Chapter 1

Introduction

1.1 Overview

Preparation of composites is an engineering technique that desires systematic and interactive tactic which aims at having a material with optimum characteristics for specific application. Composite materials usually exhibit a higher strength to weight ratio with flexible characteristics. Composites are derived from two or more materials and often possess remarkably improved physical and chemical properties as compared to individual components. Thus, composites from a multifunctional material system that delivers the required properties of a material that are not present in the individual components that contribute to making up the composites. The composition provides a combination of superior properties of two or more materials that are insoluble to each other (Lubin, 2013). In other words, Composites provide most of the benefits from one material such as polymer, metal, ceramic and other reinforcement materials usually fibers in the matrix e.g. lignocellulosic fiber reinforced polymer matrix, glass fiber reinforced polymer matrix, silicon carbide reinforced ceramic matrix and silicon carbide reinforced metal matrix.

This vital characteristic provokes many researchers to use composite materials in various applications such as automobile, packaging, furniture, building and sporting goods. In modern era, the annual growth rate of fiber-based composites in markets is expected to be 11.8% from 2016 to 2024 (Misra et al., 2015). Many types of agro-waste fibers such as hemp, wheat straw, kenaf, jute and rice husk are used as a reinforcing agent in the thermosetting polymers matrix (Urethane, Epoxy, Polyester, Polyurethane

(Jawaid et al., 2013; Merlini et al., 2011) and thermoplastics matrix (Polyethylene, Nylon, Polypropylene, Acrylonitrile-butadiene-styrene, polycarbonate, Polyvinyl alcohol, Poly-caprolactam (Cao et al., 2012; Majid et al., 2010).

1.2 Polymers

One of the remarkable achievements of the modern era is polymers which have certainly covered a broad market in many applications such as packaging, wrapping, furniture, building and automotive industries (Bajracharya et al., 2016; Díaz et al., 2018; Fazeli et al., 2018). Based on their origin, Polymers can be categorized in two ways like natural and synthetic polymers. Moreover, different types of polymers have representing different physical properties like tensile modulus and elongation limit. Synthetic polymers are petroleum derived non-biodegradable materials and natural polymers are water-based polymers originated naturally from nature like silk, wool, rubber etc. (Mogoşanu and Grumezescu, 2014). As per this classification, the polymer can be distinguished into plastics, elastomers and fibers. Plastics exhibit partially reversibility while elastomers have reversibility with long-chain extensibility. Moreover, fibers have high tensile modulus with moderate stretchability.

The massive use of synthetic polymeric products in daily life has extensively increased for many applications. These synthetic polymers are high molecular mass derived from the polymerization of petrochemicals. Polymers are generally synthesized from the reaction of a large number of smaller monomers to create a long chain molecule. In addition, many polymers such as polyethylene, polypropylene, polystyrene, polyvinyl alcohol, polyamide, and polyvinyl chloride are also widely used (Buekens and Yang, 2014). The polymers have a wide variety of characteristics. Some polymers exhibit brittle and rigid nature while others show flexibility and remarkable reversibility. There are many favourable properties of polymers that encourage their wide use in day to day life such as good moldability, low density, long life, low cost etc. Many literatures data show 39 wt. % demand for polyethylene among all the polymers while other demands for their polymers like polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate are 27 wt. %, 4 wt. %, 17 wt. % and 8 wt. %, respectively as shown in Table (1.1) (Europe, 2017).

Table 1.1 World plastics demands by different types of synthetic polymers in 2016(Europe, 2017)

Polymers	**Demand (wt. %)**
Polyethylene	39
Polypropylene	27
Polyvinyl chloride	17
Polyethylene terephthalate	8
Polystyrene	4
others	5

Synthetic polymers have some remarkably favourable characteristics for most of the applications such as low water vapor transmission rate, hydrophobicity, non-biodegradability, higher mechanical and thermal stabilities. These properties encourage people to surge the use of polymeric products for different applications. In the last few decades, worldwide consumption of polymer is near about 340 million tons in 2016

(Ritchie and Roser, 2018). Approximately 50-70% of the total non-biodegradable packaging waste generated is derived from polyethylene, polypropylene, polystyrene and polyvinyl chloride. In India, 15000 tons of plastic waste is generated every day as most of the packaging waste (Kamyotra and Sinha, 2016). Moreover, massive use is also resulting in the generation of undesirable and non-biodegradable synthetic polymeric wastes. Moreover, synthetic polymers do not degrade quickly. The Polymeric waste generation data over the years are shown in Figure 1.1.

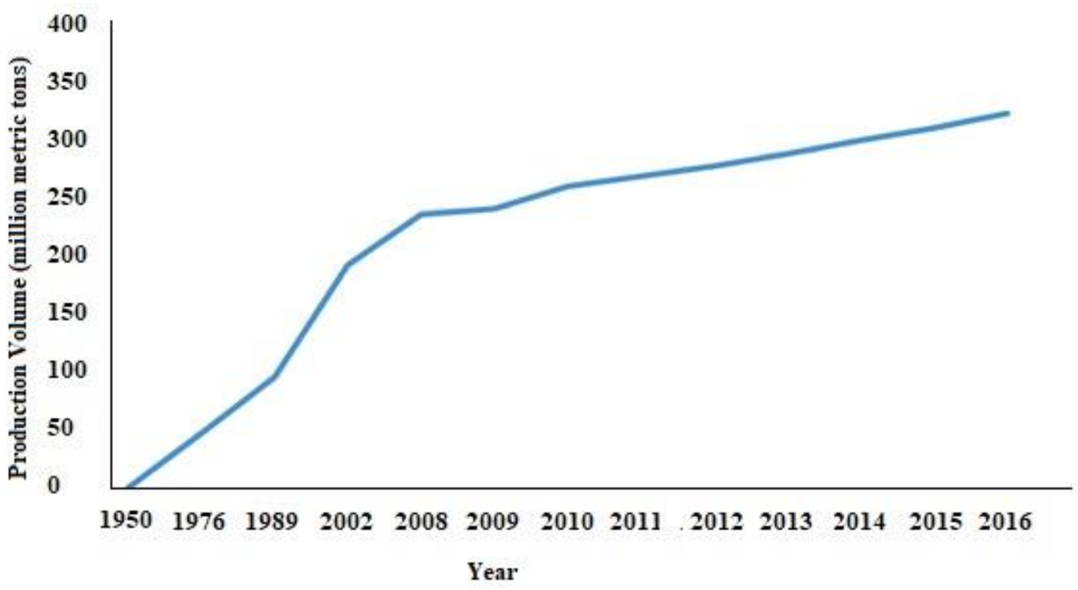

Figure 1.1 Synthetic polymers waste generation data (Ritchie and Roser, 2018).

Hike in consumption is correlated with the generation of plastics waste which is either landfilled or incinerated. In land-filled processes, polymeric waste is initially dumped inland and is allowed to gradually degrade using a different combination of chemical, biological and physical processes. It normally takes over hundred years to decompose of polymeric wastes. In Incineration process, the combustion of polymeric wastes converts it into the ash and toxic gases. The wide spectrum of toxic gases gets released into an environment causing air pollution. This process is generally used to minimize the waste generated in a short time as compared to land-filled disposal process. Hence, it's the need of the hour to find an alternative way for reducing the contribution of polymeric wastes on a global level. A recent attempt is concerning to meet environmental aspects using renewable resources in synthetic polymer matrix composites and achieving the same characteristics with affordable cost for different applications such as automotive, packaging, sensors and building sectors (Mohammed et al., 2015).

1.3 Agro-waste

Agro-waste is known as the waste which is produced from various agricultural activities. It includes manures, bedding, plant stalks, hulls, leaves and vegetable matter. In India, 910 metric tons of agro-waste is generated every year. Landfill, open burning and Incineration process are simple options for the waste disposal (Dhar et al., 2017). Abundantly available agro-waste is composed of cellulose, hemicellulose and lignin. To reduce abundantly available agro-waste, the common disposal technique used by the farmers is burning the biomass in an open atmosphere. This activity is causing a large number of undesirable gases such as carbon dioxide (CO_2), particulate matter (PM), carbon monoxide (CO) and polycyclic aromatic hydrocarbons (PAHs) released in the healthy environment and thereby significantly reducing the air quality of the surroundings day by day. So, it is needed to adopt a worth full way to utilize the agro-waste in an environmentally acceptable form. It will also help to provide farmers extra income from same agro-waste instead of burning agro-waste in an open atmosphere.

1.3.1 Classification of Agro-waste

Agro-waste is generally produced from plants residues. It can be classified in two ways, viz. agricultural residues, and industrial residues. Agricultural residues are categorized such as field residues (stems, stalks, leaves, seed pods) and process residues (husks, seeds, roots, bagasse, molasses). These are shown in Figure 1.2. Agro-wastes are low in density, biodegradable in nature, abundantly available, low in cost and easy to process. These characteristics have drawn a lot of attention in the modern era and motivate researchers to use agro-waste as a replacement of synthetic fibers in a polymer matrix for packaging applications (Chawla and Bastos, 1979; Dhakal et al., 2015).

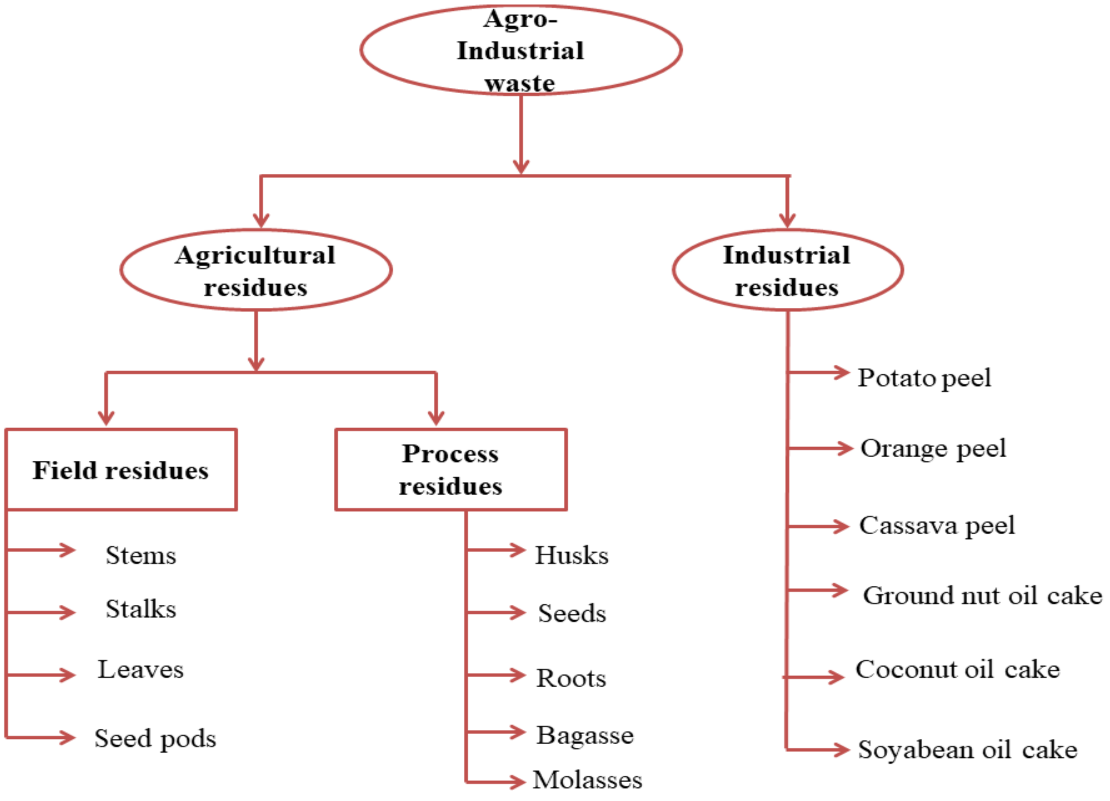

Figure 1.2 Classification of Agro-waste (Dhar et al., 2017)

1.3.2 Chemical composition of Agro-waste

The lignocellulosic fiber is composed of cellulose and hemicellulose which is strongly covered with a strong wall of lignin. The presence of proximate percentage of cellulose, hemicellulose and lignin in agro-waste can be differentiated in terms of the type of lignocellulosic fibers. This lignocellulosic property of biomass has attracted many researchers to utilize abundantly available agro-waste as a reinforcing agent in a polymer matrix (Laadila et al., 2017). The chemical composition of some of the lignocellulosic fibers is shown in Table 1.2.

Table 1.2 Chemical composition of some natural fibers.

Natural fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Hemp	57-77	14-22.4	3.7-13	(Chaitanya et al., 2017)
Banana	53.45	28.56	15.46	(Shahinur and Hasan, 2019)
Coir	43.44	0.25	45.84	(Shahinur and Hasan, 2019)
Jute	59-61	22.1	15.9	(Shahinur and Hasan, 2019)
Sisal	65-68	10-22	9.9-14	(Senthilkumar et al., 2018)
Wheat straw	38-45	15-31	12-20	(Chaitanya et al., 2017)
Bagasse	40-55.2	25.3	16.8	(Chaitanya et al., 2017)
Kenaf	72	20.3	9	(Faruk et al., 2012)
Rice husk	35-45	19-25	20	(Faruk et al., 2012)
Rice straw	41-57	33	8-19	(Faruk et al., 2012)
Flax	62-72	18.6-20.6	2-5	(S and Hiremath, 2019)
Bamboo	26-65	30	5-31	(S and Hiremath, 2019)
Ramie	68.6-76.2	13-16	0.6-0.7	(Mohammed et al., 2015)
Abaca	56-63	20-25	7-9	(Mohammed et al., 2015)
Pine apple	81	-	12.7	(Mohammed et al., 2015)
Caraua	73.6	9.9	7.5	(Mohammed et al., 2015)

Due to the environmental consideration, current trends motivate many researchers to use agro-waste to synthesize the composites for reducing the polymer consumption throughout the world and take steps towards building a sustainable environment (Faruk et al., 2012; Paul et al., 2015). These trends are pushing many authors to suggest composite industries to represent a new agro-waste fiber-based matrix. The key prospects to use agro-waste in the polymer matrix as an alternative are to gain comparable mechanical and thermal stabilities with biodegradability and reduced cost (Satyanarayana et al., 2009). In some cases, fiber based composites provide significant results as compared to carbon fiber or glass fiber-based composites. In addition, the production of waste also demands less energy which is 9.55 MJ/kg for flax stalks fibers as compared to glass fiber-based composites (54.7 MJ/kg) (Joshi et al., 2004). These characteristics are enabling the researchers to use a massive amount of lignocellulosic materials in a polymer matrix for packaging applications.

Literature confirms that composites have successfully replaced the synthetic polymers in lightweight and high mechanical stability applications. Therefore, composites are in high demand in many applications in terms of higher tensile strength, stretchability, low density and benchmark thermal stability. In composites, a fibrous reinforcing material normally light in weight gets embedded in a matrix of tough material in order to obtain the desirable properties which are not present in any individual materials. In addition, desirable properties in composites depend on the type of fibers, amount and processing techniques.

In this thesis, two types of polymers like polyethylene, polypropylene and two agro-waste viz. wheat straw, hemp fiber were chosen as potential feedstock materials to effectively convert into bio-composite packaging film using central composite design-response surface methodology. This CCD-RSM technique examined the simultaneous interactions of input variables in order to attain the desirable packaging film properties. Due to the recalcitrance nature of biomass, strong interface was missing between fiber and polymer matrix. This undesirable characteristic was removed by using certain chemical pre-treatment methods for reducing recalcitrance nature of agro-waste. This action will help to make fiber more compatible while blending in a polymer matrix. In this study, alkali pre-treatment was used to break the ester bonds between cellulose, hemicellulose and lignin and make natural fiber appropriate for blending by removing the lignin and hemicellulose contents from the natural fiber. It resulted in an increased cellulose region in the fabrication of green composites using the solution casting method.

Almost all the published literatures related to agro-waste based polymeric packaging films are on wheat straw, banana, kenaf, almond shell, seagrass, rice husk, rice straw, sisal, hemp, jute, corn stalk etc. No research work has been carried out on central composite design-response surface methodology technique-based synthesis of agro-waste based polymeric packaging film. Hence, in this thesis, optimization for independent variables such as concentrations of alkali treated-agro-waste (wheat straw, hemp fiber) and polymers (polyethylene and polypropylene) were considered to observe effective output responses viz. tensile strength, elongation at break (%) and water vapor transmission rate of agro-waste polymeric packaging film. In the first type, optimization of the simultaneously effective responses for alkali treated-wheat straw-based polyethylene/polypropylene was done. This has been described in the Optimization of polyethylene/polypropylene/alkali modified wheat straw composites for packaging application using RSM published article (Dixit and Yadav, 2019b). In the second type, optimization of output responses for alkali-treated- hemp fiber-based polyethylene/polypropylene packaging film has been carried out. Further, both types were compared with the polymeric packaging film on the basis of various characteristics i.e., water vapor permeability, water vapor transmission rate, optical characteristic, contact angle, water absorption, impact strength, morphology, crystalline and functional changes.

A brief layout of the thesis is as follows; the general overview about the recent scenario of polymer consumption, polymer waste, agro-waste and composites are discussed in **Chapter 1**. **Chapter 2** exhibits the literature review and specific objectives of the thesis. **Chapter 3** presents results and discussion based on the characterization of polyethylene/polypropylene/alkali treated-wheat straw film for packaging application and **Chapter 4** enlights results and discussion based on the characterization of polyethylene/polypropylene/alkali treated-hemp fiber film for packaging applications. **Chapter 5** contains summary of thesis and future scope. The **references** are provided at the end of the thesis.