for their biodegradability by estimating the weight loss upon burial under soil for three months.

Chapter 1 provides a general introduction to the reader about the drawbacks of greater than ever production, consumption and later generation of plastic waste which is typically indestructible for hundreds of years while explaining the basic terminology and alternate solutions to the plastic problem, mainly in the form of using renewable and biodegradable materials derived from biomass. An outline of available biopolymers and their advantages and disadvantages in brief has been described and composite films synthesized using polyvinyl alcohol and lignocellulosic biomass have been briefly discussed.

Chapter 2 is a review of current literature regarding the use of bioplastics, polyvinyl alcohol in particular. Composite films prepared by PVA and reinforced with lignocellulosic polymers, nanocomposites of PVA and nano fillers like nano cellulose and nano silica, pretreatments of lignocellulosic biomass for film preparation have been reviewed.

Chapter 3 describes the materials and methods used for the experimental work. It describes in detail the materials used and methods involved in film preparation and characterization.

Chapter 4 provides the results obtained after preparing different kinds of films and carrying out their characterization tests along with a discussion of the possible cause of findings and their correlation with findings of other workers.

Chapter 5 concludes the thesis work done and summarizes the important findings. It also makes some useful recommendations for further work in this area.

Chapter 1: Introduction

1.1 Plastic waste

More than half of all of the plastic produced in the world since the beginning of its mass production in 1950s still exists today (Geyer et al., 2017; Hoornweg et al., 2013). It is estimated that around 8 billion tonnes of plastic has been produced since industrial production began in 1950 (**Fig. 1.1**) and out of that around 6 billion tones has ended up as waste (Geyer et al., 2017) (**Fig. 1.2**). This plastic has accumulated as waste in our landfills, clogging our water ways, choking up digestive tracts of animals that accidently consume them, inadvertently reaching into systems of aquatic life in micro plastic forms (Allen et al., 2020; Barnes et al., 2009; Dris et al., 2017; Y. L. Wang et al., 2020), and ultimately collecting in the oceans in the form of a large artificial island called the great pacific garbage patch (Lebreton et al., 2018; NOAA, 2020). The great pacific garbage patch is one of the 5 such garbage patches in the oceans where all the debris in the world, mostly plastic (**Fig. 1.3**), as its density is less than water is accumulated by the ocean currents. It is roughly 1.6 million square kilometers in size and predicted to be having at least 80 thousand tones of plastic waste floating in this area (Lebreton et al., 2018). Needless to say a humongous amount of plastic has been generated and then discarded because of urbanization and modern living standards which have somehow prioritized the disposable culture. Before understanding the global pattern of plastic production and waste generation pattern, it is needed to be aware of types of different plastics. It is ironic that plastic polymers have been segregated into 7 types by the U. S. Society of the Plastic Industry, for the sake of segregating plastics after use for recycling while less than 7% of total plastic produced till today has been recycled,. The resin identification code symbols are each denoted by a number enclosed within three chasing arrows representing “recycling” and called the resin identification code (**Fig. 1.4**). These resins include:

1. Polyethylene terephthalate (PET or PETE)
2. High-density polyethylene (HDPE)
3. Polyvinyl chloride (PVC)
4. Low-density polyethylene (LDPE)
5. Polypropylene (PP)
6. Polystyrene (PS)
7. Other types of plastic (consisting of thermosets, thermoplastics, polyurethanes, polyamines and polyacrylates etc.)

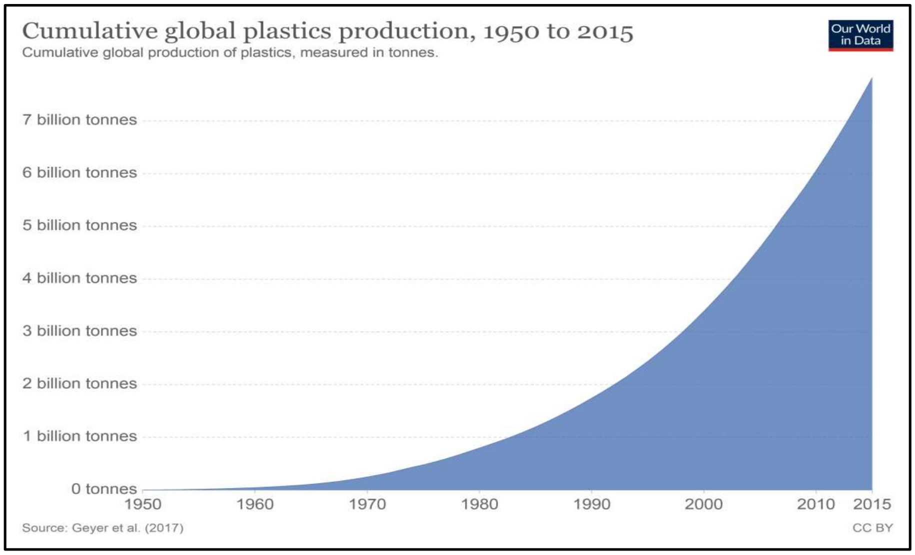


Fig. 1.1: Cumulative global plastic production since 1950s (Geyer et. al., 2017)

Be it plastic bottles of packaged drinking water, wrappers of food items, carry bags, different types of outer covering to prevent from getting wet or just versatile plastic packaging in attractive colours and completely water proof, plastics are everywhere. Plastics have changed the businesses across the world by providing a solution to logistics and increased shelf life of products and have become indispensable to human beings in only 70 years (Wong et al., 2015).

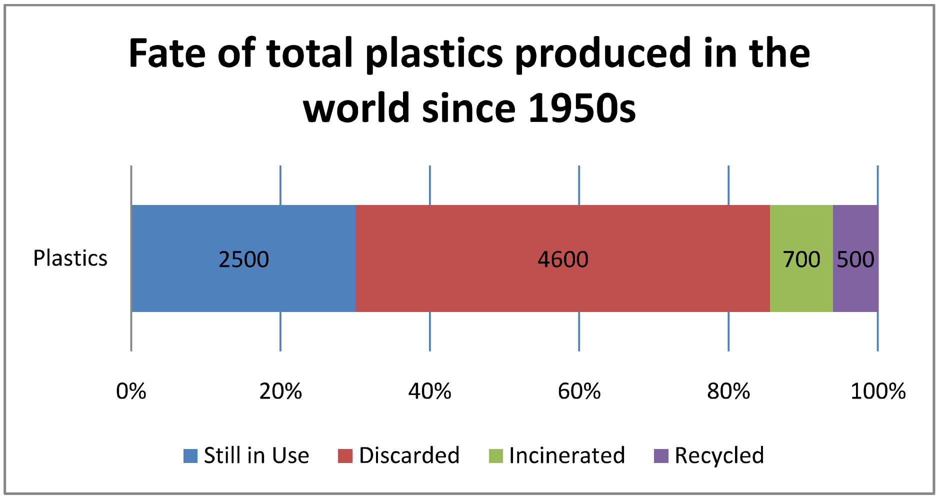
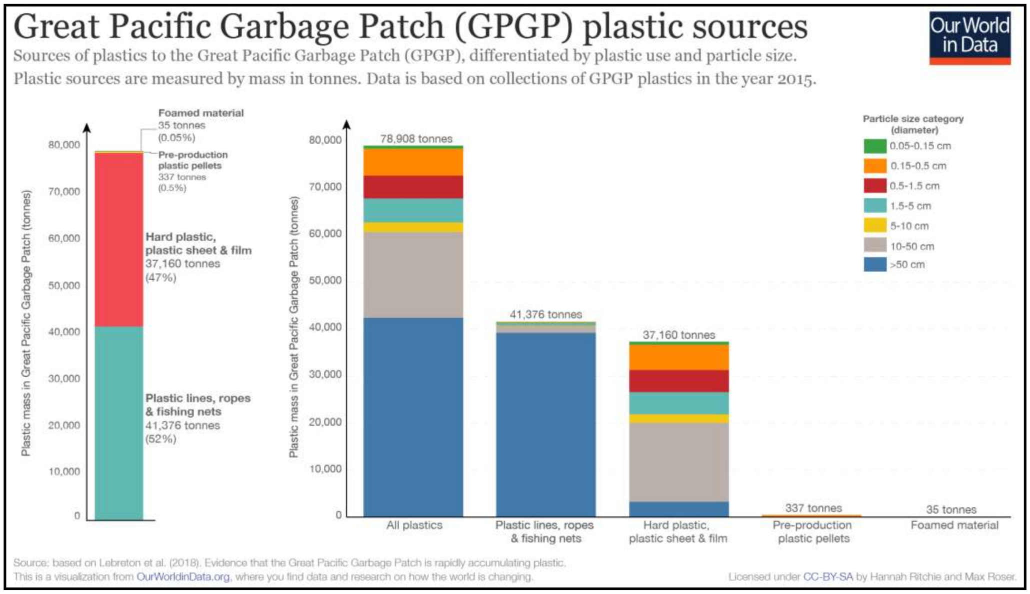

Fate of total plastics produced in the world since 1950s

Fig. 1.2: Fate of total plastic produced in the world since 1950s. All values are in Million Metric Tonnes (Geyer et. al., 2017).


Great Pacific Garbage Patch (GPGP) plastic sources

Sources of plastics to the Great Pacific Garbage Patch (GPGP), differentiated by plastic use and particle size. Plastic sources are measured by mass in tonnes. Data is based on collections of GPGP plastics in the year 2015.

Source: based on Lebreton et al. (2018). Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic.
This is a visualization from OurWorldinData.org, where you find data and research on how the world is changing.

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Fig. 1.3: Great Pacific Garbage Patch plastic source and size distribution (Lebreton et al., 2018).

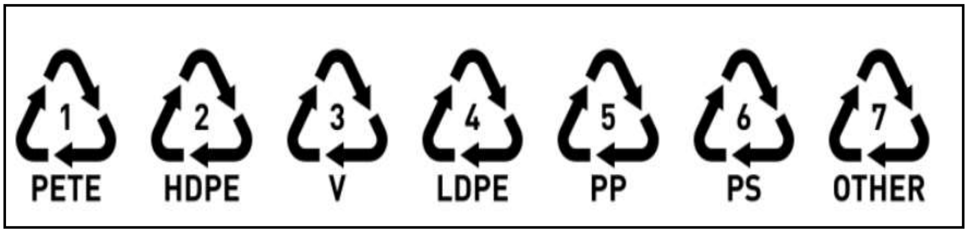

Fig. 1.4 The Plastic resin identification code (American Chemistry Council, 2016)

Around 40% of the plastic produced today is for the purpose of packaging and therefore is the quickest to be disposed off and converted to waste, typically within a period of six months (Geyer et al., 2017) . **Figure 1.5** (a) shows the production of plastics by sector and **figure 1.5 (b)** shows the production of plastics by polymer type in the year 2015. Majority of plastics produced, 42% is for the purpose of packaging and composed of PP and PE mainly. Similarly **figure 1.6 (a)** shows plastic waste generated by sector, and **figure 1.6 (b)** shows plastic waste generated by polymer type and here also the major plastic waste generated is in the form of PP and PE polymers. The second largest user sector of plastics is construction and infrastructure sector which consumes around 20 % of plastics produced globally but the plastic here has a life span of around 35 years and therefore the major waste production is due to plastics used in packaging.

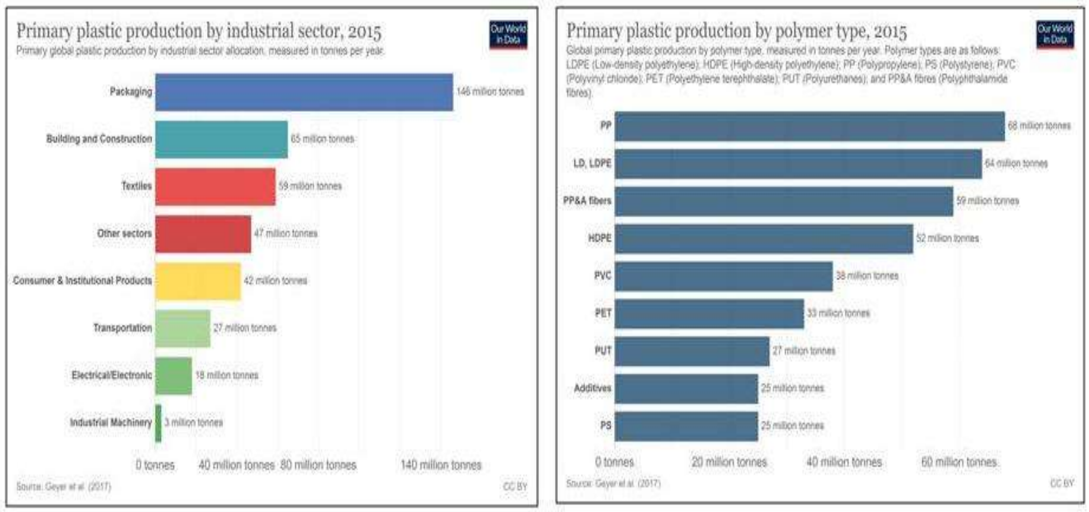

Figure 1.5(a): Plastic production in 2015 by sector; (b) Plastic production in 2015 by polymer type

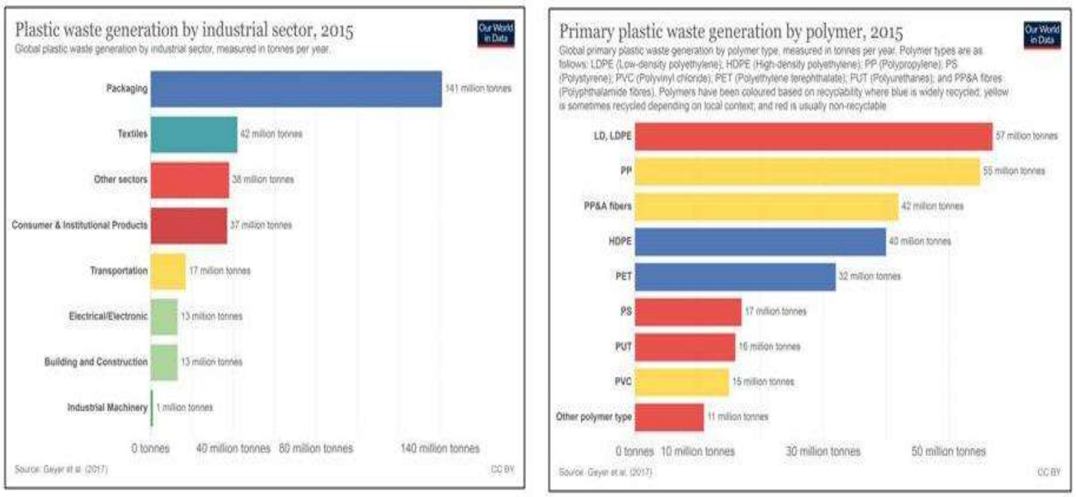

Figure 1.6 (a): Plastic waste generation in 2015 by sector; (b) Plastic waste generation in 2015 by polymer type

A quick review of India's plastic generation and consumption reveals a similar story--almost 43% of plastics consumed are PE (HDPE, LDPE and LLDPE) followed by 24% consumption of PP. Since both of these are chiefly utilized in packaging it also follows that plastics in packaging will eventually end up in waste and fairly quickly too. Although per capita consumption of plastics in India is currently at 11 kg per person as compared to that of US which is 109 kg per person or 65 and 45 kg per person for Europe and China respectively (FICCI, 2014).

Disposable plastic is the main source of problem because of its mass production, consumption and later emission as waste which is creating huge piles of garbage. Over the past decades a shifting of trends had been observed from using reusable containers towards disposable single use packaging. This has generated an enormous demand of plastic materials catering to the demands and ending in waste. It has also thus penetrated every aspect of human life including the waste generation part and plastics amount to around 26000 tonnes of waste generated every day in India only (CPCB, 2017). Per capita consumption of plastic in India is around 11 kg per person and is expected to rise to 20 kg per capita by 2022 according to reports of Tata energy research institute which would make the average consumption of plastic in India to around 20 MMT by 2022.

While plastics are a versatile group of materials their uncapped production and consumption around the world has posed serious threats to the environment. Plastics are non biodegradable which means they can be around for several hundred years filling up landfills and choking up drains and rivers (Yoon et al., 2012). Micro plastic fragments harm aquatic life when it leaches into oceans and then enter our food chain when such fish are consumed as sea food. Needless to say the world needs a sustainable alternative to plastics. The major consumption of plastics is in the form of packaging films which are mainly polyethylene and poly propylene.

The growing problem of plastic pollution requires a three pronged approach: first some way to utilize and thus degrade the accumulated plastic waste in a way that is environmentally friendly. Presently we are only aware of thermal treatment by pyrolysis that can completely breakdown plastics but it will require a great amount of energy and the gas emissions will have to be taken care of. Second, to facilitate recycling of plastics by generating awareness about plastic types for proper segregation practices which would make recycling easier. Third, to reduce the consumption of plastics so that no new plastic waste is generated; this would require alternatives to be available which are sustainable and biodegradable. The solution also needs to be less focused on chemicals and processing and more directed towards ease of production requiring little or no chemical pretreatment at all.

1.2 Biodegradability

Biodegradability is the essential attribute of any material intended to be used as an alternative to plastics. But biodegradability is a tricky term in the sense it has been used for marketing products whose biodegradability can be questioned. Mere break down of any material under suitable environmental conditions cannot be considered biodegradability. Biodegradability is a process in which any organic substance breaks down to ultimately produce carbon dioxide, biomass and water (under aerobic conditions) or methane (under anaerobic conditions) by the enzyme action of microorganisms when provided with favorable environmental conditions like temperature and humidity. Also, there must be no toxic residues during the degradation process (Rhim et al., 2013; Shah et al., 2008; Siracusa et al., 2008).

Some plastics are termed oxo-biodegradable which means they break down rapidly in the presence of oxygen and upon exposure to atmosphere into micro plastics due to additives added into them. They are not biodegraded, but only broken down to micro plastic fragments which can pollute waters/ lands and in landfill conditions produce substantial amount of methane which is a major green house gas. Some other plastics deemed to be biodegradable are termed compostable but it is to be understood that these are only compostable in an industrial composting facility which can maintain particular conditions of heat and humidity for extended periods of time. Such plastics cannot and should not be thrown away in garbage or treated at home composting facility. If these end up in landfills they merely contribute to the methane production and possibility of toxic chemical additives is always there. To prevent such misconceptions, certain standards have been developed for e.g., the standards ASTM standard D-5488-94d, European norm (EN) 13432, DIN 103.2 and ISO 472 provide definitions for biodegradability and ASTM D-6400 is US standard for solid material biodegradation by composting (Chandra & Rustgi, 1998; Fukushima & Camino, 2016; Lucas et al., 2008) .

Biodegradability is affected by both environmental factors as well as chemistry of the polymer. Environmental factors that play a role in biodegradability include the presence of right kinds of microorganisms, suitable temperature, humidity, and pH levels.

Chemical composition of the polymer like its crystallinity, additives and functional groups present and molecular weight of the polymer are some of the chemical factors affecting biodegradability (Chandra & Rustgi, 1998; Shah et al., 2008; Siracusa et al., 2008).

The process of biodegradation may consist of a number of steps including (Avérous & Pollet, 2012; E Chiellini et al., 1999; Rujnić-Sokele & Pilipović, 2017; Zhao et al., 2020):

i. Fragmentation/ biodeterioration step-- the polymer is broken down into micro pieces by microbial consortia present and growing on the surface of polymer.
ii. Depolymerisation step—the polymer is broken down into its oligomers and then into monomers by microbial action
iii. Assimilation step—microorganism take up the monomers by transportation into cells and metabolize them to produce energy and biomass
iv. Mineralization—final step where H2O, CO2, CH4 and salts are released as a result of microbial oxidation and metabolism.

Evaluation of biodegradability of polymers can be done as follows (Avérous & Pollet, 2012; E Chiellini et al., 1999; Rujnić-Sokele & Pilipović, 2017; Zhao et al., 2020):

- *Surface morphology*: Many surface characteristics are changed when biodeterioration occurs such as an increase in surface roughness, change in colour and the presence of cracks or holes.
- *Weight loss*: The weight of polymeric materials decreases with time when buried in soil or enzymatic solutions as an indicator of biodegradation.
- *Changes of properties*: Changes in dynamic, mechanical, chemical and thermal properties reflect the biodegradation of polymeric materials.

- *Product formation*: Some products such as glucose from cellulose polymeric materials or carbon dioxide (CO_2) can be used to evaluate the biodegradation of polymers.

1.3 Biopolymers

Biopolymers refer to polymers that are either have a biological origin for e.g. Originating from plants or animals; The prefix "bio" derived from Greek "bios" refers to human life. Recently the prefix has been used quite liberally leading to confusions. The European Bioplastics Association has therefore classified the polymers into 3 broad types referring to three types of bioplastics (**figure 1.7**): 1. Bio-derived and biodegradable/ compostable polymers (PLA, PHAs etc.); 2. Fossil fuel / petrochemical derived but biodegradable (PCL, PVA etc) and 3. Bio derived and non biodegradable (bio-PE, bio PET, etc.)

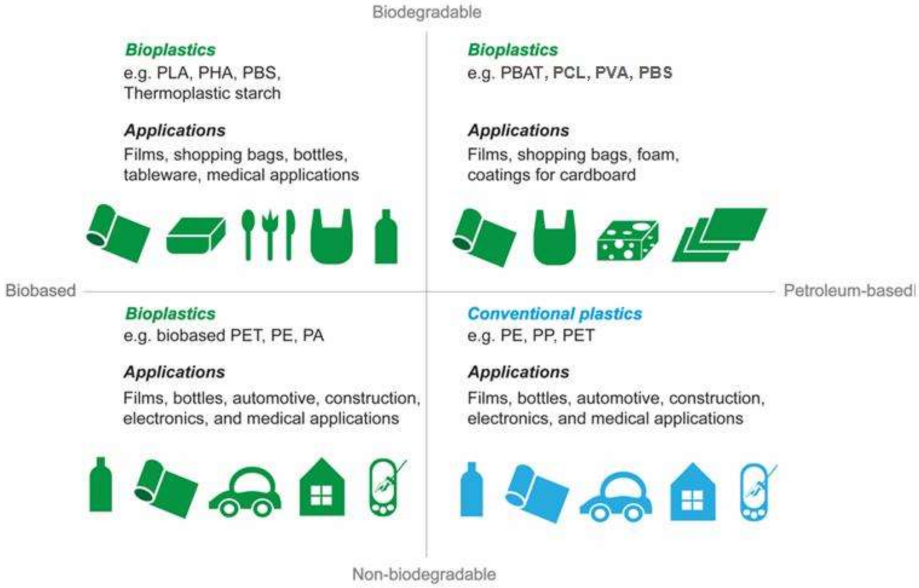

Figure 1.7: Classification of biopolymer types as per the European Bioplastics Association.

Biopolymers can also be classified according to their origin as follows (Petersen et al., 1999; van Tuil et al., 2000):

1. Polymers such as polysaccharides (e.g. cellulose, starch, chitin), lignins, proteins, and lipids directly derived from natural sources like plants or animals
2. Polymers resulting from chemical synthesis of renewable bio-derived monomers (PLA obtained by polymerization of lactic acid produced from dextrose. Also, bio derived poly ethylene produced by polymerization of ethylene derived from ethanol from sugar also falls under this category.
3. Polymers produced by microbial fermentation. Examples include Polyhydroxyalkanoates or PHAs, also consisting of polyhydroxybutyrate (PHB) and copolymers of hydroxybutyrate and hydroxyvalerate (PHBV).
4. Polymers derived by synthesis of petrochemicals; (**Figure 1.8**)

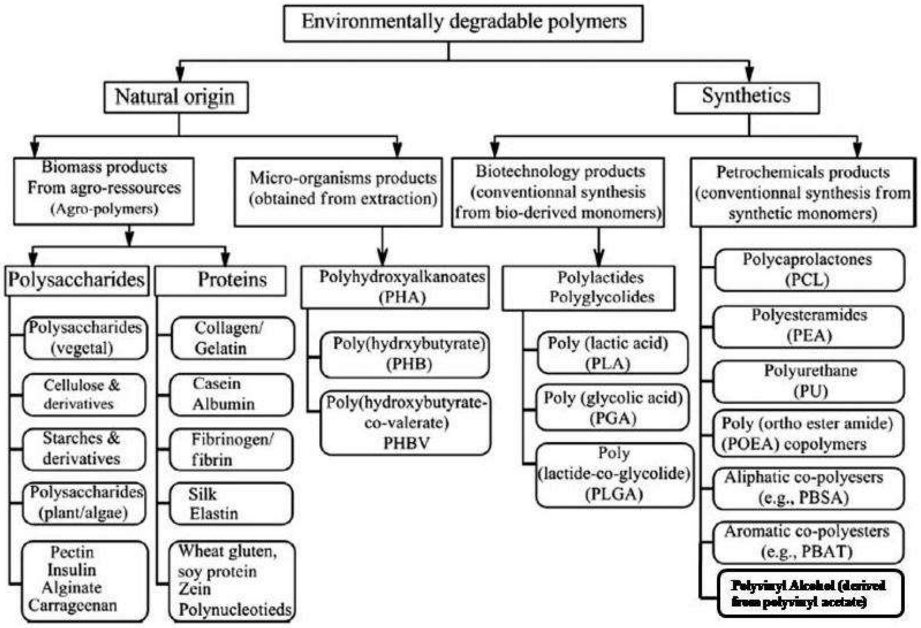

Figure 1.8: Classification of biopolymer types as per their source of origin. Adapted from (Averous & Boquillon, 2004; Satyanarayana et al., 2009).

Major focus is necessary to develop alternative to plastic. While we already have naturally occurring polymers which are also renewable (poly saccharides like cellulose and derivatives, starch, proteins like casein, gluten and carrageenan etc. hemicelluloses like xylan etc), a number of polymers have been developed over the years which have properties similar to plastics and are derived from biomass for e.g. Polylactic acid, Polyhydroxy butyrates and its derivatives etc. Such kinds of biopolymers (bioplastics) are produced as a result of bacterial fermentation. For e.g., PLA is produced by bacterial fermentation of starch to lactic acid which is polymerized to produce PLA. While other bacteria produce PHBs when grown in special media. There are some other bioplastics which are although produced synthetically from petroleum derived chemicals but are still biodegradable for instance polyvinyl alcohols, poly caprolactones etc. Some of the popular biopolymers are briefly discussed here:

1.3.1 Polylactic acid : PLA is a polyester formed by the polymerization of lactic acid (Garlotta, 2001). PLA is made from lactic acid derived from glucose rich renewable resources such as sugarcane, corn etc (Farah et al., 2016; Madhavan Nampoothiri et al., 2010). USFDA has put PLA under the GRAS category (generally recognized as safe) which means PLA is considered safe for various uses. PLA is biocompatible, has high strength, high modulus similar to PS and its films are transparent. PLA however is not efficient at moisture prevention and therefore needs either a barrier material coating (SiOx/AlOx93/ PP or PE) in order to be used as packaging for moisture sensitive items. PLA is not biodegradable as such and needs to be either recycled or treated in an industrial composting facility to completely degrade into plant fertilizer. (Farah et al., 2016; Madhavan Nampoothiri et al., 2010)

1.3.2 Polyhydroxyalkanoates: PHAs are produced by bacterial fermentation of renewable substrates. These consist of aliphatic polyesters and are stored inside cells as granules which serve as energy storage within bacterial cells. The major advantage with PHAs is their thermal and barrier properties match those of PET and PVC making them excellent alternative biopolymers but their high cost of production has inhibited their widespread use (Albuquerque & Malafaia, 2018; Pascault et al., 2012; Raza et al., 2018).

PHB is the most widely studied PHA but has poor processibility due to its crystalline nature which makes it brittle. PHBV (3-hydroxybutyrate-3-hydroxyvalerate) is the polymer formed when 3-hydroxyvalerate (HV) monomers are incorporated into the PHB polymer. It has better properties than PHB but again is costlier (Anjum et al., 2016; Y. Wang et al., 2013). In fact all the PHAs are costly due to its expensive fermentation facilities and polymer recovery systems (Snell & Peoples, 2009; Volova, 2004). Packaging likely will become the fastest growing sector for PHA in the future. Currently, widespread packaging applications of PHA films are still limited by their brittleness, high cost, and poor processibility (Volova, 2004). Strategies to improve PHA film properties include plasticization, copolymerization, blending or laminating with other polymers, such as PLA, thermoplastic starch, and PBAT, and reinforcement with inorganic or organic fillers (Khosravi-Darani & Bucci, 2015).

1.3.3 Polybutylene succinate

PBS is a biodegradable polymer formed by condensation polymerization of 1-4 butanediol (BDO) and succinic acid. While succinic acid can be synthesized by fermentation of glucose and sucrose, BDO is currently petroleum derived. But there is possibility of bio based BDO and thus PBS can be made completely bio based and biodegradable. PBS is promising biopolymer as it has mechanical properties similar to PP and PE, good thermal stability and is easily processable. Although highly crystalline nature of PBS causes it to become brittle and loose ductility over time and also makes it slower to natural biodegradation compared to other aliphatic polyesters like PHA (Zeng et al., 2012).

1.3.4 Starch based thermoplastics

Starch is a wonderful carbohydrate polymer consisting long chains of glucose which are either branched (amylopectin) or straight (amylose). Usually there is 20-25% of amylose and 75-80% of amylopectin in starch (Vilpoux & Averous, 2004). Starch is abundant and can be sourced from various crops like corn, sugarcane, maize, sweet potato etc thereby reducing its cost 81. Starch however in itself cannot form packaging films due to its hygroscopic nature, high crystallinity which makes it brittle and hard poorly processable. Also the tensile strength of starch is not suitable for packaging. Addition of plasticizers to starch combined with the thermo-mechanical treatment in extruder improves the starches' properties improve the mechanical and barrier properties (Vilpoux & Averous, 2004) . Starch has been combined with several biopolymers to improve its properties. Starch has been combined with PVA, PLA, PBS, PHA, PCL, PBAT, PP and PE also to improve flexibility and barrier properties. Future research to improve performance, stability, safety, and lower cost, including inclusion of organic or inorganic fillers, is needed to facilitate widespread use of starch-based films in the packaging industry (Ortega-Toro et al., 2017; Versino et al., 2016).

1.3.5 Polyvinyl alcohol

PVA is a biodegradable and non toxic polymer derived from petrochemicals. It is not formed via polymerization of vinyl alcohol; instead it is formed by the hydrolysis of polyvinyl acetate in presence of caustic to generate polyvinyl alcohol in varying degrees of hydrolysis. The molecular weight and degree of hydrolysis of PVA in general dictates its properties **figure 1.9**. For example, tensile strength, water, block and solvent resistance are found to increase with increasing molecular weight and degree of hydrolysis; whereas the flexibility, solubility and water sensitivity decrease (Mousa et al., 2016; Tang & Alavi, 2011).

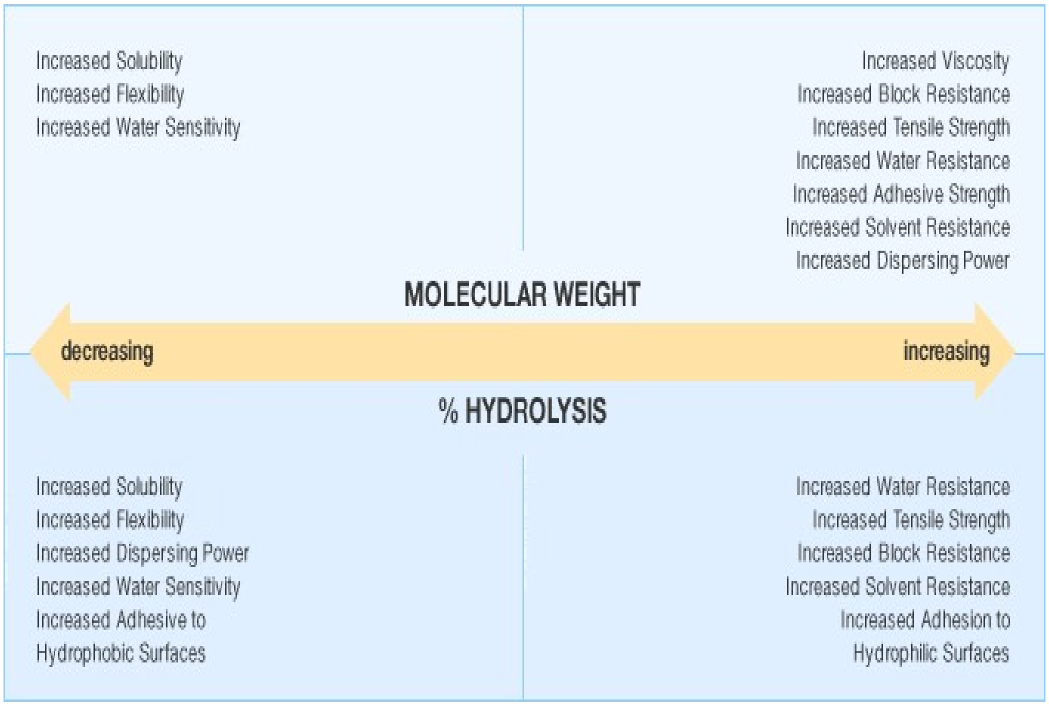

Figure 1.9: Changes Occurring in the Properties of Polyvinyl Alcohol as the Degree of Hydrolysis and Molecular Weight Change. (Tang & Alavi, 2011)

PVA has high mechanical strength and good chemical resistance but is susceptible to moisture and therefore does not possess good barrier properties (Emo Chiellini et al., 2003; Xiong et al., 2008). Barrier properties and thermal stability can be improved by addition of plasticizers which greatly improve the processibility also. PVA is a semi crystalline polymer comprising mainly amorphous phases with only a small amount of crystallinity (Guimarães et al., 2015) and consists of 1, 3-diol units or1, 2-diol units, depending on the hydrolysis degree of poly(vinyl-acetate).

The presence of many hydroxyl groups on the PVA surface makes it one of the most hydrophilic polymers with high moisture sensitivity, and hence its resulting blends and composite materials have become popular for packaging applications (Mousa et al., 2016).

While PHAs, PHBs are excellent materials of choice, they are produced via bacterial fermentation and not economical yet. PLA is promising material and somewhat cheaper too but requires industrial composting facility to be able to degrade naturally otherwise its degradation is similar to other plastics. Poly vinyl alcohol like PLA is cheaper, economical and is comparatively easier to biodegrade without composting. It is readily soluble in water and does not pose any harm to aquatic life at up to 5% v/v concentration. PVA can also be cast easily into films and processed just like plastic polymers.

Lignocellulosic biomass is the most abundant renewable material available throughout the globe. Recent research has been focused on the use of these bioplastics - biomass composite materials as an alternative to plastics thereby increasing the economical viability of such solutions. Lignocellulosic biomass has also been reported to improve the overall mechanical and barrier properties of resulting composites.

Over the years PVA has been used with polymers like starch, chitosan etc and lignocellulosic polymers from a number of agricultural biomass which is treated as waste. The agricultural residue like stalks, straw and husk from food crops, cobs of corn, hemp fibre, pineapple leaf fibre, coconut coir, kenaf fibre etc are a rich source of cellulose, hemicelluloses and lignin. These natural polymers have impressive properties at both macro and micro scale. Cellulose, when extracted, shows remarkable strength in its nano form. Lignin and hemicellulose also have interesting properties. The extraction and separation of cellulose, hemicelluloses and lignin is not quite economical yet and therefore products based on these are not widespread among the in the general public as of yet.

Our focus has been on utilizing the properties of natural lignocellulosic polymer thereby eliminating the need of extracting cellulose or any other component. This will not only reduce the costs but also be more environmentally friendly as fewer chemicals will be consumed in the manufacturing of final product.

So far very few researchers have investigated the utilization of untreated lignocellulosic polymers in preparation of packaging films and with little accomplishment. Utilizing agri-residue in film preparation poses challenges in manufacturing process, co-polymer choice; suitable cross linker and plasticizer which are efficient yet non toxic to the human and environment and above all, the finished product must meet the criteria of mechanical strength and barrier properties being at least comparable to available plastic based packaging material.

Among the various agri-residues investigated banana has remain omitted. India produces around 3 crore metric tonnes of banana per year followed by china which produces around 1 crore metric tonnes per annum. Banana production is peculiar in way that the once the plant has given fruit, it is cut and a new plant emerges from the same tuber. The cut pseudostem is either left to rot in the fields or on the highway either way it is not being utilized to its full potential. Total amount of pseudostem generated per year is 2 -3 times the amount of banana produced i.e., around 6 – 9 crore metric tonnes annually.

Banana pseudostem fibres have been traditionally used in India, Indonesia and Malaysia for preparation of banana silk, banana pith powder has been used as staple food and banana leaves have long been used as dining plate in southern India. Banana plant has therefore been maximally utilized but the pseudostem—the major part of banana plant--remains underutilized. Banana pseudostem contains over 85% water and dry mass of banana pseudostem contains about 70 percent cellulose, 15 percent lignin and 6-15% hemicellulose. Banana pseudostem fibres are extracted by pulverizing the dried stem. These fibres show excellent mechanical properties and have been found to be quite compatible with polymers like polyvinyl alcohol due to their fairly low lignin content. Banana pseudostem is abundantly available at a cheap price.

The present work focuses on providing an alternative to single use petroleum derived plastic packaging film while also utilizing a renewable source of biomass which was being treated as agricultural waste. This would help in reducing the dependency on petroleum derived plastics and also solve the problem of agricultural waste while being completely biodegradable and having properties similar and comparable to plastics we have so grown used to these past years.

Considering the mounting environmental issues due to single use non-biodegradable petroleum based plastics and polymeric films, several research groups across the globe have shown interest in developing bio-degradable polymeric films and/or film composites using renewable and eco-friendly natural raw materials. Several of the abundantly available lingo-cellulosic agricultural and non-agricultural waste biomasses (such as banana trunk, barley husk, wheat straw, etc., have the potential to be converted into bio-degradable films in admixture with other natural polymers. India is one of the largest producers of banana which generates large mass of leaves and trunk in the field after harvesting the fruits. Having little or no value as a fodder in most places these are left as waste biomass in the fields to decay in natural way. The banana trunk, in particular, has the characteristics appropriate for use in developing biodegradable packaging films.

In view of this the broad objectives of the present work is to develop processes for using banana trunk biomass as a natural ingredient with appropriate natural and relatively more easily biodegradable synthetic polymers and to characterize the prepared films to ascertain the process conditions and finally evaluate their use suitability.