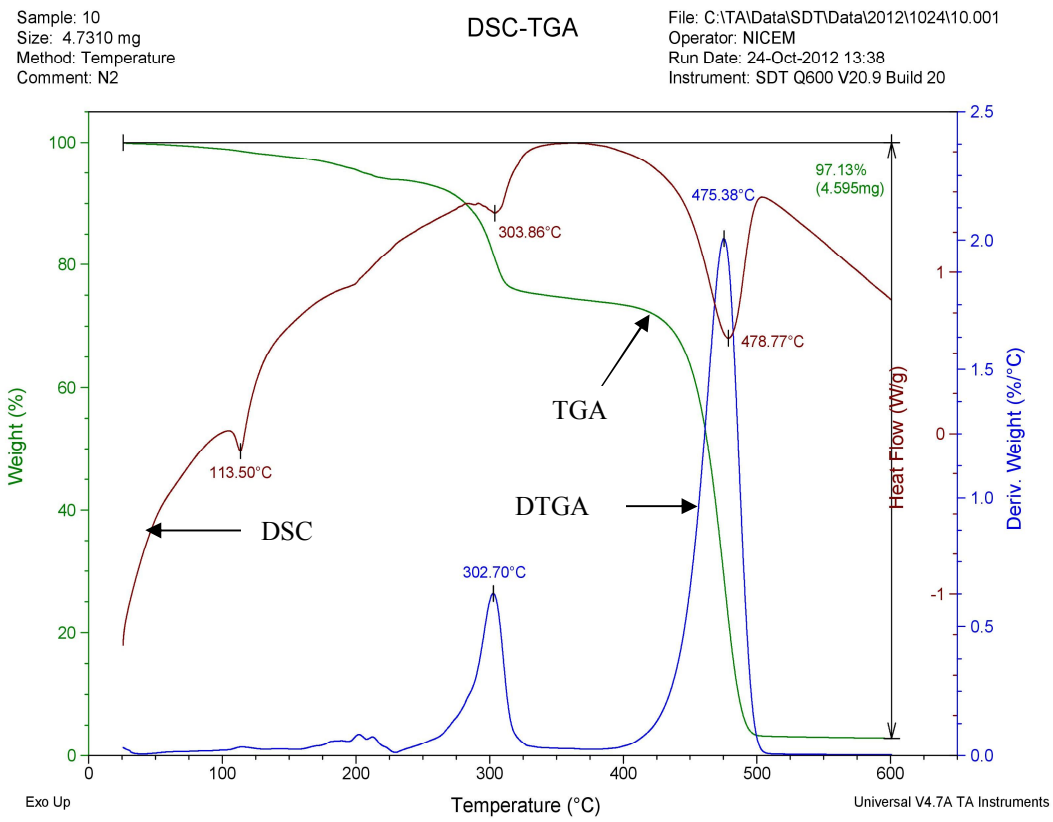


Figure 7m: LDPE/SDCA (70/30) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

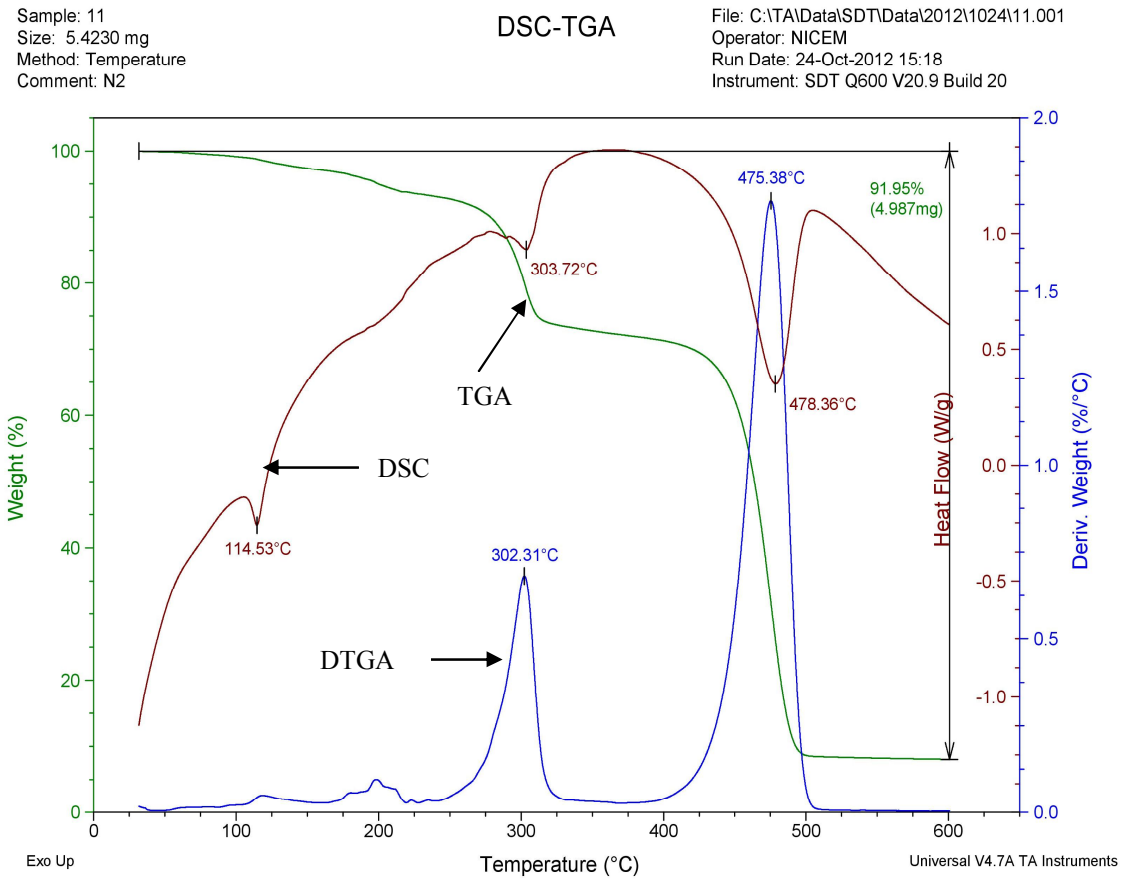


Figure 7n: LDPE/SDCA (60/40) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key — **TGA**

DSC

DTGA

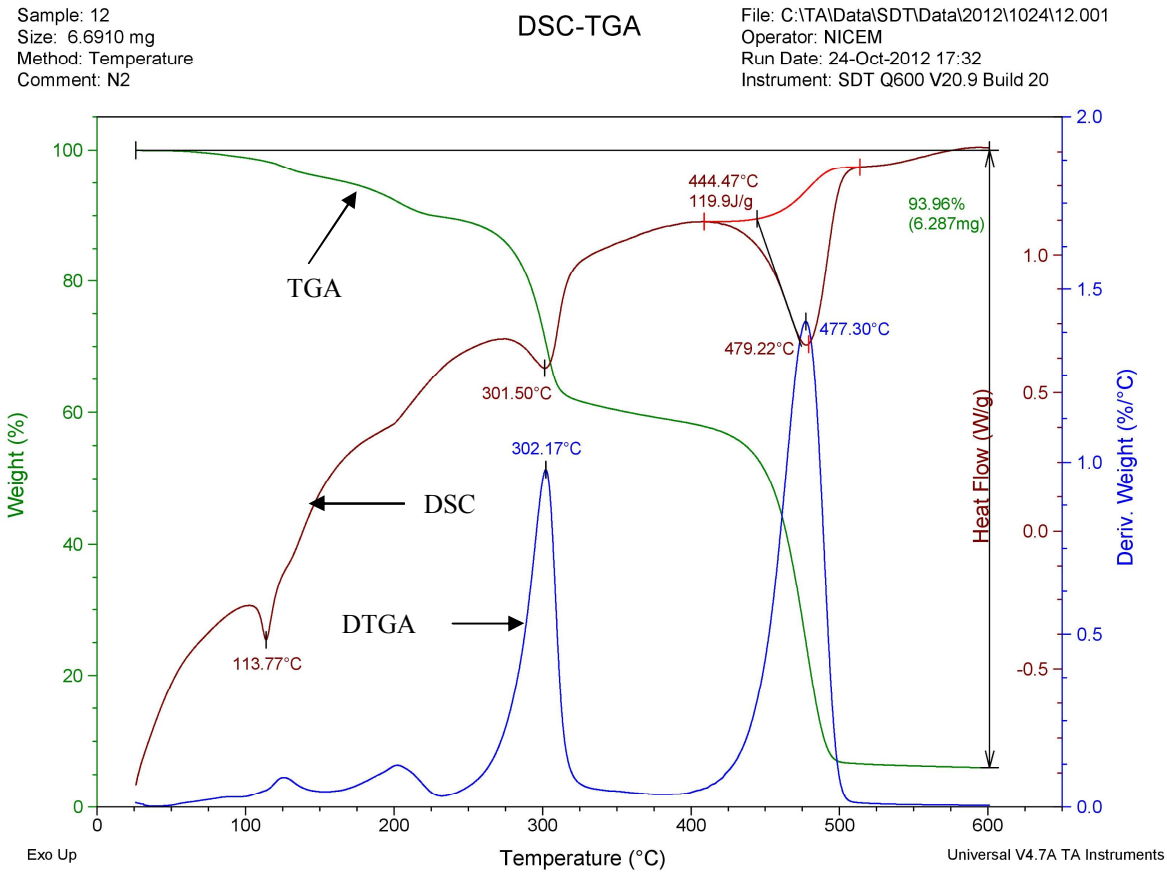


Figure 7p: LDPE/SDCA (50/50) Thermal Curves indicating the loss of weight with temperature (TGA), heat flow through the sample and transition temperature points (DSC).

Key

TGA

DSC

DTGA

Table 7: TGA Percentage weight loss at different Temperatures

Sample	Percentage Decomposition (%)									
	100 °C	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	600 °C
LDPE	00	00	00	00	00	00	05	17	100	100
STARCH	15	15	15	15	40	75	78	80	82	83
TPS	05	07	10	15	55	77	80	82	84	86
SDCA	03	08	18	25	62	70	75	78	80	82
LDPE/TPS 90/10	00	00	00	00	05	08	08	30	100	100
LDPE/TPS 80/20	00	00	00	04	13	13	13	35	98	98
LDPE/TPS 70/30	00	02	05	08	28	30	30	45	96	96
LDPE/TPS 60/40	00	04	05	08	27	30	30	45	96	96
LDPE/TPS 50/50	00	04	05	07	25	39	39	50	92	92
LDPE/SDCA 90/10	00	00	00	03	05	07	07	25	100	100
LDPE/SDCA 80/20	00	02	04	06	15	15	15	40	98	99
LDPE/SDCA 70/30	00	03	06	08	25	25	25	46	97	97
LDPE/SDCA 60/40	00	04	05	10	23	25	25	45	92	92
LDPE/SDCA 50/50	00	05	10	15	30	43	44	52	94	94
LDPE/STA 80/20	00	00	00	00	10	12	12	25	98	99

4.5.2 Differential Scanning Calorimetry (DSC)

The heat flow through the samples under investigation during the differential scanning calorimetry was studied with the view to determine the transition points particularly the melting points (T_m), glass transition points(T_g) and Decomposition temperatures (T_c) using symultanic thermal analyzer SDT Q600.

The peak from the Starch DSC curve (figure 7a) at 74 ^oC corresponds to the temperature at which moisture content starts to vaporized. After the vaporization of the moisture content the heat continue to flow through the starch until the starch is decomposed as indicated by the decomposition (peak) temperature at ≈ 302 ^oC after which the rate of heat flow slows down for the rest of the starch decomposition process. The DSC curve from figure 7b for the thermoplastic starch (TPS) indicated a melting point of ≈ 161 ^oC which also overlaps with the desorption of water. The decomposition temperature for the TPS was indicated at ≈289 ^oC. It may be observed that the decomposition peak which is at relatively lower temperature as compared to that of native starch is wider in size covering more temperature range for complete decomposition of TPS confirming the better thermal stability of TPS as compared to native starch.

The SDCA melting point is indicated at ≈ 139 ^oC by the DSC curve Figure 7c.Thedecomposition temperature is at ≈301 ^oC which appear as a glass transition (T_g), this behaviour may be related to the amorphous characteristics of the material. The LDPE (Figure 7d), melting point is indicated by the DSC curve at ≈ 114 ^oC, the decomposition temperature was shown at ≈ 481 ^oC.

Figures 7f –7p showed the TGA/DSC curves of various composites each of which LDPE is the matrix and either TPS or SDCA is a filler component. It may be observed that in all these composites the melting point is around 114 ^{o}C. which is the melting point of LDPE as indicated in figure 7d, this suggests immiscibility between the composite components as indeed shown in the scanning electron microscopy of the samples and also suggested by WAXD.

The DSC curves of the LDPE/TPS composites indicated Tg values representing the decomposition temperatures of the starch fillers (TPS) i.e Tc or Tg at ≈ 250 ^{o}C - 305 ^{o}C, this is more prominent with LDPE/TPS (80/20) – LDPE/TPS (60/40). However LDPE/SDCA exhibited their Tc at ≈ 250 ^{o}C - 305 ^{o}C for the starch component (SDCA).

The Tc for the LDPE component were indicated between 478 ^{o}C and 482 ^{o}C in all the composites i.e both LDPE/TPS and LDPE/SDCA composites.

The LDPE/SDCA (50/50) (Figure 7p) DSC Curve showed the heat of decomposition or ester bond breakage (C=O) to be 119.9KJ at 444.47 ^{o}C.

4.6 Moisture Absorption

Table8: Percentage water absorption

Days Sample	0	7	14	21	28	35	42	49	56
LDPE	0	0	0	0	0	0	0	0	0
LDPE/TPS 90/10	0	1.85	2.21	2.21	2.29	2.47	2.47	2.47	2.47
LDPE/TPS 80/20	0	3.16	3.54	3.79	3.91	4.23	4.29	4.36	4.36
LDPE/TPS 70/30	0	6.03	7.43	8.34	8.75	8.92	9.73	9.91	10.31
LDPE/TPS 60/40	0	12.56	13.28	13.7	13.85	13.99	14.99	14.99	14.99
LDPE/TPS 50/50	0	20.65	21.1	21.32	21.98	22.21	22.5	22.5	22.95
TPS	0	100	100	100	100	100	100	100	100
LDPE/SDCA 90/10	0	0.82	0.98	1.31	1.55	1.72	1.88	1.88	1.96
LDPE/SDCA 80/20	0	3.75	5.57	6.71	8.08	9.1	10.01	10.24	10.69
LDPE/SDCA 70/30	0	15.8	13.98	12.98	12.87	12.32	11.54	11.21	11.05
LDPE/SDCA 60/40	0	20.68	20.09	18.3	17.26	16.82	16.67	16.52	16.07
LDPE/SDCA 50/50	0	35.75	35.57	35.01	34.36	33.99	33.71	33.43	27.19
SDCA	0	-100	-100	-100	-100	-100	-100	-100	-100
LDPE/STA 80/20	0	3.47	3.91	4.14	4.57	5.13	5.59	5.59	5.59

Introduction of water absorbency to hydrophobic materials may be used as an indication of degradation possibility, this could be related to susceptibility of the material to microbial attack. Table 8 and figure 8(a – c) showed the results of water uptake of samples under investigation. The results indicated that the moisture uptake increases with time of immersion and filler concentration for both the LDPE/TPS (Figure 8a) and the LDPE/SDCA (Figure 8b). It may also be observed that there is very high rate of moisture uptake within the first few days of immersion, however in later days the rate of water uptake greatly decreases though without reaching equilibrium in the case of LDPE/TPS. Similar results were obtained by various researchers (Danjaji et al 2001, Chuayjuljit et al 2009) .

The absorption of water is related to its rate of diffusion into the composites. Moisture uptake in Starch - LDPE composites is mainly due to the starch particles; exposed starch granules or those at or near the surface absorb moisture faster than those in the interior. The decrease in the rate of moisture uptake with time of immersion could be due to a concentration gradient across the two materials. Initial water molecules added to starch particles have been found to be strongly bonded as in a hydrate. When all the available hydroxyl groups are used up in this way, further water absorbed is held less firmly (Danjaji ,et al 2002).

In the LDPE/SDCA composites (Figure 8b) the percentage weight of the material decreases with time of immersion after reaching a peak, this behaviour is more clearly manifested in composites with higher concentration of fillers. The 100% SDCA completely dissolved in water within 24hours during the water absorbency test, indicating that the starch was actually hydrolysed when reacted with the carboxylic acid. Clarke and

Gillespie (1932) mentioned that Carboxylic acids can hydrolyse starch at a higher rate than even mineral acids (Jancy and Raja, 1999). The decrease in percentage weight of the LDPE/SDCA composite after absorbing maximum amount of water could thus, be attributed to loss of material after dissolution of some fraction of the starch-dicarboxylic acid present from the composite.

Generally the LDPE/SDCA composites have greater water susceptibility as compared to LDPE/TPS. This phenomenon is clearly shown in figure 8c.

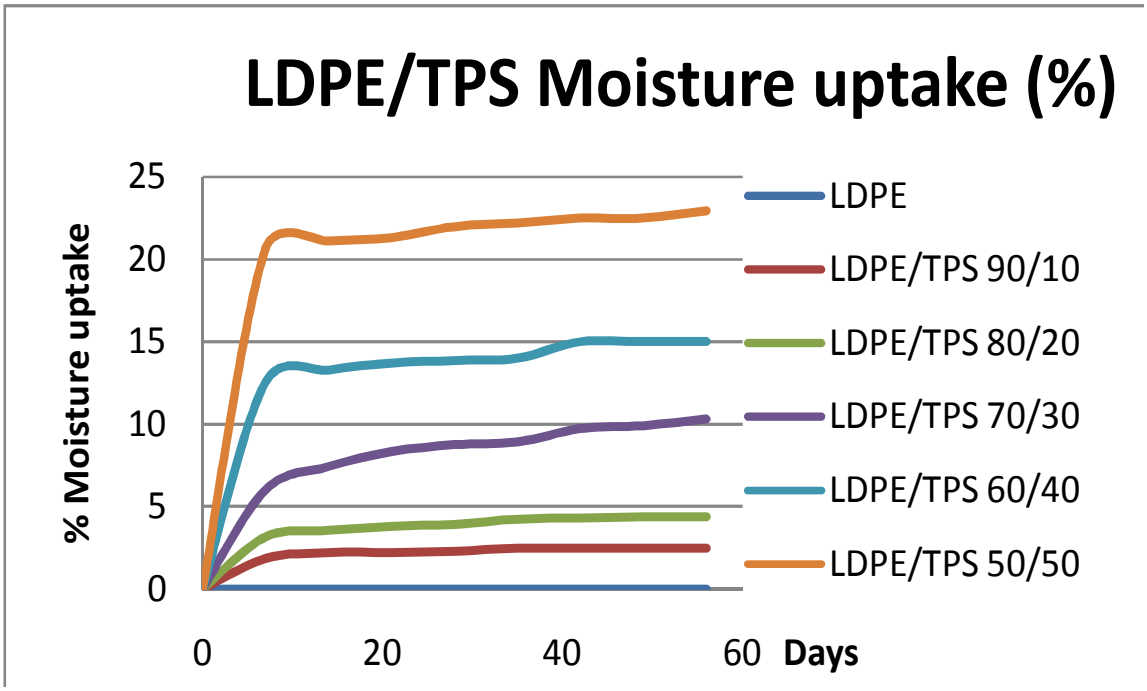


Figure 8a: LDPE/TPS Rate of water absorption with time

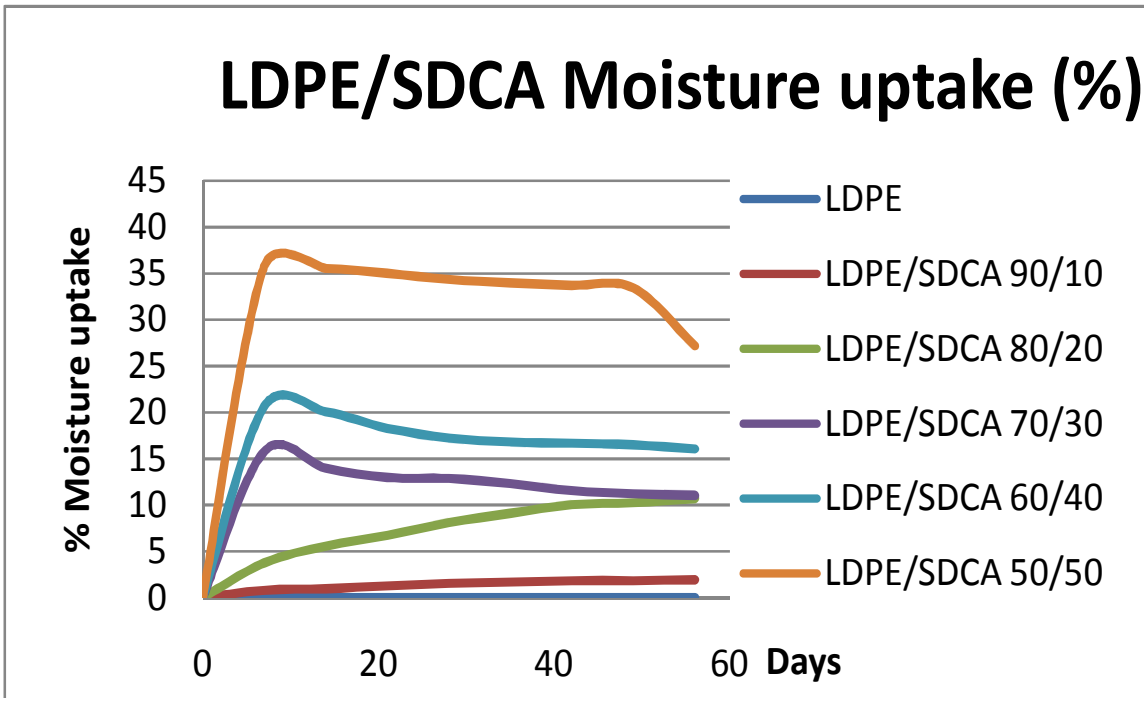


Figure 8b: LDPE/SDCA Rate of water absorption with time

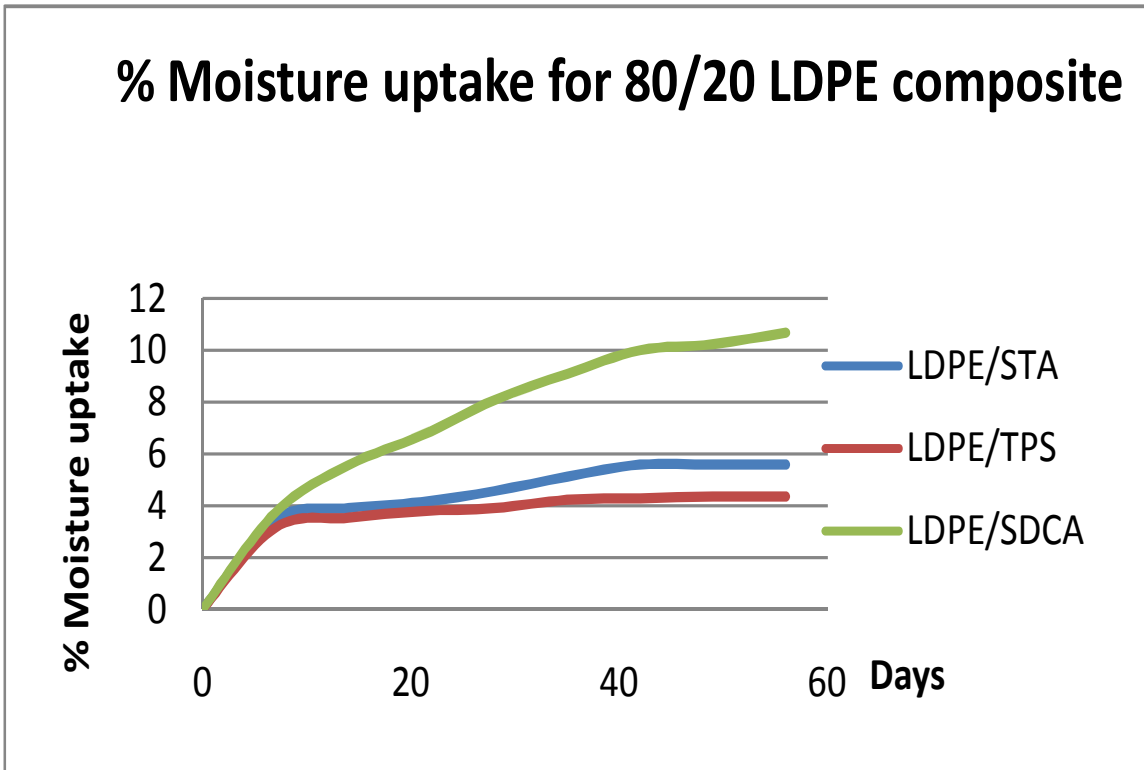


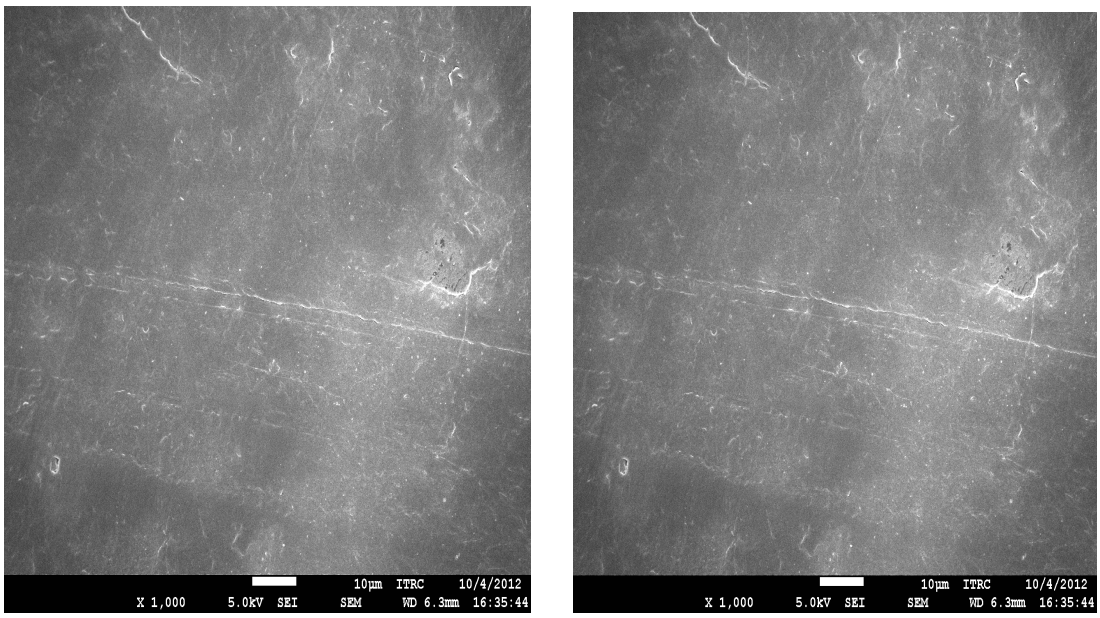
Figure 8c: Rate of water absorption with time for 80/20 LDPE/STA, 80/20LDPE/TPS and 80/20LDPE/SDCA composites.

4.7 Soil Burial Test

The samples for soil burial tests were buried at an agricultural garden at Seoul South Korea during the rainy season i.e between the months of August 2012 and October 2012 to a soil depth of 15cm from the surface ground, and about 300mm in between each other. The samples were unearthed after 63 days, carefully washed thoroughly with tap water followed by distilled water and then allowed to dry in an open air for 7 days. The morphology of the samples was studied before and after the test using Scanning Electron Microscope Jeol JSM 7600F. The weight of the samples was also measured before and after the soil burial from which the percentage weight loss was determined (Table 9). The Micrograph of the sample before and after the soil burial test is shown in plateIII (a –L). It may be observed that there is no remarkable change between the LDPE micrographs before and after the soil burial (plate IIIa, I & ii). How ever, remarkable changes appeared on the composites, the degraded samples appeared whitish and brittle with pores. Leading to increase in surface area of PE matrix and providing susceptible groups for its biodegradation (Park et al, 2002).

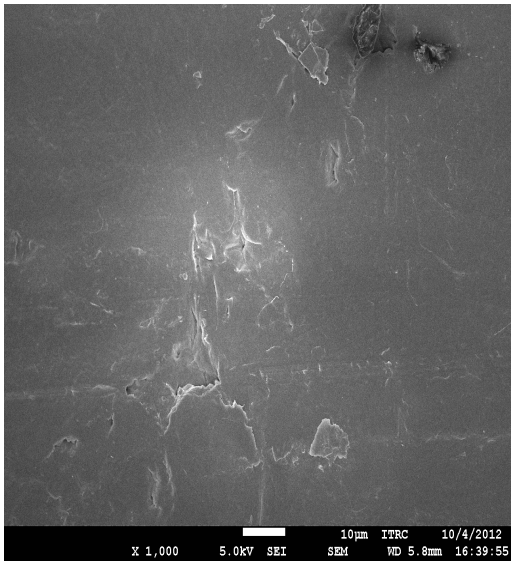
Table 9 and figure 9 showed the percentage weight loss of the samples after the soil burial. It may be observed that the % weight loss increases with increasing filler content for both the LDPE/TPS and LDPE/SDCA. This is due to the action of microbes present in the soil consuming the filler (starch derivative) or leaching action on the material. The more the amount of starch on the composite sample the higher the action of the microbes on it.

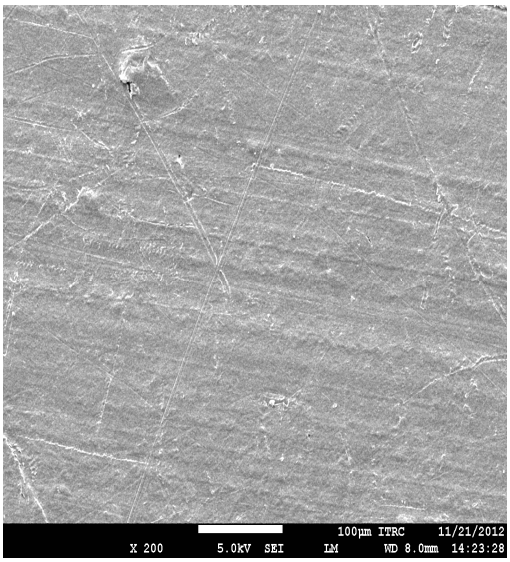
Both results showed that LDPE/SDCA composite are more susceptible to soil degradation as compared to the LDPE/TPS composites. This is due to the fact that SDCA is more hydrophilic than the TPS and therefore more likely to be attracted by microorganisms and consumed.



(i) before burial **(ii) after burial**

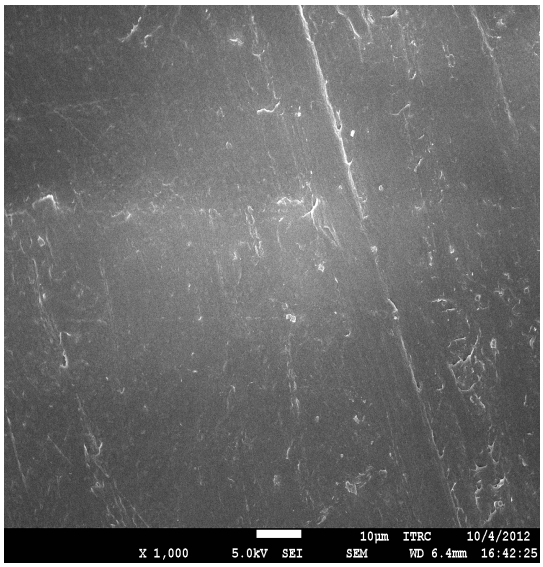
Plate III (a): Scanning electron microgrograp of 100% Low density polyethylene (LDPE) showing the effect of soil burial degradation after 63 days.

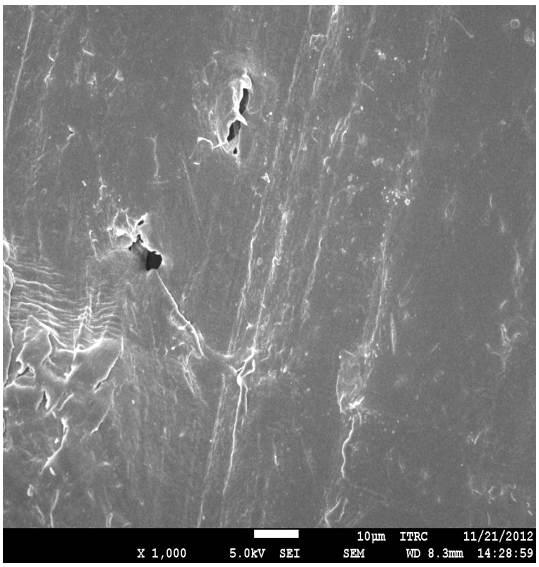




(i) before burial **(ii) after burial**

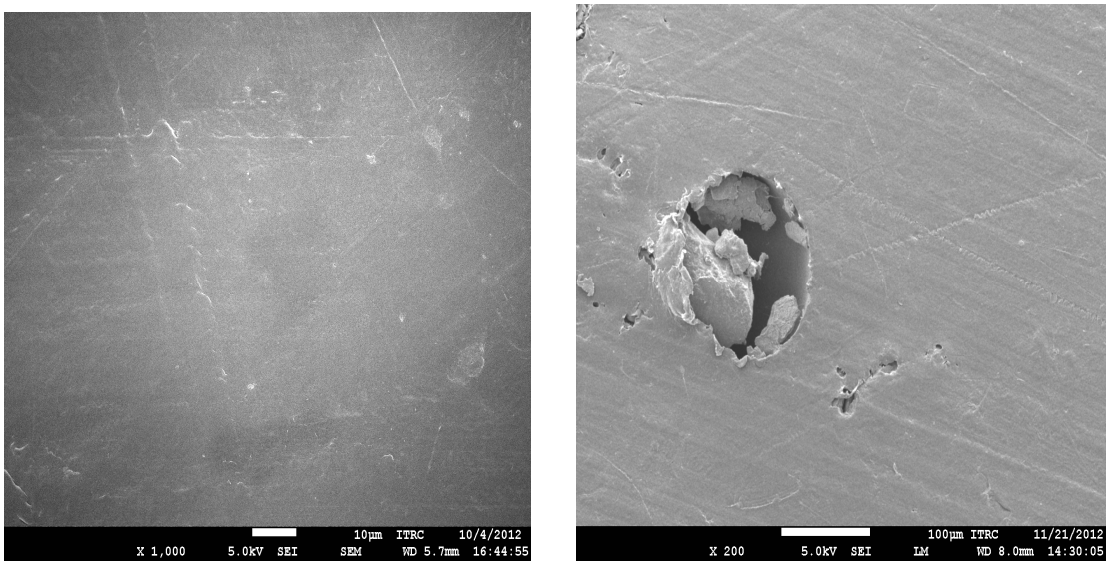
Plate III (b): Scanning electron micrograph of LDPE/TPS (90/10) showing the effect of soil burial degradation after 63 days.





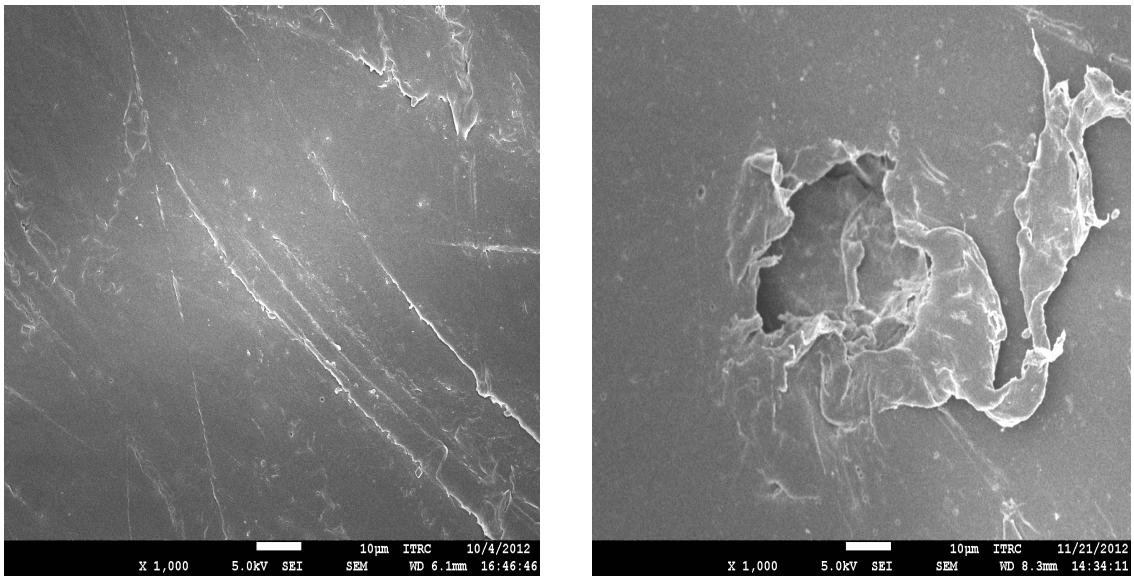
(i) before burial **(ii) after burial**

Plate III (c): Scanning electron micrograph of LDPE/TPS (80/20) showing the effect of soil burial degradation after 63 days.



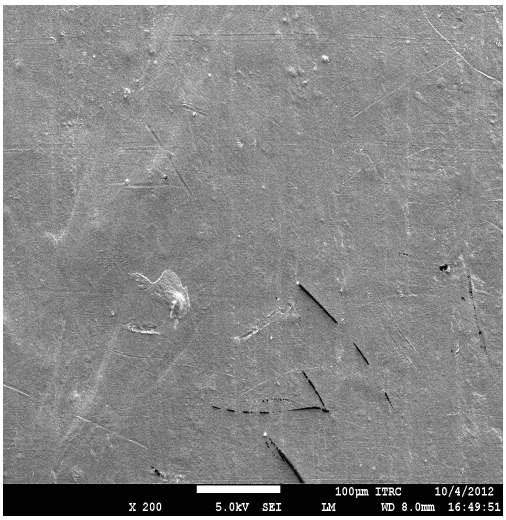
(i) before burial **(ii) after burial**

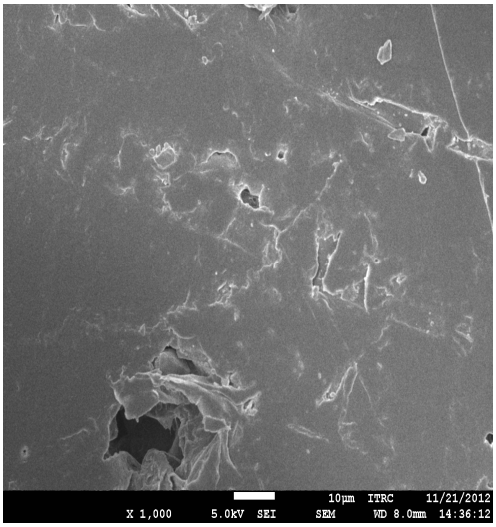
Plate III (d): Scanning electron micrograph of LDPE/TPS (70/30) showing the effect of soil burial degradation after 63 days.



(i) before burial **(ii) after burial**

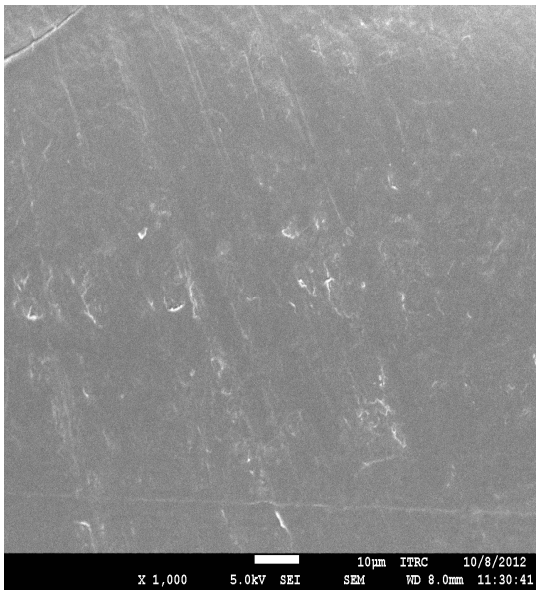
Plate III (e): Scanning electron micrograph of LDPE/TPS (60/40) showing the effect of soil burial degradation after 63 days.

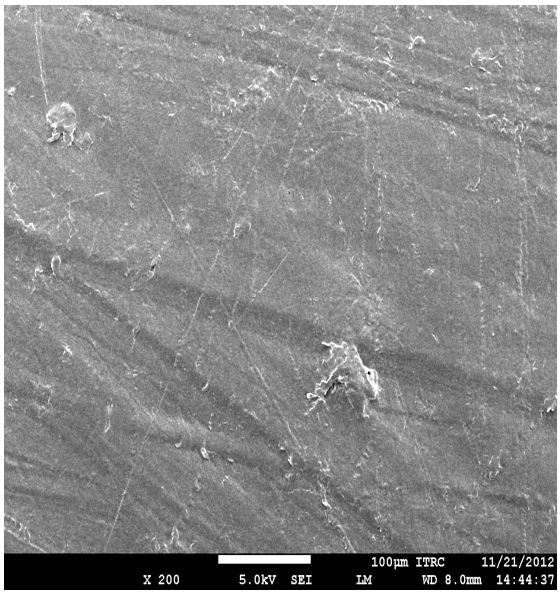




(i) before burial **(ii) after burial**

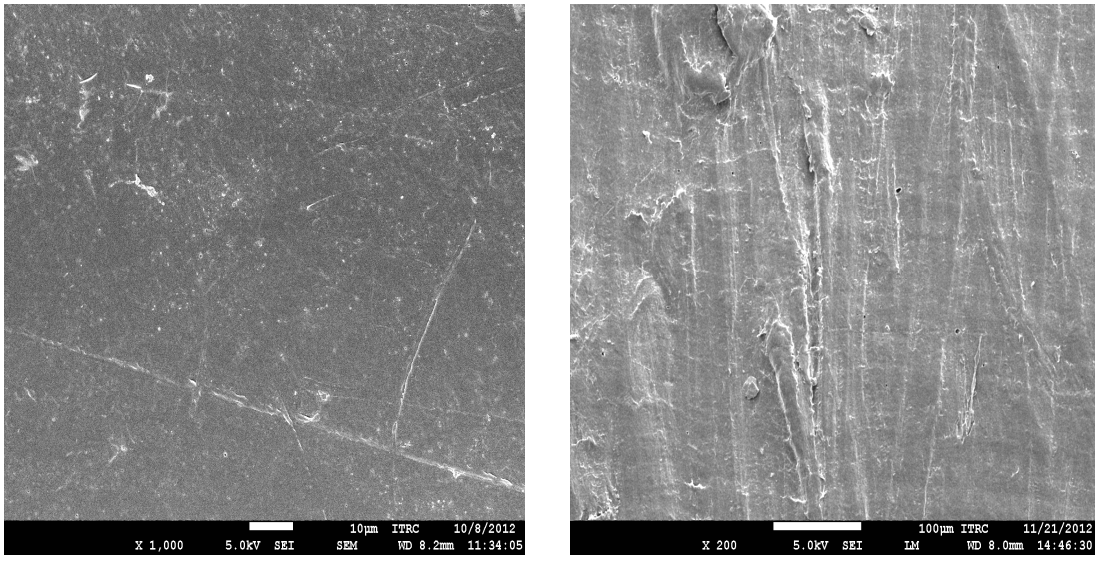
Plate III (f): Scanning electron microgrograp of LDPE/TPS (50/50) showing the effect of soil burial degradation after 63 days.





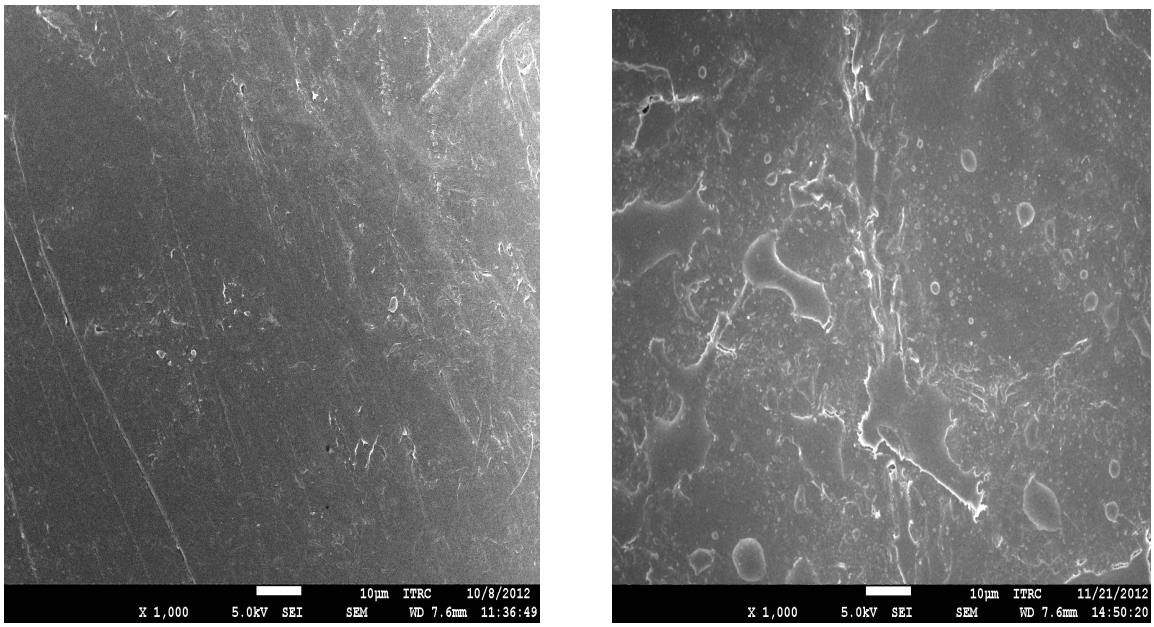
(i) before burial **(ii) after burial**

Plate III (g): Scanning electron microgrograp of LDPE/SDCA (90/10) showing the effect of soil burial degradation after 63 days.



(i) before burial **(ii) after burial**

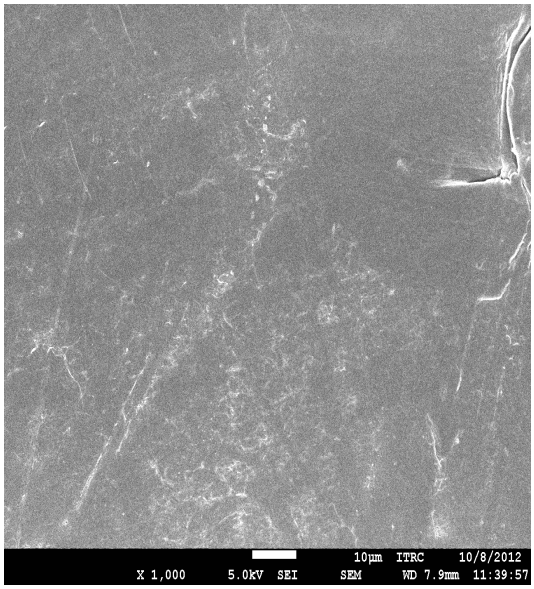
Plate III (h): Scanning electron micrograph of LDPE/SDCA (80/20) showing the effect of soil burial degradation after 63 days.



(i) before burial **(ii) after burial**

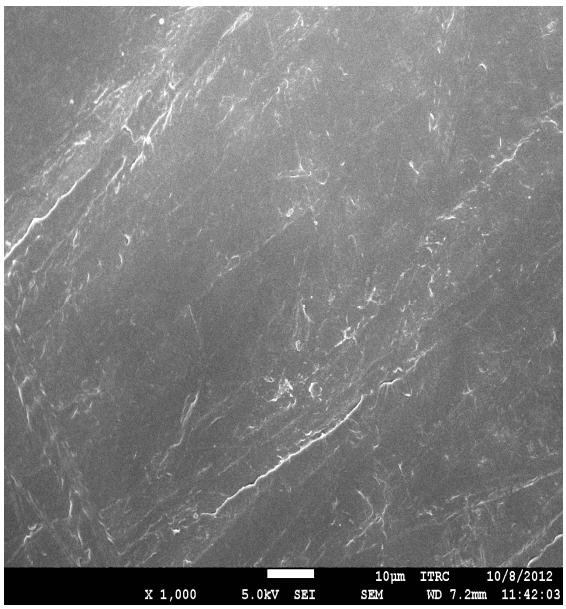
Plate III (i): Scanning electron micrograph of LDPE/SDCA (70/30) showing the effect of soil burial degradation after 63 days.

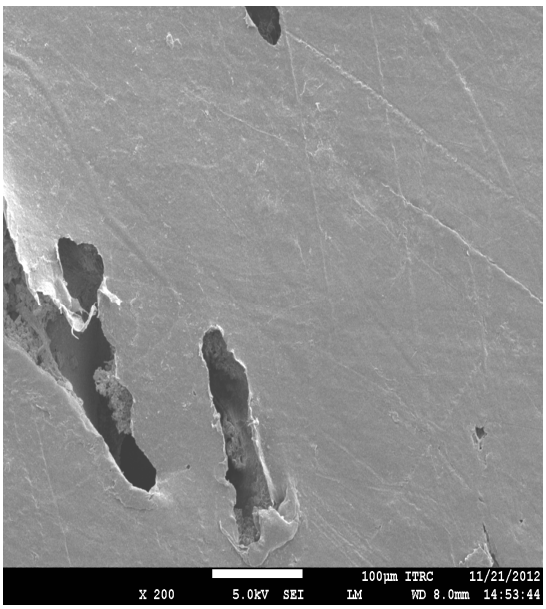




(i) before burial **(ii) after burial**

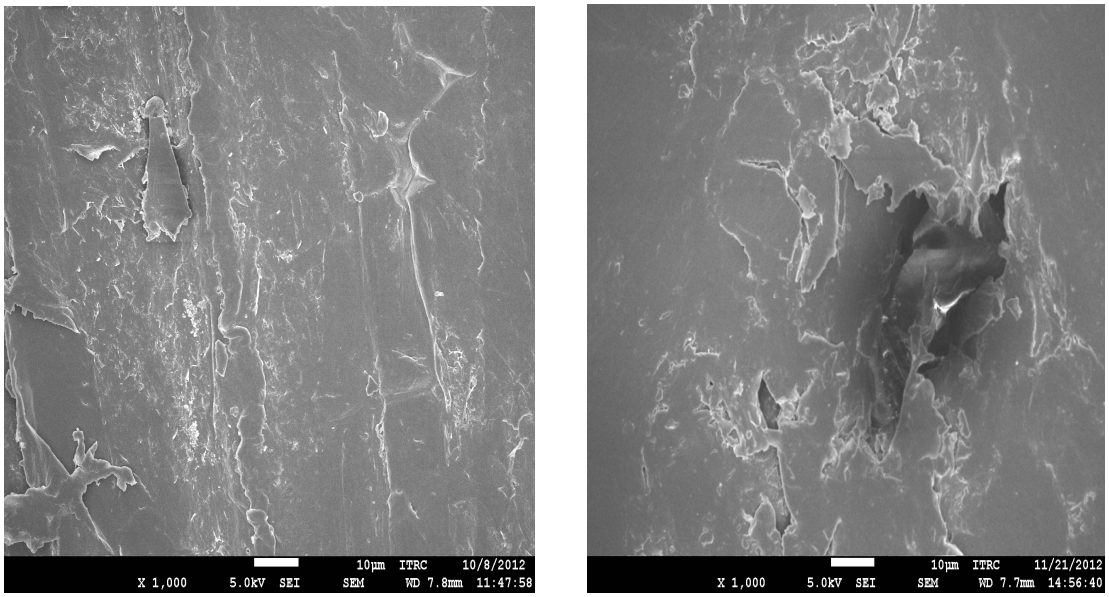
Plate III (j): Scanning electron microgrograp of LDPE/SDCA (60/40) showing the effect of soil burial degradation after 63 days.





(i) before burial **(ii) after burial**

Plate III (k): Scanning electron microgrograp of LDPE/SDCA (50/50) showing the effect of soil burial degradation after 63 days.



(i) before burial **(ii) after burial**

Plate III (L): Scanning electron microgrograp of LDPE/STA (80/20) showing the effect of soil burial degradation after 63 days.

Figure 9: Soil burial degradation (percentage weight loss)

Sample	Weight before burial (g)	Weight after burial (g)	Percentage weight loss (%)
LDPE	1.340	1.286	0.04
LDPE/TPS (90/10)	1.672	1.559	6.76
LDPE/TPS (80/20)	1.233	1.096	11.11
LDPE/TPS (70/30)	1.689	1.423	15.75
LDPE/TPS (60/40)	1.489	1.069	28.14
LDPE/TPS (50/50)	1.792	1.112	37.95
TPS	1.407	0.000	100
LDPE/SDCA (90/10)	1.560	1.416	9.23
LDPE/SDCA (80/20)	1.151	0.947	17.72
LDPE/SDCA (70/30)	1.534	1.138	25.81
LDPE/SDCA (60/40)	1.426	0.945	33.73
LDPE/SDCA (50/50)	1.691	0.899	46.84
SDCA	1.070	0.000	100
LDPE/STA (80/20)	1.766	1.518	14.04

Figure 9 shows the effect of soil degradation on weight of the samples after 63 days burial.

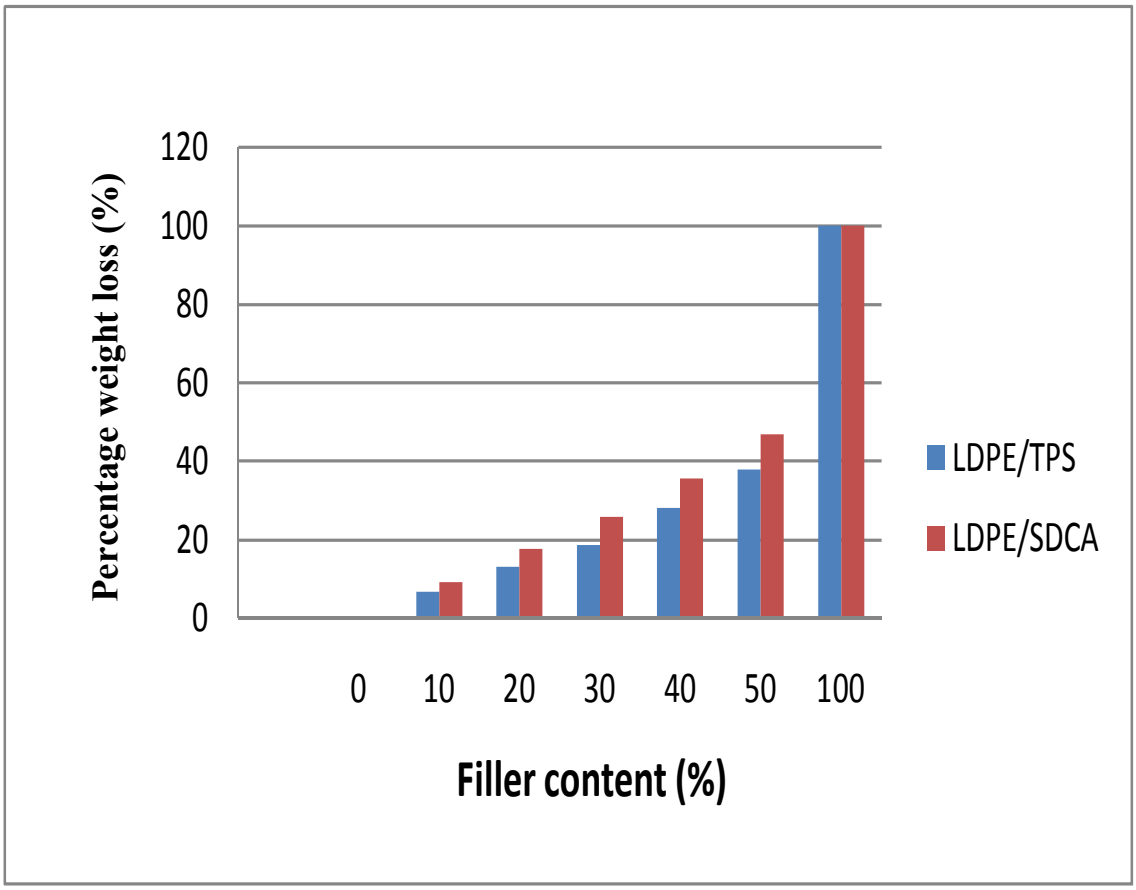


Figure 9: percentage weight loss of LDPE/TPS and LDPE/SDCA due to Soil burial degradation on the filler content after 63 days.

CHAPTER FIVE

SUMMARY, CUNCLUSION AND RECOMMENDATIONS

5.1 Summary

Thermoplastic starch (TPS) was prepared from potato starch by extrusion through a twin-screw co - rotating extruder HAAKE Rheomex OS PTW16 at a temperature range of 160^{o}C - 170 ^{o}C using Glycerol as plasticizer. The starch and the glycerol were initially mixed in the ratio 100:30 respectively before feeding into the extruder.

Similarly, Potato starch and Oxalic acid were thoroughly mixed in the ratio 100:20 respectively and fed through a twin-screw co - rotating extruder HAAKE Rheomex OS PTW16 at a temperature range of 90^{o}C - 100 ^{o}C to obtain starch dicarboxylic acid compound (SDCA). Thermoplastic starch - low density polyethylene (LDPE/TPS) composites were prepared by melt blending Low density polyethylene (LDPE) with thermoplastic starch, their mechanical, thermal and biodegradable properties were then investigated. Low density polyethylene filled with starch dicarboxylic acid compound LDPE/SDCA composites were prepared by melt blending Low density polyethylene with starch dicarboxylic acid compound, their mechanical, thermal and biodegradable properties studied.

The Fourier transform infra-red spectroscopy (FT-IR) was used to investigate interaction between Low density polyethylene (LDPE) and the starch derivatives Thermoplastic starch (TPS) and starch dicarboxylic acid compound (SDCA). The FT-IR spectra suggests replacement of Hydroxyl bonds between the starch polymer chains with weaker

hydrogen bonds between the starch and the plasticizer, and partial ester formation between the starch and the dicarboxylic acid.

The crystallinity of the samples were studied using X – ray diffractometer, it was shown that the complexation of the LDPE with the TPS/SDCA have taken place on the amorphous region and thus, the crystalline region is not affected. Scanning Electron microscopy (SEM) and other investigations suggest immiscibility between the composite components i. e the LDPE (matrix) and the TPS/SDCA as fillers. Mechanical properties i.e response to applied forces and deformation of the samples were studied using UTM (WITHLAB WL2100) and a dynamic mechanical analyzer DMA Q800. The LDPE/TPS were found to have better mechanical properties as compared to LDPE/SDCA.

Thermal properties of the samples were investigated employing symultanic thermal analyzer SDT Q600 to study the transition temperatures. Thermoplastic starch (TPS) starch dicarboxylic acid compound (SDCA) and low density polyethylene (LDPE) were shown to have improved thermal stability while in the composite than in their respective pure states.

The water absorbency studies indicated that LDPE/SDCA composites are more susceptible to water attack than the LDPE/TPS. All the composte samples were shown to be biodegradable on soil burial studies and the extent of degradation is in direct relation with the quantity of the filler.

5.2 Conclusion

Thermoplastic starch - low density polyethylene (LDPE/TPS) composites and low density polyethylene filled with starch dicarboxylic acid compound LDPE/SDCA composites were prepared, their mechanical, thermal and biodegradable properties investigated.

Various investigations suggest immiscibility between the composite components i. e the LDPE (matrix) and the TPS/SDCA as fillers. It was shown that the complexation of the LDPE with the TPS/SDCA have taken place on the amorphous region and therefore the crystalline region is not affected.

The tensile strength was found to decrease with increase in filler concentration in both LDPE/TPS and LDPE/SDCA composites which may be attributed in both cases to poor adhesion between the matrix and the fillers as a result of incompatibility. However, LDPE/TPS exhibited a relatively greater strength as compared to LDPE/SDCA, thus indicating that TPS tends to be more compatible with the LDPE than the SDCA. The DMA analysis indicated that both the storage and loss moduli of the LDPE/TPS and LDPE/SDCA composite samples decreases with increase in temperature. The LDPE/SDCA composites were shown to have the ability to dissipate higher energies due to their amorphous characteristics as compared to LDPE/TPS composites. The LDPE/TPS were found to have relatively better thermal stability as compared to LDPE/SDCA. The biodegradation studies reveal that the LDPE/SDCA composite are more susceptible to soil degradation as compared to the LDPE/TPS composites. The dissolution of Starch dicarboxylic Acid (SDCA) in water makes it readily useful in food and pharmaceutical industries.

5.3 Recommendations

Various plasticizers should be employed in the preparation of the thermoplastic starch and the visco-elastic properties of the TPS studied. Efforts should also be put towards improving the thermal and mechanical properties of thermoplastic starch by employing various agencies.

Enzyme hydrolysis and microbial attack (microbial culture test) should be carried out especially for the Starch dicarboxylic acid compound to explore other uses particularly in the food industry. Other dicarboxylic acids in addition to oxalic acid should be employed in further studies.

High density polyethylene HDPE, Polypropylene (Pp) and other similar polymers should be employed in further studies.

Other area of studies for the LDPE/TPS and LDPE/SDCA should focus especially on weather degradation and durability tests.

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