CHAPTER 3: MATERIALS, METHODOLOGY AND CHARACTERIZATION

3.1 Materials

3.1.1 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol or PVA is recognized as one of the very few vinyl polymers that is soluble in water and is in the family class of poly(hydroxylate)s (Chiellini, Corti, D'Antone, & Solaro, 2003). PVA has been available since around 1924, and due to their solubility-swellability in water, an inexpensive and harmless solvent, this polymer covers a wide range of applications in different industrial commercial segments. PVA is produced commercially from the parent homopolymer polyvinyl acetate or PVAc. The acetate group in polyvinyl acetate is dissolved in an alcohol such as methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide (Marten & Zvanut, 1992) (Sato, Yamuchi, & Okaya, 1998). The resulting hydrolysis reaction removes the acetate or ester groups from the PVAc molecules, and replaces it with hydroxyl groups without disrupting their long chain structure. The chemical structure of the resulting vinyl alcohol repeating unit is given in Figure 3.1

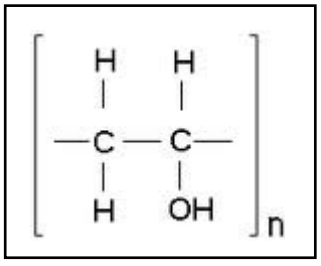

Fig. 3.1 The chemical structure of PVA

PVA with its many hydrophilic groups exhibits a high affinity for organic substances containing hydroxyl groups such as starch and cellulose, but is highly resistant towards different kinds of oil, and many organic solvents such as aliphatic and aromatic hydrocarbons, ethers, esters and ketones (Patachia-Bodonea, 2003). PVA provides a unique combination of properties whereby it has excellent film forming ability, high tensile strength and flexibility, high oxygen and aroma barrier properties, and it is environmentally friendly where it biodegrades easily in aqueous environments. PVA also has other exceptional properties such as good thermal stability, lack of static charge, excellent adhesion to organic and inorganic materials and good abrasion resistance. Physically, PVA takes the form of a white or cream coloured granular powder and as a film PVA is translucent and resistant to tearing and punctures. PVA is also odourless, tasteless, non-toxic and non-carcinogenic (Flieger, Kantorova, Prell, Rezanka, & Votruba, 2003).

PVA has a melting point between 180°C - 190°C. For this reason most of the plastic items made based on PVA are mainly obtained using casting techniques. This limits the methods used to form plastics from PVA because of the close proximity between its melting point and decomposition temperature. PVA decomposes rapidly above 200°C, and the degradation process releases water from the polymer matrix, accompanied by the formation of volatile degradation products, such as acetic acid, acetaldehyde, and crotonaldehyde (Chiellini, Corti, D'Antone, & Solaro, 2003). The acid produced can further catalyzed the degradation and changes the polymer colour due to the formation of polyene structures (Tsachiya & Sum, 1969).

PVA is a highly crystalline synthetic polymer and its crystallinity is attributed to the hydrogen atoms and hydroxyl groups (-OH) having roughly similar sizes, which tend to allow closer packing structure within the crystal lattice.

PVA has various applications in the food and consumerable industries and the uses of PVA include:

- As a reinforcement in concrete in the form of PVA fiber
- As a mold release because materials do not stick to it
- As a water soluble film used for packaging
- As a textile sizing agent
- As a bonding or coating agent
- As an embolization agent in medical procedures
- Used in protective chemical resistant gloves
- Used in eye drops and hard contact lens solution as a lubricant

3.1.2 Starches

3.1.2.1 Rice

Rice is an annual grass that grows in the tropics. Roughly half of the world's population, including all of East and South East Asia depends on rice as a main source of nourishment and rice is considered one of the most important commercial food crops. The rice is the second cereal most cultivated in the world after maize (corn) (Wang, Chen, & Li, 2007). The natural habitat of rice plant is tropical marshes, but now it is cultivated in a wide range of subtropical and tropical habitats. Rice plants thrive under extremely moist conditions and moderate temperatures. Rice or *Oryza sativa* is a member of the grass family *Gramineae*. It is an erect plant that grows to a height of 1-2 m, has long flat leaves with branching stems ending in a pinnacle bearing flowers that produce the fruit, or grain. The fruits are known as caryopsis or grains, are one-seeded,

and contain large concentration of starch (answers.com, 2011). Figure 3.2 shows the image of the rice plant *Oryza sativa.*

Fig. 3.2 The rice plant *Oryza sativa.* (Rice, 2011)

A rice grain contains about 94% of starch, 5% of proteins and 1% of lipids (International Rice Research Institute (IRRI), 2011). Rice is also made into flour or starch for use in the food and animal feed products. Rice starch has found many applications in diverse consumer and industrial sectors because of its many excellent characteristics. Table 3.1 lists the starch granule properties and general chemical characteristics of the rice starch.

Table 3.1 Starch granule properties and general chemical characteristics of rice starch

(BeMiller & Whistler, 1996) (Satin, 2011) (Tester, Karkalas, & Qi, 2004) (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005) (Puncha-arnon, Pathipanawat, Puttanlek, Rungsardthong, & Uttapap, 2008) (Singh, Kaur, Sandhu, Kaur, & Nishinari, 2006) (Vandeputte, Vermeylan, Geeroms, & Delcour, 2003) (Dias, Muller, Larotondo, & Laurindo, 2010) (Schoch, 1942)

Characteristics	
Type/origin	Grain
Average size of granule (diameter in μm)	2-9
Shape of granule	Polyhedral (angular)

Amylose content (%)	10-15
Amylopectin content (%)	85-90
Moisture content (%)	13
Ash (%)	0.13
Lipid (%)	0.8
Phosphorus (5)	0.013
Gelatinization temperature (°C)	65 – 85

Figure 3.3 shows the rice starch granule image scanned with an electron microscopy with a magnification of 3000x.

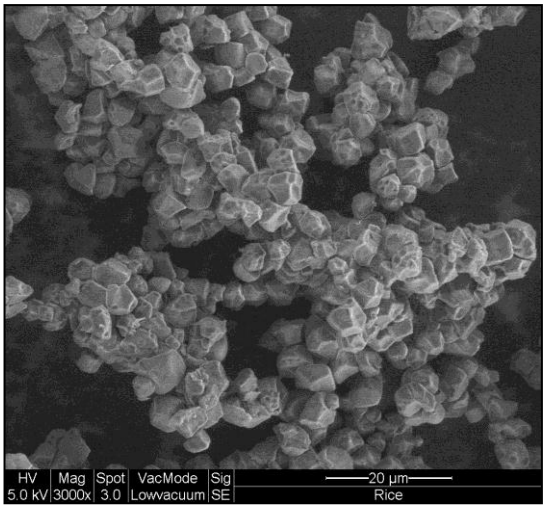

Fig. 3.3 Rice starch granule

Rice starch has by far the smallest granule size of all the commercial starches in the market today. A smaller granular size means a much higher concentration of particles in a specific area and a much greater specific surface. This characteristic makes rice starch very suitable for applications in laundry sizing and for skin cosmetics. Being the smallest starch granule makes it possible for rice starch to absorb more products on its surface, such as flavours and emulsifiers. One of rice starch special characteristic is that it is easily digestible. It is one of the main reasons why rice starch is widely used in

baby food and other special dietary foods. Rice starch has also been made into biodegradable packaging (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998) (Bourtoom & Chinnan, 2008) (Parvin, Rahman, Islam, Khan, & Saadat, 2010).

3.1.2.2 Tapioca

Tropical root and tuber crops are important food crops in the humid tropics such as Malaysia. Tapioca (*Manihot esculenta Crantz*), also called cassava is a starch containing root crop that provides one of the cheapest source of calories. Tapioca is only commercially cultivated mainly for its starchy roots which is one of the most important product synthesized by its plant that is consumed as food, animal feeding and used in the industrial processes. The tapioca plant is a perennial woody shrub with edible roots belonging to the dicotyledon family *Euphorbiaceae*. The plant grows up to a height of 1-3 m tall and several roots may be found on each plant (Onwueme & Alves, 2002).

Figure 3.4 shows the image of the tapioca plant and its tuberous roots.

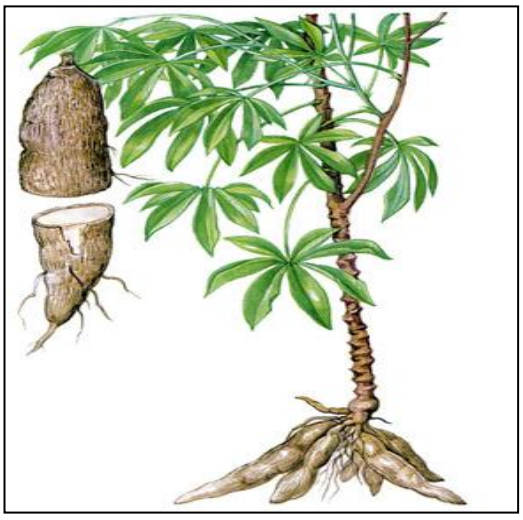

Fig 3.4 Tapioca plant and its tuberous roots.

The underground tuberous storage roots is long and tapered, with firm homogeneous chalk-white flesh encased in a detachable rind, about 1 mm thick, and it can measure up to about 1m in length and over 10 cm in diameter (Jansson, Westerbergh, Zhang, Hu, & Sun, 2009). A typical starch content of the tapioca plant is about 20-30% (Tonukari, 2004). The high starch production from the roots attributes together with the unique properties of its starch makes tapioca suitable for food and non-food applications. Table 3.2 lists down the starch granule properties and general chemical characteristics of tapioca starch.

Table 3.2 The starch granule properties and general chemical characteristics of tapioca starch

(O'Hair, 1990) (Peroni, Rocha, & Franco, 2006) (Mishra & Rai, 2006) (Moorthy, 2002) (Pickard, Asaoka, & Blanshard, 1991)

Characteristics	
Type/origin	Tuber or root
Average size of granule (diameter in μm)	15
Shape of granule	Round
Amylose content (%)	13-21
Amylopectin content (%)	79-87
Moisture content (%)	7.5
Ash (%)	0.21
Lipid (%)	0.1-0.5
Phosphorus (5)	0.007
Gelatinization temperature (°C)	66 – 72

Figure 3.5 shows the tapioca starch granule image scanned with an electron microscopy with a magnification of 3000x.

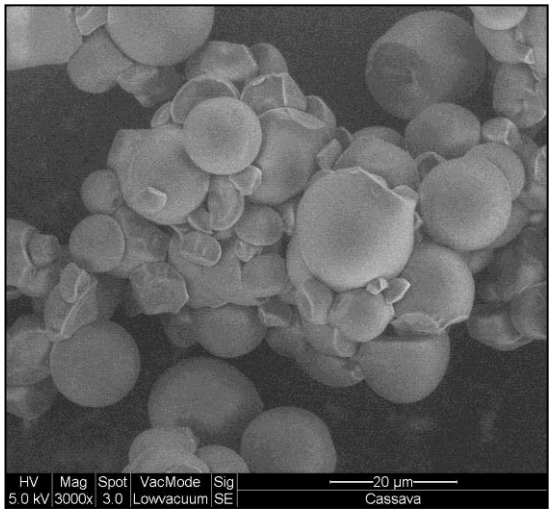

Fig. 3.5 Tapioca starch granule

Tapioca plant can grow in conditions of low nutrient availability and able to survive drought and because of this tapioca ranks very high among crops that increases its production yearly and this will lead to higher amount of starch available making it cheaper for industrial processes, and opening up new markets. Tapioca starch is widely used in every sector of the food and non-food industries. In the pharmaceuticals industry, the starch serves as a filler material and bonding agent for making tablets. The starch also acts as a thickener for soups, baby foods and other liquid foods. In the foam, paper and rubber industry, tapioca starch is also used to produce biodegradable packaging (Salgado, Schmidt, Ortiza, Mauri, & Laurindo, 2008) (Chuayjuljit, Hosililak, & Athisart, 2009) (Larotonda, Matsui, Soldi, & Laurindo, 2004).

3.1.2.3 Sago

The palms (*Palmae*) constitute as one of the oldest plant families on Earth. The sago palm (*Metroxylon sagu Rott.*) is an extremely hardy plant and is regarded as one of the potential underutilized food palms and thrives well in the harsh swampy peat environment and tropical rain forests in South East Asia. Sago starch is the only example of commercial starch that is derived from the stem of the sago palm (Karim, Tie, Manan, & Zaidul, 2008). Sago palm is a hapaxantic (flowers once before dying), monocotyledonous plant belonging to the genus *Metroxylon Rottbuell* (Uhl, 1987). The sago palm plant can grow up to a height of 6-10 m, with the circumference of the trunk reaching to 1.2 m. During its vegetative state, just before flowering, the plant converts its stored nutrients into starch, which fills the trunk. The sago palm pith is saturated with starch from the base of the stem upwards and upon reaching maturity at 9-12 years of age the trunk will be fully saturated with starch almost to the crown (Lim, 1991) (Yatsugi, 1986). Figure 3.6 shows the image of the sago palm *Metroxylon sagu Rott.*

Fig. 3.6 The sago palm *Metroxylon sagu Rottb.* (Sago, 2011)

Sago is the powdery starch made from the processed pith found inside the trunks of the sago palm. The sago starch obtained from the sago plant is made according to the following steps (Shipman, 1967):

1) Felling of the sago palm plant.
2) The trunk of the plant is split lengthwise
3) The pith is removed from the trunk
4) The pith is crushed and kneaded to release the starch
5) The extracted starch is then washed and strained from the fibrous residue of the pith
6) The raw starch suspension is collected and dried in the sun or kiln

The amount of starch that a mature sago palm tree can produce reaches about 250 kg (dry weight per plant) (Flach, 1997). The starch content of the pith obtained from commercially harvested sago palm varies from 18.8% to 38.8% (Wina, Evan, & Lowry, 1986). As the sago starch is utilized in many aspects in the food and non-food industries, numerable researches have been done on the characteristics and functional properties of the starch itself. Table 3.3 lists the starch granule properties and general chemical characteristics of the sago starch.

Table 3.3 Starch granule properties and general chemical characteristics of sago starch (Karim, Tie, Manan, & Zaidul, 2008) (Wang, Powell, & Oates, 1995) (Swinkels, 1985) (Ahmad, Williams, Doublier, Durand, & Buleon, 1999)(Ahmad & Williams, 1998) (Ito, Arai, & Hisajima, 1979)

Characteristics	
Type/origin	Pith
Average size of granule (diameter in μm)	30
Shape of granule	Oval or polygonal and truncated
Amylose content (%)	27

Amylopectin content (%)	73
Moisture content (%)	10.6 – 20
Ash (%)	0.1 – 0.4
Lipid (%)	0.1
Phosphorus (%)	0.02
Gelatinization temperature (°C)	69 - 72

Figure 3.7 shows the image of sago starch scanned with electron microscopy with a magnification of 3000x.

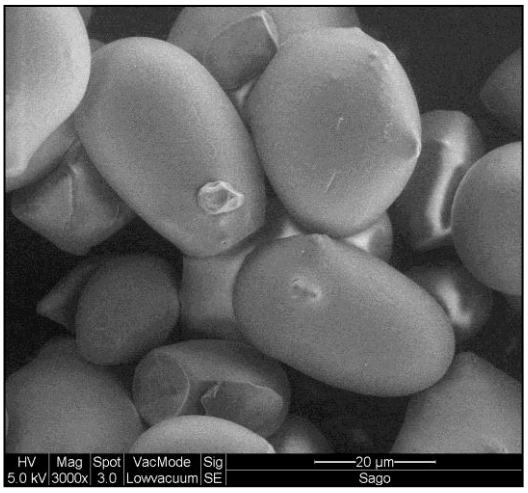

Fig. 3.7 Sago starch granule

Sago starch has a multitude of uses. As there is a strong and growing demand for sago starch, efforts have been made to convert sago palm into plantation cultivation. More diversified researches have been undertaken aimed at increasing the utilization of sago starch. In the production of packaging material, sago starch has been used in producing biodegradable packaging (Griffin, 1994) (Ishiaku, Pang, Lee, & Mohd Ishak, 2002). In the food sector, sago starch is used in the production of monosodium glutamate (MSG), glucose, caramel, syrups and others (Singhal, Kennedy, Gopalakrishnan, Kaczmarek,

Knill, & Akmar, 2008). The starch also acts as an ingredient in noodles, vermicelli, biscuits and many other foods. Refined sago starch is also used as coatings in the paper industry, as adhesives for textiles and plywoods and as a stabilizer in pharmaceuticals (Singhal, Kennedy, Gopalakrishnan, Kaczmarek, Knill, & Akmar, 2008).

3.1.3 Natural Fibers

3.1.3.1 Bamboo

Bamboo is the common term applied to a vast group of large woody grasses that belongs to the perennial grass family *Poaceae*, subfamily *Bambusoideae* (Scurlock, Dayton, & Hames, 2000). Among many natural fibrous plants, bamboo is one of the fastest growing grass plants, attaining maturity within 5 years and it is also a high yield renewable resource. Bamboos occur mostly in natural vegetation of tropical, subtropical and temperate regions and grow abundantly in most of the tropical countries. In Malaysia, bamboo is found in abundance and it is widely scattered in about 5% of the total forest reserve area (Mohmod & Mustafa, 1992). In general, bamboos can be classified into two categories that is monopodial (spreading or running kind of bamboo) and sympodial (clumped kind of bamboo). Most of the tropical bamboos are sympodial (Li, 2004). Figure 3.8 shows the Malaysian tropical bamboo called the *buluh minyak* or *bambusa vulgaris*.

Fig. 3.8 *Buluh minyak* or *bambusa vulgaris* (Buluh_minyak, 2011)

Clumping bamboos, such as the genus *bambusa vulgaris*, develop from branched clusters of rhizomes that turn upward as soon as they are formed; each rhizome develops a new clump close to the parent plant. All bamboos grow to full height and girth in 3-4 months. Within these 3-4 months, the clump of young shoots grows vertically, with no branching. After attaining, its full height, the pulpy wall of the culms start to dry and hardens and the culms begin to sprout branches and leaves and this is when the shoot is considered a fully matured culm (Bamboo, 2011). The structure of bamboo consists of solid nodes and internodes or culms at regular intervals. The solid nodes have high density and high silica content. The culms are the most distinguishable part of the bamboo plant species. They are usually cylindrical and hollow and vary in sizes, diameter, colours and textures.

The bamboo culms outermost layer, the bark, consists of epidermis cells that contain a waxy layer called cutin. The tissue of the culm contains parenchyma cells and the vascular bundles. Vascular bundles are commonly known as bamboo fibers. The bamboo fibers are scattered all over any piece of bamboo, where the average volume

percentage of fibers in a piece of bamboo is approximately 32% (Ray, Das, & Mondal, 2004). Bamboo fibers are relatively long (1.5-3.2 mm) compared to hardwood fibers (Scurlock, Dayton, & Hames, 2000). The *buluh minyak* or *bambusa vulgaris* has long and slender fiber with an average fiber length of 2.8 mm and width of 0.013mm. The average density of bamboo fiber is 0.8 g/cm^3 (Jain, Kumar, & Jindal, 1992). The chemical compositions of bamboo are similar to those of hardwoods, except for the high ash and silica contents. The α-cellulose, hemicellulose and lignin content of bamboo is 26-43%, 20-25%, and 21-31%, respectively (John & Anandjiwala, 2007).

In nature, bamboo can be considered a natural lignocellulosic material because it consists of cellulose fibers imbedded in a lignin matrix. Even though bamboo culms do not have the structure of true wood, they are very hard because they resemble unidirectional fiber reinforced composites with many modes along its length. The superior strength of bamboo fibers is an important factor when it is used as filler in biodegradable packaging. Because of this unique characteristics and high strength, also, bamboo has multitude of uses. In Asian countries, bamboo has been used in household utilities such as containers, woven mats, handicrafts, chairs etc. Many Asian species of bamboo have strong, light and flexible stems, which have been used as a primary material for the construction of houses, scaffolding, ladders and fences (Das & Chakraborty, 2006). It has also been widely used in building applications such as flooring, ceiling, walls, window frames and doors.

3.1.3.2 Kenaf

Kenaf or *Hibiscus cannabinus L.* is a warm season annual fiber crop native to tropical and subtropical Africa and Asia. It is a herbaceous plant that belongs to the dicotyledonous family *Malvaceae* and is a close relative to roselle, cotton, okra and jute

(Webber III & Bledsoe, 2002). Kenaf is considered a hardy plant that requires minimum of fertilizers, pesticides and water in comparison to conventional crops and can be grown under a wide range of weather conditions. Kenaf has a high growth rate; the stems of the plant which fibers are extracted from can rise to heights of 4-6 m, with a stem diameter of 2-5 cm, in just about 4-5 months (Mossello, et al., 2010). Due to the fast growth, the kenaf plants are poised to be introduced as a new annually renewable source of industrial purpose and can provide necessary biomass to partially alleviate the wood's fiber deficit. Figure 3.9 shows the image of the kenaf plant.

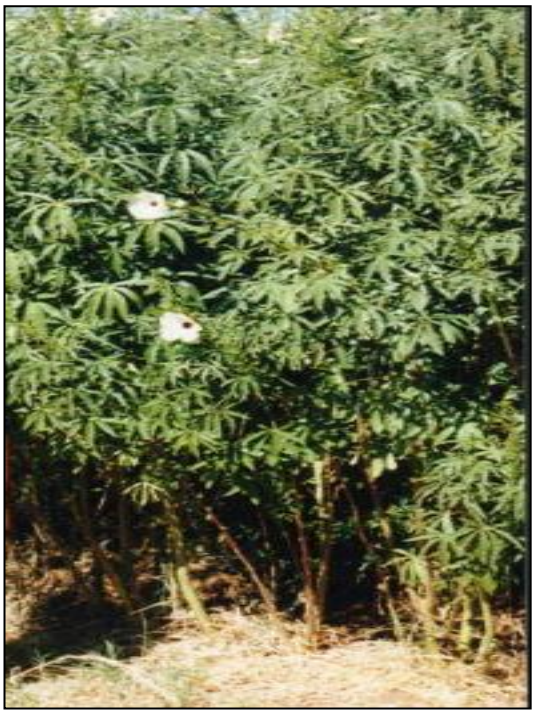

Fig. 3.9 The kenaf plant (*Hibiscus cannabinus L.)*

As a dicotyledon plant, kenaf has two distinct kinds of fibers; long coarser bark fibers, which account for 32-35% of its fibrous part, and short finer core fibers, which account for 65-68% in place of the middle hollow core (Summerscales, Dissanayake, Virk, & Hall, 2010). Fiber from the bast portion of the stem is about 2.32 mm in length and

resembles softwood fibers while those from the core are shorter, 0.74 mm and resembles hardwood fibers (Ververis, Georghiou, Christodoulakis, Santas, & Santas, 2004). The density of the kenaf fiber is 0.275 g/cm^3 (Dutt, Upadhaya, Singh, & Tyagi, 2009). The kenaf bast fiber is comparatively long and slender and this could prove advantageous in manufacturing products such as high grade pulps for the paper industry, protective packaging for fruits and vegetables, fillers, composite board and textiles. The short core fibers are thicker and have a lower mechanical strength and could be used to manufacture products such as animal bedding, poultry litter, bulking agent for sewage sludge, and horticultural mixes (Mossello, et al., 2010).

For industrial applications, the overall basic information about the chemical composition of a fiber is necessary. Kenaf bast and core fibers were quite different in respect to their chemical component. In general, the kenaf bast fibers were higher in α-cellulose, extractive and ash content, while the kenaf core fibers were higher in hollocellulose and lignin (Abdul Khalil, Ireana Yusra, Bhat, & Jawaid, 2010). The α-cellulose, hemicellulose, and lignin content of the kenaf stem are 60%, 12.65%, and 17.8%, respectively (Yan, Xu, & Yu, 2009). The low lignin content in kenaf plant is reflected in lower pulping chemicals, energy consumption and bleaching requirements which makes it suitable to be an alternative to wood in the paper industry (Webber III & Bledsoe, Kenaf yield components and plant composition, 2002). The high α-cellulose content in kenaf is believed to provide high strength that serve to be beneficial to the manufacturing of fiber end products such as biodegradable packaging. Figure 3.10 shows the kenaf fibrous stalks.

Fig. 3.10 The kenaf stalks (Kenaf, 2011)

The kenaf plant is composed of multiple useful components (e.g. stalks and seeds) and within each of this plant there are various usable portions:

- Stem - cordage fiber in products such as rope, twine, carpet, backing, and burlap.
  - building materials such as fibreboard or particleboard
  - as natural fillers for injection moulded and extruded biodegradable plastics (Webber III & Bledsoe, Kenaf: Production, Harvesting and Products, 1993)
  - used as a fiber crop for the manufacture of newsprint and other pulp and paper products.
  - as high protein animal feed.
- Seeds - yield a vegetable oil that is edible
  - oil is also used for cosmetics, industrial lubricants and as bio-fuel

  (Kenaf (Hibiscus cannabinus L.), 2011)

3.1.3.3 Roselle

Roselle or *Hibiscus sabdariffa* is a dicot plant of the *Malvaceae* family originating from Africa. Roselle is currently being cultivated in tropical regions of India and parts of

Asia, Australia and America (Gomez-Leyva, Costa, Muraira, Espino, Ramirez-Cervantes, & Andrade-Gonzalez, 2008). The species *hibiscus sabdariffa* comprises of a large number of cultivated types which, on the basis of their growth and end use, are categorized into two non-fixed varieties that is; the more important economically is *Hibiscus sabdariffa var. altissima Wester*, which is cultivated for its jute-like fiber in India, The East Indies, Nigeria and in tropical America. This type of hibiscus family is commonly confused with, *hibiscus cannabinus L.*, a somewhat similar but more widely exploited as a fiber source. The *hibiscus sabdariffa var. altissima* is a rigorous, erect, single stemmed, high yielding plant that grows to a height of 3-5 m high and is sparsely branched. The stem of this variety is green and it produces green, red-streaked inedible calypses. The *var. altissima* are grown as a fiber crop. The fibers obtained from the stems of the plants are used for bags, twines, carpet yarn, textiles and paper pulping. Figure 3.11 shows the *Hibiscus sandariffa var. altissima.*

Fig. 3.11 *Hibiscus sabdariffa var. altissima* (hibiscus sabdariffa var. altissima, 2011)

The other distinct variety of roselle is the *Hibiscus sabdariffa var. sabdariffa* where it is commercially cultivated for its edible calypses (Sie, et al., 2011). The true roselle embraces a shorter and woodier based sushrub that can grow to 2-2.5 m tall. The stem

of the plant is red and the leaves are arranged alternately in the stems. Figure 3.12 shows the *Hibiscus sabdariffa var. sabdariffa.*

Fig. 3.12 The *Hibiscus sabdariffa var. sabdariffa*

In Malaysia, the *Hibiscus sabdariffa var. sabdariffa* has been promoted as a cash crop for commercial planting since it is considered as a unique plant because the calyx of the flowers is used to produce drinks, jellies, wines etc. The calypses of the plant also has high medicinal values. Since the roselle has high commercial values and it is cultivated widely in Malaysia, the harvesting of only it calypses will produce an abundance of plant stem that has high strength fiber. Figure 3.13 shows the stems of the roselle plant.

Fig. 3.13 The roselle stems
(Discover the many uses of the Roselle plant, 2010)

The abundance availability of high strength roselle fibers can be a major factor in producing good quality sustainable fillers for producing biodegradable packaging for industrial applications. The roselle fibers are typical of fibers from the bast plants. Fiber from the bast portion of the stem is about 2.78 mm in length and while those from the core are shorter, 0.79 mm (Dutt, Upadhaya, Singh, & Tyagi, 2009). The density of the roselle fiber is 0.281 g/cm^3. The α-cellulose, hemicellulose, and lignin content of the roselle stem are 48.6%, 22.8%, and 19.2%, respectively (Dutt, Upadhaya, Singh, & Tyagi, 2009). Roselle contains higher α-cellulose than kenaf and can be characterized as promising for pulp and paper manufacture from the chemical composition point of view.

3.1.3.4 Napier Grass

Napier or Elephant grass (*Pennisetum purpureum*) is a robust species of grass native to the tropical grasslands of Africa. Napier grass is best suited planted in high rainfall areas, but it is drought tolerant and can also grow well in drier areas. It is a tall perennial plant that grows up to a height of 2.4 m, rarely up to 7.5 m, with hairy leaves 30-120 cm

long and 1.5 cm broad (Pennisetum purpureum, 2010). The stalks of the Napier grass are very coarse, tufted and grows in large bamboo-like clumps (Pennisteum purpureum - Factsheet, 2010). Figure 3.14 shows the Napier/Elephant grass.

Fig. 3.14 The Napier/Elephant grass

Napier grass has a high growth rate and it is considered as one of the highest yielding tropical forage grass. Due to the fast growth and good fiber quality, there has been increasing interest in Napier grass, primarily for its potential use as a forage grass in providing high quality animal feed and as a bio-fuel crop (Woodard & Sollenberger, 2010). One of the disadvantages of growing Napier grass is that it is an aggressive plant that spread through the ground. If it is not controlled, it can invade crop fields and become a weed.

The Napier grass stalks contain about 30-40% crude fiber and they are relatively short compared to bast fibers from other perennial plants (Van Dam, Chikafumbwa, Jamu, &

Costa Pierce, 1993). Figure 3.15 shows the stalks of Napier grass where the fibers are extracted from.

Fig. 3.15 Napier grass stalks

The chemical composition of Napier grass does not vary much from other perennial plant mentioned in this study. The grass content of cellulose, hemicelluloses, pectin, lignin and ash are 43.3%, 28%, 19.5%, 17.3% and 5.3%, respectively (Hoa, 2008). The high α-cellulose content of the grass makes Napier an alternative and cheaper source of material to act as filler in producing plastic products. The grass is available abundantly in nature and the extraction of its fiber is simple, and cheap. In addition, the density of Napier grass is less compared to that of bast fibers and that makes it suitable in making composites used in lightweight structures. The raw fiber materials can be blended with a polymer matrix and processed as biocomposites for automobile dashboards, carpet padding or as a "substitute for fibreglass and synthetic fiber", and as fiber for injection moulded and extruded plastics. The Napier grass is one of the grass fibers that is used as reinforcements in the development of new composites for lightweight structures (Rao, Prasad, Ranga Babu, Rao, & Gupta, 2007).

3.2 Methodology

3.2.1 Surface treatment of natural fibers

The natural fibers used in this study such as bamboo, kenaf, roselle and Napier grass were preconditioned before the cellulose was extracted. The fibers were chopped to an approximate length of 1 cm. Then they were washed thoroughly with distilled water to eliminate any dirt or other unwanted residues and dried in a convection oven at 100°C for over 24 hours.

A dewaxing process was carried out that is boiling the fibers in a mixture of toluene and ethanol in a soxhlet extractor for 6 hours. The volume ratio of toluene and ethanol were 2:1. The dewaxed fibers were then taken out from the extractor and washed with ethanol for 30 minutes and dried again in the convection oven for 24 hours.

The pre-treated fibers were then mix with 0.1 M NaOH in 50% volume of ethanol at 45°C for 3 hours under continuous stirring with an overhead stirrer. The overhead stirrer's speed was maintained at around 300 rpm. Then the fibers were bleached with hydrogen peroxide at pH 11.5 (buffer solution) and at 45°C: (a) 1.0% H_2O_2, (b) 2.0% H_2O_2, (c) 3.0% H_2O_2 and (d) 4.0% H_2O_2 for 3 hours each under continuous agitation. The mixture is then treated with 10% w/v NaOH and 2% w/v $Na_2B_4O_7.10H_2O$ at room temperature for 15 hours under continuous stirring. Lastly, the mixture was treated with 70% HNO_3 and 80% HAc at 90°C for 20 minutes to neutralize the treated fibers.

The extracted cellulose was washed with ethanol and distilled water and dried at 60°C in the oven until constant weight is achieved. This alkali treatment procedure was adapted from the work done by Sun et. al with slight modifications (Sun & Sun, 2002).

3.2.2 Sample preparation of PVA/starch and PVA/starch/fiber composites

A series of two set of samples that are the PVA/starch and PVA/starch/treated fibers composites were prepared by varying the starch and fiber content by using water as the solvent. The different composition of the blends formed by this solution casting technique is presented in Table 3.4 and 3.5. PVA in the form of powder were added to water and the mixture was heated up to 90°C while continuously stirring. The working temperature was maintained at 90°C because if the temperature goes up to 100°C, the transparent PVA solution will become slightly yellow due to partial degradation. The overhead stirrer's speed was maintained at about 100 rpm. If the blending speed goes higher, more bubbles in the PVA solution will be generated due to the contamination of air and if the operating speed is less than 60 rpm then a small amount of PVA slurry will be deposited at the bottom so proper blending speed of the stirrer should be maintained throughout the experiment. When the PVA has completely dissolved into the solution, the temperature of the mixture solution was lowered to 80°C maintaining stirring but avoiding frothing. Starch was then added to the mixture and the temperature and stirring was maintained for 3 hours to gelatinize the starch. In the preparation of the PVA/starch/fibers composites, when the starch was completely gelatinized, the pre-treated fibers were added and the mixture was stirred continuously for another 2 hours. The mixture was then removed from the heat and distributed onto levelled petri dishes. Air bubbles were removed by flaming and each solution was dried for 24 hours at 50°C. Complete drying was avoided as some moisture is required for the biocomposite films to remain flexible and not to crack.

Table 3.4 and 3.5 compiles the different associations that have been carried out. For example, biocomposites in the table that is denoted as 'PVA/1TS/1KF' means that the

composite was prepared by mixing 10g of PVA with 1g of tapioca starch and 1g of treated kenaf fibers.

Table 3.4 The compositions of the blended biocomposite films of PVA and different starches

Sample	PVA (g)	Starch (g)
PVA/1TS	10	1
PVA/3TS	10	3
PVA/1RS	10	1
PVA/3RS	10	3
PVA/1SS	10	1
PVA/3SS	10	3

* TS = tapioca starch, RS = rice starch and SS= sago starch

Table 3.5 The compositions of the blended biocomposite films of PVA with different starches and different treated fibers

Sample	PVA (g)	Starch (g)	Fibers (g)
PVA/1TS/1BB	10	1	1
PVA/1TS/3BB	10	1	3
PVA/1TS/1KF	10	1	1
PVA/1TS/3KF	10	1	3
PVA/1TS/1ROS	10	1	1
PVA/1TS/3ROS	10	1	3
PVA/1TS/1NP	10	1	1
PVA/1TS/3NP	10	1	3
PVA/1RS/1BB	10	1	1
PVA/1RS/3BB	10	1	3

PVA/1RS/1KF	10	1	1
PVA/1RS/3KF	10	1	3
PVA/1RS/1ROS	10	1	1
PVA/1RS/3ROS	10	1	3
PVA/1RS/1NP	10	1	1
PVA/1RS/3NP	10	1	3
PVA/1SS/1BB	10	1	1
PVA/1SS/3BB	10	1	3
PVA/1SS/1KF	10	1	1
PVA/1SS/3KF	10	1	3
PVA/1SS/1ROS	10	1	1
PVA/1SS/3ROS	10	1	3
PVA/1SS/1NP	10	1	1
PVA/1SS/3NP	10	1	3

* TS = tapioca starch, RS = rice starch and SS= sago starch
BB = bamboo fiber, KF = kenaf fiber, ROS = roselle fiber and NP = napier fiber

3.3 Testing and Characterization

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. The infrared portion of the electromagnetic spectrum is generally categorized into three regions that is the near-, mid- and far-infrared. The

near- or high energy infrared lies approximately between 14000-4000 cm^{-1} and this portion of the electromagnetic wave region excites overtone or harmonic vibrations. The mid-infrared, approximately 4000-400 cm^{-1}, has been used to study the fundamentals vibrations and associated vibrational-rotational aspects of a molecular structure in a material. The analytical technique that uses this method of identifying compounds and investigates sample composition based on the vibrations of chemical molecular structure is in the form of absorption spectroscopy. The far-infrared, approximately 400-10 cm^{-1}, has low energy and has been used in the study for rotational spectroscopy.

Fourier Transform Infrared Spectroscopy is a powerful analytical tool for characterizing and identifying organic and inorganic molecules. The FTIR is an instrument that exploits the fact molecules absorbs specific frequencies that are characteristic of their structure and records spectra between the 4000 cm^{-1} down to 400 cm^{-1} portion of the electromagnetic wave region that corresponds to the absorption energy by a molecule as the component atoms vibrate about the mean centre of their chemical bonds. Molecules are flexible, moving collections of atoms. The atoms in a molecule are constantly vibrating around their average positions. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule generates oscillating electric field with the same frequency of the incident infrared radiation. The infrared radiation absorbs by molecules in a sample is projected in the form of infrared spectrum that represents a fingerprint of a sample with absorption peaks that are unique to the frequencies of vibrations between the bonds of the atoms making up the material (Introduction to Fourier Transform Infrared Spectroscopy, 2010). Like a fingerprint no two unique molecular structures produce the same infrared spectrum. FTIR is also a non-destructive instrument that can identify chemicals which can be either organic or inorganic.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of the raw samples and biocomposite films were recorded on a Nicolet iS10 spectrometer

(ThermoScientific, USA). For the raw materials such as pure PVA, different starches and different fibers, the test samples were pulverized with KBr and pressed into transparent discs for analysis. The samples from the biocomposite films were taken at random and data were collected over 32 scans with a resolution of 4 cm^{-1} at room temperature. The samples were scanned from 700 to 4000 cm^{-1}. Samples were scanned in duplicate and the resulting spectrum was analyzed using the Omnic Spectra software.

3.3.2 X-Ray Diffraction (XRD)

X-ray diffraction is a versatile, non-destructive analytical technique that reveals detailed information about the chemical composition, crystallographic structure and physical properties of organic and inorganic materials. It provides information that includes types and nature of crystalline phase's present, structural makeup of phases, degree of crystallinity, amount of amorphous content and size and orientation of crystallites (Exova, 2010). X-ray diffraction is also a common technique for qualitative and quantitative analysis of crystalline compounds. This technique is based on observing the scattered intensity of an x-ray beam hitting a sample as a function of incident and scattered angle. An x-ray diffractometer consists of three basic elements that is an x-ray tube that generates the x-ray radiation of a certain wavelength, a sample holder, and an x-ray detector to detect the diffracted x-ray beam. Copper is the most common target material for single crystal diffraction with CuKα radiation of 1.5418 Å. The workings of an x-ray diffractometer is that the sample rotates in the path of the collimated x-ray beam at an angle θ while the x-ray detector is mounted on an arm to collect the diffracted x-rays and the arm rotates at an angle of 2θ (X-ray Scattering Technique,

2010). The reflection of the x-ray beam on planes of atoms in the material creates a series of spots called the diffraction pattern. As the sample is rotated at different angles, the diffraction pattern will change. By varying the orientation angles, and recording the 2θ data, a three-dimensional atomic structure can be calculated. The basic law that governs the calculation of *d* i.e. the distance between a series of parallel planes in a molecule is the Bragg's Law:

$$n\lambda = 2d\sin\theta$$

where n = 1, 2, 3,…(usually taken as 1)

λ = wavelength (1.5418 Å for copper)

d = interatomic spacing in angstroms

θ = the diffraction angle in degrees

The x-ray diffraction patterns were recorded on a SIEMENS D5000 x-ray diffractometer using copper anode x-ray tube (CuKα radiation, λ = 1.5418Å). The starch and natural fibers were packed tightly in sample holders. The biocomposite films were places in a sample holder for x-ray diffractometry. Both types of samples were exposed to the x-ray beam at 40 kV and 40 mA. The scanning region of the diffraction angle (2θ) was from 5° to 80° at 0.10° step size with a scan step time of 3 s.

3.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or TGA is one of the members of the thermal analysis techniques family that is used to characterize a wide variety of polymeric materials. TGA is also a thermal measurement technique commonly employed in research and testing to determine material characteristic such as the thermal degradation temperature and absorbed moisture and volatile contents of a material. Basically, TGA provides quantitative measurements of the rate of change in the mass of a sample associated with transition and thermal degradation in a controlled atmosphere. It can also be used for the identification of compounds present in mixtures of materials. When these mixtures or blends are heated in a controlled manner, the thermogram curve produced consists of all possible weight losses from all components superimposed on each other. Characteristic thermogravimetric curves are given for specific materials and chemical compounds due to unique sequence from physicochemical reactions occurring over specific temperatures ranges and heating rate. If careful interpretation and identification of the individual thermal events is carried out, the components that make up the mixtures or blends can be identified.

The essential component in TGA is a thermobalance (recording balance), furnace, temperature programmer, sample holder and an enclosure for establishing the required atmosphere. The sample holder in the form of a platinum/aluminium pan is place in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere inside the enclosure with the sample may be purged with an inert gas such as nitrogen or helium to prevent oxidation or other undesired reactions. Thermal analysis is carried out by raising the temperature gradually according to a certain heating rate and plotting the loss/gain weight against the temperature. After the

data is obtained, the results from the thermogravimetric analyses are usually reported in the form of curves relating mass lost/gain from the sample against temperature. TGA measurements can provide valuable information that can be used to select materials for certain end-use applications and to predict product performance and improve product quality.

Thermogravimetric analyses were performed by using a Diamond TG/DTA instrument from Perkin Elmer, USA. The samples, weight varied from 2-5 mg, were measured in hermetically sealed aluminium crucibles in the presence of nitrogen atmosphere (flow rate of 20 ml/min). The samples were heated from 50°C to 900°C with a heating rate of 10°C/min. The results were evaluated with the PYRIS Software package.

3.3.4 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis or DMTA is a thermal analysis technique used to study the viscoelastic behaviour of a material. DMTA works by applying a sinusoidal stress to a sample of known geometry, and the resultant strain is measured. The DMTA determines changes in the sample properties resulting from changes in five experimental variables that are temperature, time, frequency, force and strain. When the changes in the five experimental variables are measured, this allows the determination of complex modulus. Two major kinds of test modes can be used to probe the viscoelastic properties of a material: temperature sweep and frequency sweep tests. A common test method involves measuring the complex modulus using a single frequency and constant deformation (strain) amplitude while varying temperature. When the temperature is varied, this will lead to variation in the complex modulus. Generally, the complex

modulus measured are the storage modulus, E', that measures the elastic response or stored energy, the loss modulus, E", that measure the viscous response or energy dissipated, and tan delta (δ), that measures the damping properties of a material. Damping is a dimensionless property and is the measure of how well a material will absorb or lose energy.

One important application of DMTA is measurement of the glass transition temperature of polymers. The glass transition temperature is the temperature that indicates the relaxation in a polymer where a material changes from being a glass-like manner material to a rubber-like manner material. The test method that is often used to characterize the glass transition temperature of a polymer is the temperature sweep test. Determining the glass transition temperature of a polymer is important because it characterizes the polymer's mechanical properties at that certain temperature and this determines the choice of a given polymer in a particular application.

DMTA is particularly useful for evaluating viscoelastic materials that have mechanical properties, which exhibit time, frequency, and/or temperature. DMTA is a versatile technique that complements the information by the more traditional thermal analysis techniques such as DSC and TGA and it can be said that DMTA is the most sensitive of all thermal analytical techniques.

The viscoelastic behaviour of the biocomposites films were tested on a Dynamic Mechanical Thermal Analyzer DMTA861 by Perkin Elmer, USA, working in tensile mode in constant stress. Samples for DMTA testing with dimensions of 10 mm × 5 mm × 0.05 mm were cut from the selected biocomposites films and fixed in a steel clamp. The temperature profile ranged from -40°C to 150°C at a 2°C/min heating rate. When the dynamic mechanical spectroscopy was employed within the linear viscoelastic

regime to determine T_g, the storage and loss modulus (E' and E") and loss tangent (tan δ = ΔE'/E") were measured as a function of temperature at constant frequency, 1 Hz. The results were evaluated with the STAR Software package.

3.3.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry or DSC is a thermal analysis technique that measures the amount of heat necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in a heated or cooled environment at a controlled heating rate. The basic principles of DSC is that it monitors heat affects associated with the physical transformation of the sample such as phase transitions where more or less heat will need to flow to the samples depends on whether the transformation process is exothermic or endothermic. The difference in the heat flow to the sample and a reference at the same temperature is recorded as a function of temperature. DSC can be used to measure a number of characteristic properties of a sample such as fusion and crystallization events as well as glass transition temperature. Determining the glass transition temperature is important since the mechanical behaviour of polymers changes markedly at the glass transition. In the DSC experiment, T_g is manifested by a drastic change in the baseline, indicating a change in the heat capacity of the polymer. No enthalpy is associated with such transition; therefore the effect in the DSC curve is slight.

The essential components in a DSC are the sample and reference crucibles, heaters, temperature programmer and an enclosure for establishing the required atmosphere. The sample and reference crucible is in the form of a platinum/aluminium pan and each pan sits on a heater. The heater heats the pan at exactly the same heating rate. The

atmosphere inside the enclosure with the sample may be purged with an inert gas such as nitrogen or helium to prevent oxidation or other undesired reactions. The difference in heat energy required to maintain the sample and reference pans at a nearly identical temperature is provided by the heat changes in the sample.

Differential Scanning Calorimetry (DSC) analyses were performed by using a Mettler Toledo DSC822 instrument equipped with an intra-cooler. The samples, weight varied from 1-3 mg, were measured in hermetically sealed 40 μl aluminium crucibles in the presence of nitrogen atmosphere (flow rate of 50 ml/min). An empty pan was used as a reference. The samples were heated from -30°C to 150°C with a heating rate of 5°C/min. The glass transition temperature of the specimens was determined from the mid-point of the heat capacity change observed on the second run to eliminate the effect of sample history. The results were evaluated with the STAR Software package.

3.3.6 Mechanical Testing – Tensile Test

In many applications in the consumer industries, the mechanical properties of a material play a vital role even though the primary function of the end-product is electrical, magnetic, optical or biological. The mechanical properties, among all of the properties of polymeric materials, are often the most important properties because nearly all service conditions and the majority of end-use applications involve some degree of mechanical loading. Understanding the strength and endurance of a product is beneficial to the end-user and also to the supplier of the products. Information on mechanical properties of polymeric materials such as tensile, flexural compression and shear helps optimized the material formulations, processes and quality control, and all of these

properties can be derived from a universal testing machine. The universal testing machine allows a polymeric sample to be stretch (tensile), bend (flexural), squash (compression) or pull (shear) until it ruptures or breaks. One of the common tests done on the universal testing machine to determine important mechanical properties of a polymeric sample is the tensile test.

Tensile test, also known as tension test, is probably one of the most fundamental mechanical tests that can be performed on a material and it is a test in which a sample is subjected to uniaxial tension until failure. Tensile test, in a broad sense, is the measurement of the ability of the polymeric material to withstand forces that tend to pull it apart and to what extent that material stretches before breaking. The tensile strength of the plastic often is the primary concern and the strength of interest may be measured in terms of either the stress necessary to cause appreciable amount of plastic deformation or the maximum stress the material can withstand. Also of interest is the materials' ductility, which is a measure of how much it can be deformed before it fractures. All of these measureable quantities can be derived from the stress-strain curves that the tensile test produces.

The short-term tensile test ASTM D638 is one of the most widely used mechanical tests for plastics for determining mechanical properties such as tensile strength, yield strength, yield point and elongation. The specimen's shape is usually defined by the standard or specification being utilized. Most tensile specimens are designed to have the center section narrower than the ends, and thus commonly called "dogbone"specimens. The shape of the specimen for the tensile test is important because it is crucial to avoid having a break or fracture within the area being gripped.

Tensile strength (TS), Young's modulus (YM), and percent elongation at break (%E), were evaluated for each of the biocomposite films using an INSTRON 3345 testing

machine in tensile mode. The measurements mentioned were carried out following ASTM D 638 standard method. Crosshead speed was 5 mm/min and the load cell was 100 N. Both gauge length and grip distances were 7.5 mm and 25.4 mm. respectively. The specimens were cut in dumbbell shapes with a die of ASTM D638 type V. The thickness of the films was measured using a digital thickness gauge 'Mitutoyo', Japan at 5 random positions around the biocomposite film. All the samples were preconditioned at ambient temperature (25°C) and 50% relative humidity for 48 hours, and tests were performed under the same conditions. An average value of at least five replicas of each specimen was taken.

3.3.7 Biodegradable Test – Soil Burial Test

Biodegradation, bio-recycling and composting are attractive solutions to eliminate polymeric wastes. From a general viewpoint, regardless of the type of the plastics application, biodegradability is monitored through direct and indirect methods aimed at showing the plastic's property changes. Test methods to determine biological action on biodegradable plastic materials have been available for different classes of plastic materials. Visual examination by optical, scanning microscopy and measurements of molecular weight changes and of weight loss are the most commonly used strategies to determine biodegradation. A large number of standardized methods have been developed for different environments, and with the use of different analytical methods. Different type of analytical methods used to determine biodegradability are like standards ASTM G21-96 (Standard practice for determining resistance of synthetic polymer materials to fungi), ASTM G29-96 (Standard practice for determining algal resistance of plastics films) and etc (Muller, 2003).

The soil burial test method involves burial of specimens in different kinds of soil. This kind of biodegradation method involves the enzymatic action of living organisms (micro/macro) in the soils. Almost all microbial degradation is carried out by both fungi and bacteria. Molecular degradation of the polymeric materials is promoted by enzymes in the soil and can occur in aerobic and anaerobic conditions, leading to complete or partial removal of the specimen from the environment.

The biodegradability of different biocomposite films was determined by exposing the samples to compost soil (soil containing manure). The soil burial experiment was done in two kinds of environment: simulated burial in compost soil in the laboratory and burial in compost soil in an uncovered area outside the laboratory. The indoor soil burial experiment was carried out in a series of plastic boxes (60 cm × 30 cm × 30 cm) containing compost soil whilst the samples for the outdoor experiment was buried in compost soil in an uncovered area. The biocomposite film samples with dimension of 3 x 5 cm were buried perpendicularly at a depth of 15 cm beneath the surface and separated from each other in a distance of 7 cm. The soil was kept moist by sprinkling water at a regular time interval to maintain about 50% humidity. The soil burial degradation test was done in the duration of 70 days. To evaluate the biodegradation of the biocomposite films, variations in film morphology and the time by which films disintegrated, and weight loss were recorded. To determine the weight loss in the specimens, at predetermined intervals, the film were carefully removed from the compost soil, dry cleaned with a brush, and washed gently with distilled water to remove the soil. The specimens were the dried in an oven until constant weight was obtained. The weight of each sample was routinely measured before and after degradation.

3.3.8 Scanning Electron Microscopy (SEM)

The scanning electron microscope or SEM is a type of microscope that images the surface of a specimen by using high-energy electron beam. It is a method for high-resolution imaging of surface of solid samples. Basically, SEM uses a focused beam of electrons to generate a variety of signals at the surface of the solid specimens. The signals that are derived from the electron-sample interactions reveal information on the external morphology or texture about the sample. The advantages of SEM over light microscopy include higher resolution that make closely spaced specimens be magnified at much higher level and tremendous depth of field, that provides an almost 3-D image to analyze, as compared to flatter image optical microscope produces.

Listed below is the summarized version of the method on how the scanning process of SEM is done:

i. A beam of electron is produced at the top of the microscope by an electron gun. Metals such as tungsten are used as a thermal emission source to produce electrons. Tungsten is normally used because it has the highest melting point and lowest water vapour pressure of all metals and because of its low cost.
ii. The electron beam produced travels a vertical path through the SEM chamber, which is held in vacuum. The SEM chamber is vacuum to allow the electrons to travel freely from the source to the sample and then to the detector. Without vacuum, the electron beam would encounter constant interference from air particles in the atmosphere.

iii. The beam goes through electromagnetic fields and lenses, which would focus the beam down towards the sample.

iv. Once the electron beam hits the sample, electrons and x-rays are ejected from the sample.

v. Detectors collect these x-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a monitor and this produces the final image.

To produce images using the SEM, samples or specimens must be electrically conductive, at least at the surface of the sample and electrically grounded. This is to prevent the accumulation of electrostatic charge at the surface of the sample that causes scanning faults and image defects. Non-conductive specimens are coated with an ultrathin coating of electrically conducting material, commonly gold, deposited on the sample either by sputter coating or by high vacuum evaporation. Another requirement for a sample to be viewed by SEM is that the sample must be dry or moisture free because SEM uses high vacuum in order for it to be operational. A dry sample is usually mounted on a specimen stub using an adhesive such as electrically conductive double sided adhesive tape before examination in the SEM microscope.

The scanning electron micrographs were taken by means of a LEICA SEM microscope. The images taken were from the granular structure of starches, the morphology of the natural fibers after subjecting it to chemical surface treatments, the surface morphology of the biocomposite films, the Instron fragile fracture surface of the composite sample, and the morphology of the biodegraded samples. The biocomposite films fractured by the Instron Testing Machine were mounted with the fractured surfaces facing up. All the

samples were coated with gold using a vacuum sputter coater and mounted on top of prepared metal stubs using conductive double-sided adhesive tapes.