Chapter 2

Literature review and objectives

This chapter deals with literature review for the fabrication of packaging film based on polyethylene, polypropylene and agro-waste as a feedstock. This chapter is divided into different sections which cover packaging raw materials, various synthesis processes and a brief compilation of published literature based on packaging feedstocks. Based on research gap, the objectives of the thesis have been finalized.

2.1 Literature review

2.1.1 Feedstocks for packaging application

2.1.1.1 Polyethylene

Polyethylene is a thermoplastic polymer resulting from the polymerization of long-chain ethylene monomer ($CH_2=CH_2$). The two famous categories of PE, viz. high-density polyethylene (HDPE) and low density polyethylene (LDPE) are generally used as a feed in the packaging industry. The density and melting point of HDPE are 0.941 g/cm^3 and 130-135 °C. Moreover, these properties are significantly higher as compared to LDPE (1700 g/mol). In addition, these characteristics are also correlated with a lower flexibility limit.

Low density polyethylene is tremendously used in applications such as packaging, households and mobile manufacturing units because of its remarkable properties such as thermal characteristics, hydrophobicity, superior mechanical stability and low cost. These features have attributed considerable attention to the packaging industry. PE is frequently used in several applications such as plastic bags, wrapping equipment, bottles, containers, trash bags, laminations and nutrition packaging applications. Many researchers used PE for the fabrication of packaging film in their published articles (Azlin-Hasim, Cruz-Romero, Morris, Cummins, & Kerry, 2015; Colín-Chávez, Soto-Valdez, & Peralta, 2014; Gaikwad, Singh, & Lee, 2017; Jiang, Wei, Cheng, & Zhu, 2018; Peyroux et al., 2016; Peyroux et al., 2015; Semanová, Skláršová, Šimon, & Šimko, 2016) that demonstrate the suitability of PE in packaging applications.

2.1.1.2 Polypropylene

Polypropylene (PP) is one of the frequently used thermoplastic polymers synthesized from the polymerization of propylene monomer. PP has a semi-crystalline structure which is similar to the PE. PP has exceptional mechanical strength with outstanding resistance to stress as compared to PE. The melting point of PP is 160-165 ^{O}C with 0.85-0.95 g/cm^3 density. These characteristics enable PP applications in various industries such as packaging, containers and plastic products. Some authors used protein and silicate-coated PP composites to obtain the desired mechanical strength for packaging film applications (Lee, Son, & Hong, 2008; Roes, Marsili, Nieuwlaar, & Patel, 2007). Some literature also enlightens the use of PP composites film to restrict the interaction of feed with outer surroundings (Lebossé, Ducruet, & Feigenbaum, 1997; Zobel, 1985).

2.1.1.3 Agro-waste

Composites based on agro-waste have attracted the attention of researchers in the Nanocomposite field due to prominent advantages such as low weight, biodegradable in nature and easy availability as compared to synthetic polymer (Thakur, Thakur, & Gupta, 2013). Moreover, the regulations related to the environmental aspects have also forced the researchers to use natural fibers for synthesizing green composites. Many researchers used lignocellulosic fibers such as jute, kenaf, banana, hemp, wheat straw, corn stalks in developing green film. These films also exhibit many desirable characteristics such as water barrier, strength, and biodegradability assuring their applications for packaging (Averous, Fringant, & Moro, 2001; Ganjyal, Reddy, Yang, & Hanna, 2004; Islam, Rahman, & Hasan, 2019; S & Hiremath, 2019; Sayeed, Sayem, & Haider, 2019).

India is the key producer of wheat throughout the world which signifies the existence of maximum crop residue after cultivation. Devi et al., 2017 reported the generation of 110.3 tons of wheat straw in India during 2014-15 in their article. This report assures abundantly availability of wheat straw in India. Excessive availability pressurizes farmers to burn wheat straw and contributes to air pollution which originates severe health issues for human beings. Along with such issue, it may also note that wheat straw is also cellulose-rich biomass assuring its potential uses for packaging applications (Yang, Bai, & Wang, 2018). Several researchers have found suitable use of wheat straw in a polymer matrix for packaging applications (Alemdar & Sain, 2008; S Panthapulakkal & Sain, 2015; Tajeddin, 2015).

Hemp fiber is also lignocellulosic biomass, which exhibits the strongest and durable characteristics among all other natural fibers. These prominent properties make hemp fibers favourable source of cellulose fiber for synthesizing green composites having excellent thermo-mechanical properties for packaging applications (Czigány, 2006; Dhakal et al., 2015; Khan et al., 2018; Liu, Thygesen, Summerscales, & Meyer, 2017; Madhusudhana, Desai, & Venkatesha, 2018).

2.1.2 Composite materials

Composite preparation technique involves providing a way to meet the desirable characteristics from the combination of two or more materials. In other words, composites are composed of two or more materials for getting a superior property which is not present in any discrete material. So, composites are a multifunctional material system that delivers the required properties of a material that are not present in the individual materials that contribute to making up the composites. Bio-composites derived from abundantly available agro-waste based polymer composites have attracted many researchers to replace key petroleum-derived non-biodegradable materials for many industrial applications i.e., packaging, furniture goods, automotive parts, sporting goods, wrapping, and building(Iwata, 2015; Tsuchiya, Ifuku, Koyama, & Numata, 2019). Moreover, agro-wastes represent remarkable mechanical properties in addition to low cost and biodegradability. Bio-composites also have shape versatility characteristic over a wide range of applications using established solution casting technique (Numata & Kaplan, 2010). Many researchers have worked on incorporation of agro-waste in polymer matrix showing suitability for various uses such as furniture, sports, disposal, packaging, roof panel, aerospace and automotive industries (Arrakhiz et al., 2012; Etaati, Wang, Pather, Yan, & Mehdizadeh, 2013; Khan et al., 2018; Madhusudhana et al., 2018). These qualities make bio-composites comparable to other synthetic composites.

2.1.3 Agro-waste characterization

Agro-waste plays a vital role in composite preparation for the fabrication of green packaging film. Therefore, agro-waste characterization is very crucial to observe its surface morphology, crystalline behaviour, functional changes and cellulose percentage for reinforcement of polymer composites. Many researchers have used several characterization techniques such as Scanning Electron Microscope, Fourier Transformed Infrared Spectroscopy, and X-Ray Diffraction. Zegaoui et al., 2018 used TGA and FTIR analyses to examine the effect of alkali treatment on hemp fiber for polymer blending. Arrakhiz et al., 2012 investigated the thermal stability of chemically treated-alfa fiber reinforced polypropylene composites for different industrial applications. Arrakhiz et al., 2013 evaluated the functional changes in chemically modified doum fiber for green reinforcement applications. Pracella et al., 2006 used SEM, TGA, FTIR analyses for suitable enhancement in stiffness of the treated-fiber reinforced polypropylene composites. Alemdar et al., 2008 used SEM, TGA, XRD, FTIR analyses techniques on hemp fiber in order to observe the considerable changes in fiber for suitable packaging, furniture and automotive applications. Lu et al., 2013 studied the thermal and functional changes in treated-hemp fiber for significant improvement in fiber-polymer matrix interface.

It is clear from the above literature review that agro-waste characterization is essential to observe desirable modifications that are responsible for its uses in the present packaging film study.

2.1.4 Packaging film characterization

Packaging film synthesized from agro-waste and polymers were characterized by many researchers using several analytical techniques such as SEM (scanning electron microscope), FTIR(Fourier transformed infrared spectroscopy), TGA (Thermogravimetric analysis), XRD (X-ray diffraction), mechanical test, dart impact test, contact angle, water vapor transmission rate, water vapor permeability and optical characteristics test. Alemdar et al., 2008 prepared thermoplastic starch/wheat straw packaging film and analysed packaging film using SEM, TGA, tensile modulus, strain modulus and young modulus tests. Many authors performed a tensile test, flexibility test, water absorption, thermal stability, impact test for natural fibers such as hemp, basalt, wheat straw reinforced high-density polyethylene packaging film. The concluded results indicated the suitability of natural fiber in a polymer matrix for packaging applications (Babaei, Madanipour, Farsi, & Farajpoor, 2014; Lu & Oza, 2013; Roumeli et al., 2015; Sarasini et al., 2018; Zabihzadeh, 2011). Tejeddin et al., 2015 performed a tensile strength test for low-density polyethylene/wheat straw-based composite film for packaging applications and observed the influence of Maleic Anhydride Polyethylene and Polyethylene Glycol as a compatibilizer on the film. Authors investigated tensile strength, flexural strength, tensile modulus, a flexural modulus of polypropylene/wheat straw composites for various applications such as automotive, construction and packaging (Suhara Panthapulakkal & Sain, 2006). This study examined the tensile strength and fracture toughness of alkali treated-hemp fiber incorporated polypropylene composites for automobiles, military, construction, packaging, aerospace and railway coach applications (Etaati, Pather, Fang, & Wang, 2014). Some authors evaluated tensile strength, FTIR, TGA, Young’s modulus of chemically treated natural fibers reinforced polypropylene composites for a variety of applications (Arrakhiz et al., 2013; Arrakhiz et al., 2012). Authors prepared chemically modified wheat straw reinforced polystyrene film and characterized it by SEM, TGA, XRD, tensile test, water vapor transmission rate, soil biodegradable test, water absorption test and contact angle for checking the suitability of the film for packaging applications (Dixit & Yadav, 2019). Thus, it is very important to examine the characteristics of synthesized film for packaging film based on various analytical techniques.

2.1.5 Types of synthesis process involved

In order to meet the standards of packaging film, various types of process techniques are used for synthesizing composites based on natural fiber and polymer. Out of the available techniques, extrusion, injection, melt mixing and solution casting method have been discussed below.

2.1.5.1 Extrusion molding

The extrusion process generally uses a die to obtain composites in the desired shape. This process starts with the feeding of thermoplastic materials in to the funnel shaped container (Hopper). From this hopper, the raw materials are delivered to the heated barrel and pushed out the molten plastics through a custom die for forming a rod or tube like structure. This process is beneficial for manufacturing a two-dimensional regular cross section area of the desired product. This admired quality has received industrial attentions to synthesize polymer composites. In this process, feedstocks are kept in the hopper for melting. After melting, the mixture is transferred towards extruder in order to get the desired shape of an object. Many authors used different type of extruders for synthesizing polymer composites based as Hemp Hurd (Khan et al., 2018), Hemp fiber (Dhakal et al., 2018; Lu & Oza, 2013), corn stalk (Ganjyal et al., 2004), clove essential oil (Mulla et al., 2017), doum fiber (Arrakhiz et al., 2013) and wheat straw (Tajeddin, 2015; Yang et al., 2018) for green packaging applications.

2.1.5.2 Injection molding

The injection molding is one of the famous methods to manufacture polymer-based composites based on the molten die-casting method. It can be divided into three ones viz. feed zone, compacting zone and metering zone. In feed zone, polymer and natural fibers are added in the hopper for melting. Further melt composites are compacted in a compact zone. Subsequently, in order to achieve the three dimensional desired shapes of the composites according to the requirements, compacted composites are sent towards the molding section. This technique is frequently applied to prepare products of complicated shapes like automotive components, medical and electronic equipment. In recent scenario, many researches are accomplished using injection manufacturing process for reinforcement applications and assuring the suitability of this method for obtaining the required properties (Babaei et al., 2014; Bourmaud, Le Duigou, & Baley, 2011; Etaati et al., 2014; Sarasini et al., 2018; Zabihzadeh, 2011).

2.1.5.3 Melt mixing method

Melt mixing is an adorable method to synthesize natural fiber-based composites of thermoplastics or elastomeric polymeric matrix for various types of industrial applications (Rane, Kanny, Abitha, & Thomas, 2018). Initially, a polymer is melted with the required appropriate amount of natural fibers with the help of extruder. This process is conducted under the presence of various inert gases such as nitrogen, argon, or neon. In this method, polymer can be mixed with the natural fibers by applying sufficient shear force to form a desired product in the absence of organic solvents. Many works of literature supported the use of melt mixing process for achieving required promising properties of desirable reinforcement packaging application (Islam et al., 2019; Roumeli et al., 2015; Sánchez-Safont, González-Ausejo, Gámez-Pérez, Lagarón, & Cabedo, 2016).

2.1.5.4 Hand layup method

Hand layup is a cost-effective method to fabricate a woven composite based on natural fiber and polymer. A gel coating is applied in the mold for the soft removal of the composites without any cracks. Further, reinforcing material is placed in the mold and used brush to apply the thermoplastic resin on the filler material. Further, a roller is used to prepare a composite in order to a uniform resin distribution. After the curing process, the film is easily detached from the mold surface (S & Hiremath, 2019). Many articles have favoured this process for preparing a composite film of natural fiber and polymer (Dhakal et al., 2018; Gamage, Park, & Kim, 2009; Madhusudhana et al., 2018).

2.1.5.5 Solvent casting Method

Solvent casting is a cost-efficient technique to synthesize natural fibers based polymer composites that may be utilized in many applications such as building materials, packaging goods, furniture products and membrane formation with superior mechanical properties. This process is also considered as a better replacement of the extrusion method to obtain a film with excellent characteristics. In this method, a polymer is dispersed in solvent at the required temperature. Further, the required amount of natural fiber is incorporated into the solution. Subsequently, the resultant solution is cast on a glass plate of known thickness for drying purposes in order to remove the solvent present in the composite film. This process is demonstrated as the simplest way to synthesize a film with desirable characteristics. Many authors synthesized promising composite packaging film based on many natural fibers such as banana (Srivastava, Singh, Mishra, & Srivastava, 2019), kenaf (Islam et al., 2019), rice straw (Perumal et al., 2018), jute (Orasugh et al., 2018), rice husk (Kargarzadeh, Johar, & Ahmad, 2017), wood cellulose (Sirviö, Kolehmainen, Liimatainen, Niinimäki, & Hormi, 2014), hemp (Luzi et al., 2016) and wheat straw (Alemdar & Sain, 2008).

2.1.6 Previous research on composites & packaging film

Many kinds of research have been discussed in this section systematically according to feedstock's materials for packaging applications.

2.1.6.1 Incorporation of a reinforcing agent in Polymer composites

Daramola et al., 2020 studied the mechanical stability of chitosan particles incorporated high density polyethylene composites using compression moulding technique. The results showed that the impact strength of composites had proportionally increased from 2 to 10 wt.% chitosan particles. The higher tensile strength i.e. 23.14 MPa of HDPE composites was observed at 2wt% chitosan particles. So chitosan particles have significantly performed as filler in polymer matrix for reinforcement applications.

Boonsiriwit et al., 2020 have used alkali treated- halloysite nanotubes clay fillers in low density polyethylene matrix for minimizing the production of ethylene gas and synthesized a suitable packaging film for cherry tomato. The water barrier property has increased by 10% with reliable ethylene absorption capacity at 5 wt.% alkali treated- halloysite nanotubes clay particles incorporated LDPE composites showing suitability for packaging applications.

Zia et al., 2019 prepared LDPE/curcumin based composites using extrusion technique and studied the physicochemical properties of curcumin based composites for packaging applications. Reported results showed that 55% reduction in WVTR with 10% enhancement in contact angle was observed in 5% curcumin reinforced LDPE composite film as compared to pure LDPE film assuring its suitability for packaging applications.

This study explored the manufacture of linear low-density polyethylene/cinnamon essential oil/nano-silver/nano-copper composites for active packaging applications. Moreover, the authors of this paper demonstrated decrement of transmittance at 800 nm with surging the concentration of silver-copper nanoparticles in the composites for chicken meat application (Ahmed et al., 2018).

Zegaoui et al., 2018 chose alkali-treated hemp fiber as a filler in cyanate ester/ benzoxazine resin matrix for packaging, electronic substrate and adhesive applications and observed an effect on tensile strength, strain, tensile modulus and water absorption of the prepared composites. The findings of this study assure the successful replacement of polymer resin with treated-hemp fiber in order to attain the benchmark mechanical stability in terms of tensile strength, strain and tensile modulus.

Khan et al., 2018 prepared extruded polylactic acid/hemp Hurd/glycidal methacrylate-grafted (GMA) composite and utilized injection molding. Further, the authors examined crystalline changes and thermo-mechanical stability of the synthesized composite. Results showed that increasing the GMA contribution (20% w/w) in composite was responsible for 94% retaining polymer strength with a desirable range of thermal-mechanical stability for packaging and disposal goods applications.

The study of Jo and others evaluated the mechanical properties of nano-silver incorporated polyethylene and polypropylene-based film for food packaging applications using the melt extruding method. SEM result showed the even distribution of silver content in the film with comparable tensile and antimicrobial properties as compared to commercial low-density polyethylene film for effective food packaging applications (Jo et al., 2018).

In another study, Mulla et al., 2017 prepared linear low-density polyethylene film using the extrusion process and modified the film surface using chromic acid treatment. Further, clove essential oil was spread over the film surface using a sterile spreader. The concluded results of this study are assured the suitable use of chromic acid and clove essential oil with desirable characteristics like microbial safety, increased oxygen transmission rate and required mechanical strength for food packaging applications.

Sabetzadeh et al., 2016 examined the effect of nano clay on low-density polyethylene/thermoplastic starch/linear low-density polyethylene-based packaging film on the basis of transparency and morphological properties. Authors concluded that packaging film synthesized by using 5 phr nano clay embedded exhibited promising properties for packaging applications.

Khalaj et al., 2016 prepared iron particles reinforced polypropylene/montmorillonite (nano clay) composite film. Further, the authors observed a combined effect of iron nanoparticles and nano clay on a water barrier and mechanical properties of the synthesized film. The use of clay decreased the water migration barrier property with enhanced mechanical stability in the resultant composite film showing reliability for active packaging applications.

Authors of another published work incorporated soy protein isolated in polyethylene/polypropylene matrix using hand layup technique and investigated the effect of soy protein isolate in composites for sprout packaging applications. Results revealed that soy protein isolate based composite favoured the microbial safety of sprout. So this finding signified a superior food packaging (Gamage et al., 2009).

Table 2.1 Literature review for the incorporation of a reinforcing agent in a polymer matrix for packaging applications.

Raw materials (Reference)	Parameters	Pre-treatment	Method	Results					Applications
HDPE, chitosan (Daramola et al., 2020)	Chitosan (2%-6%)		Compression molding	**HDPE** IS= 200 KJ/m^2 FM= 1100 MPa FS = 21 MPa	**HDPE/2% Chitosan** IS= 250 KJ/m^2 FM= 1200 MPa FS = 40 MPa	**HDPE/4% Chitosan** IS= 210 KJ/m^2 FM= 1600 MPa FS = 55 MPa	**HDPE/6% Chitosan** IS= 208 KJ/m^2 FM= 1150 MPa FS = 40 MPa	**HDPE/8% Chitosan** IS= 208 KJ/m^2 FM= 1150 MPa FS = 40 MPa	Reinforcement
LDPE, Halloysite nanotubes (HNTs) Boonsiriwit et al., 2020	HNTs (1%-5%)	Alkali treatment of HNTs	Extrusion	**LDPE** TS= 17.43 MPa EAB = 321% WVTR = 12.20 g.m^2/day Ethylene absorption capacity (µL/100 cm^3)= 0.98	**LDPE/1%HNTs** TS= 17 MPa EAB = 315 % WVTR = 12.10 g.m^2/day Ethylene absorption capacity (µL/100 cm^3)= 3.15	**LDPE/3%HNTs** TS= 16.07 MPa EAB = 298 % WVTR = 13 g.m^2/day Ethylene absorption capacity (µL/100 cm^3)= 3.87	**LDPE/5%HNTs** TS= 13.17 MPa EAB = 235% WVTR = 13.50 g.m^2/day Ethylene absorption capacity (µL/100 cm^3)= 5.27		Packaging
LDPE, Curcumin (Zia et al., 2019)	Curcumin (1%-7%)		Extrusion	**LDPE** WVTR = 360 g.m^2/day CA = 101.2^O	**LDPE/5% Curcumin** WVTR = 160 g.m^2/day CA = 110.7^O				Packaging
CE, BOZ (Zegaoui et al., 2018)	HF (6%-24%)	NaOH treatment of Hemp fiber (THF)	Hydraulic hot-press	**CE/BOZ** TS=28.05 MPa TM =1.60 GPa Strain = 2.10% WAB = 0.75 %	**CE/BOZ/THF(20%)** TS=55.74 MPa TM =3.47 GPa Strain = 1.38% WAB= 5%				Packaging
PLA (Khan et al., 2018)	GMA (1%), TBPB (0.5%), HH (10-30%)		Extrusion and injection	**PLA** TS= 65MPa EAB= 4.5% FS= 100 MPa	**PLA/ 30% HH** TS= 45MPa EAB = 2% FS= 60 MPa	**GMA-g-PLA/ 30%HH** TS= 50 MPa EAB = 2.1% FS= 80 MPa			Packaging and Disposable goods
LDPE, PP (Jo et al., 2018)	Ag content (0-240mg)/ Kg of LDPE Ag content (0-290 mg)/ kg of PP		Extrusion	**Ag (0 mg)/ Kg of LDPE** TS =28 MPa EAB = 600% YM= 170 MPa	**Ag (240 mg)/ Kg of LDPE** TS =23MPa EAB = 600% YM= 480 MPa	**Ag (0 mg)/ Kg of PP** TS =52 MPa EAB = 1000% YM= 1200 MPa	**Ag (290 mg)/ Kg of PP** TS =40 MPa EAB = 800% YM= 1000 MPa		Food Packaging

LLDPE, , CEO (Ahmed et al., 2018)	silver-copper (Ag-Cu) nanoparticles (NPs)		Compression molding	**LLDPE** Thickness= 0.096 mm T at 800 nm= 90%	**LLDPE/2% Ag-Cu** Thickness= 0.098 mm T at 800 nm=10.20%	**LLDPE/4% Ag-Cu** Thickness= 0.103 mm T at 800 nm= 9.46%	**LLDPE/4% Ag-Cu/50%CEO** Thickness= 0.107 mm T at 800 nm= 2.86%	Chicken meat Packaging
LLDPE, CLO (Mulla et al., 2017)	CA treatment of film		Extrusion	**LLDPE** TS= 8.18 MPa EAB = 620 % TM= 59MPa Transparency(%)=1.19 OP= 1.02x10^{-16} (Kg.m/m^2.d.Pa)	**LLDPE/CA** TS= 6.59 MPa EAB = 496% TM= 48 MPa Transparency(%)=1.5 OP=1.62 x10^{-16} (Kg.m/m^2.d.Pa)	**LLDPE/CLO** TS= 6.43 MPa EAB = 501% TM= 47MPa Transparency(%)=1.73 OP=1.74 x10^{-16} (Kg.m/m^2.d.Pa)		Food Packaging
LDPE, LLDPE thermoplastic starch (Sabetzadeh et al., 2016)	Nanoclay content (1-5 phr)		Extrusion	**At 0 phr nanoclay** TS= 12 MPa IS= 5.90 KJ/m^2 WAB =12% Optical transparency(%) = 78 EAB = 370%		**At 5phr nanoclay** TS= 16 MPa IS= 8 KJ/m^2 WAB =10.5% Optical transparency (%) = 76 EAB = 350%		Packaging
PP (Khalaj et al., 2016)	Iron particles (0.05 wt%-0.2 wt%), OMMT (1wt%-4 wt%)		Extrusion	**PP** TS= 28 MPa Water transmission rate= 1.8 g/m^2.hr Oxygen transmission rate =0.6 cc/ m^2.hr		**PP/ 2wt%OMMT/0.05 wt% iron particles** TS= 32 MPa Water transmission rate= 1.4 g/m^2.hr Oxygen transmission rate =0.6 cc/ m^2.hr		Food Packaging

<table>
<tr>
<td>WSNF, TPS
(Alemdar & Sain, 2008)</td>
<td></td>
<td colspan="2">Chemical treatment process steps
1-Soaked in NaOH
2- treated with 1 M HCl $85^{O}C$ for 2 hours
3- treated with 2 W/V% NaOH at 85 ^{O}C for 2 Hours</td>
<td>Solution casting method</td>
<td colspan="2">TPS
TM= 111MPa
YS= 4.45 MPa
SM= 112 MPa</td>
<td colspan="2">TPS-2 wt% NF
TM= 151MPa
YS= 5.32 MPa
SM= 173 MPa</td>
<td colspan="2">TPS-5 wt% NF
TM= 192 MPa
YS= 5.92 MPa
SM= 201 MPa</td>
<td colspan="2">TPS-10 wt% NF
TM= 271MPa
YS= 7.71 MPa
SM= 308 MPa</td>
<td>Packaging</td>
</tr>
<tr>
<td>PP, PE, SPI
(Gamage et al., 2009)</td>
<td colspan="2">Anti-microbial
(0.6 %-1.2 %)
(MA)</td>
<td></td>
<td>Hand lay up</td>
<td>PP/PE
TS=65 MPa
EAB(%)=45</td>
<td colspan="2">SPI
TS= 38MPa
EAB(%)=50</td>
<td>SPI-MA0.6
TS= 40MPa
EAB(%)= 44</td>
<td>SPI-MA0.8
TS= 39 MPa
EAB(%)=45</td>
<td colspan="2">SPI-MA1.0
TS= 39 MPa
EAB(%)=44</td>
<td>SPI-MA1.2
TS= 39 MPa
EAB(%)= 45</td>
<td>Sprout Packging</td>
</tr>
</table>

2.1.6.2 Incorporation of agro-waste in Polyethylene/Polypropylene composites

Suffo et al., 2020 investigated the thermo-mechanical properties of LDPE/sugar-beet agro-waste composites for reinforcement applications. In this study, different percentages of sugar-beet (20-50%) have been incorporated in LDPE matrix and observed the effect on impact strength, young modulus and elongation at break properties of the resultant composites. The remarkable young modulus i.e. 551.31 MPa with considerable impact strength of 50wt% agro-waste incorporated in LDPE matrix assured its suitability for reinforcement applications.

An article by Sarasini et al., 2018 elucidated the thermal and mechanical stabilities of basalt, hemp and basalt-hemp fibers incorporated in high-density polyethylene/maleic anhydride high-density polyethylene composites for package trays, door panels and dashboard applications. They concluded that 30 wt.% basalt fiber and 15 wt.% basalt/15 wt.% hemp fiber-based polymeric film had higher tensile strength compared to pure high-density polyethylene film and assured its suitability for different industrial applications.

Tajeddin, 2015 prepared bio-composite based on extruded low-density polyethylene/wheat straw. Moreover, the authors also observed the effect of maleic anhydride polyethylene and polyethylene glycol as a compatibilizer on tensile strength, flexure and impact strength of composites for packaging application. Maleic anhydride polyethylene compatibilizer improved the tensile strength of the prepared composite based on wheat straw fiber with no significant effect on impact strength.

Roumeli et al., 2015 synthesized high-density polyethylene/ compatibilizer maleic anhydride/hemp fiber composites using melt mixing method and observed tensile strength, elastic modulus, elongation and impact strength of the prepared composites for packaging application. Their results revealed that composite based on hemp fiber had higher elastic modulus as compared to pure high-density polyethylene film with less impact strength.

Babaei et al., 2014 synthesized high-density polyethylene/wheat straw flour/ azodicarbonamide /nano clay composites using injection molding machine for different kinds of applications such as automotive, packaging and thermal insulation and examined the effects of nano clay and azodicarbonamide in the composite. The effect of increasing the percentage of nano clay in composites is responsible for increasing tensile and impact strength. Moreover, increasing the concentration of azodicarbonamide in composites affects the properties significantly.

In another study, Etaati et al., 2014 investigated dynamic mechanical responses for short hemp fiber reinforced polypropylene composites using injection molding. Moreover, maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted poly (ethylene octane) (MAPOE) were used as a compatibilizer to obtain a strong matrices. As an outcome, MAPP compatibilizer based hemp fiber reinforced polypropylene composite had better mechanical stability (tensile strength, elastic modulus, storage modulus) as compared to other prepared composites.

Etaati et al., 2013 explored the utilization of hemp fiber in polypropylene/maleic anhydride grafted polypropylene matrix for automotive, construction and packaging applications and studied the effect of hemp fiber and compatibilizer contributions in a polymer matrix on the basis of tensile strength. The results indicated that polymeric film incorporated with 40% hemp fiber and 5% maleic anhydride grafted polypropylene had higher tensile strength as compared to pure polypropylene film.

Bourmaud et al., 2011 aimed to investigate the mechanical stability of recycled polypropylene/hemp fiber composites after numerous injected series and created interest towards recycling of polypropylene/hemp fiber composites for the savage of environmental considerations. The tensile strength and tensile modulus of recycled polypropylene/ hemp fiber composite after 7 cycles were 25.9 MPa and 4239 MPa which was much higher as compared to recycled polypropylene after 7 cycles. The outcomes of this study provoked many industries to adopt this technique for several industrial applications.

In a study, Zabihzadeh, 2011 synthesized composites using natural fillers such as wheat straw, poplar and pine based high-density polyethylene using maleic anhydride grafted polyethylene as a compatibilizer in order to obtain strong fiber-polymer interfacial interactions for a variety of applications by injection molding. Moreover, authors also visualized the impact on properties such as water absorption, water diffusion coefficient and thickness swelling of the resultant composites. Concluded results went to the favour of using pine natural fiber to obtain strong adhesion between fiber and high-density polyethylene as compared to other bio composites for reinforcement applications.

Alemdar & Sain, 2008 investigated tensile strength, young modulus and storage modulus properties of chemically modified wheat straw incorporated thermoplastic starch using solution casting method for packaging application. Results revealed that 10 wt.% of chemically treated wheat straw-based composite film had higher mechanical stability with significant improvement in degradation temperature as compared to pure thermoplastic starch film.

Table 2.2 Literature review for native- agro-waste incorporated polyethylene and polypropylene matrix for packaging applications.

<table>
<tr><th>Raw materials (Reference)</th><th>Parameters</th><th>Method</th><th colspan="10">Result</th><th>Application</th></tr>
<tr><td>LDPE, Sugar beet waste (SB)
(Suffo et al., 2020)</td><td>SB
(20%-50%)</td><td>Extrusion</td><td colspan="2">LDPE
IS= 67 KJ/ m^{2}
YM = 199.82 MPa
Stress at break= 490.75%</td><td colspan="2">80%LDPE/ 20% SB
IS= 50 KJ/ m^{2}
YM = 315.52 MPa
Stress at break= 50.33%</td><td colspan="2">70%LDPE/ 30% SB
IS= 49 KJ/ m^{2}
YM = 305.15 MPa
Stress at break= 33.16 %</td><td colspan="2">60%LDPE/ 40% SB
IS= 18.6KJ/ m^{2}
YM = 199.82 MPa MPa
Stress at break= 8.78%</td><td colspan="2">50%LDPE/ 50% SB
IS= 14.9 KJ/ m^{2}
YM = 551.31 MPa
Stress at break= 4.13%</td><td>Packaging</td></tr>
<tr><td>HDPE
(Sarasini et al., 2018)</td><td>HF
(10-30%),
BF (10-40%),
MAPE (0.8-1.2%)</td><td>Injection</td><td colspan="3">HDPE
TS= 20 MPa
Strain = 30%</td><td colspan="4">65%HDPE/30%BF/ 5%MAPE
TS= 50MPa
Strain = 7.25%</td><td colspan="2">65%HDPE/ 15%HF/15% BF/5%MAPE
TS= 47.5MPa
Strain = 7.5%</td><td colspan="1">65%HDPE/30%HF/ 5%MAPE
TS= 37.5MPa
Strain = 7.5%</td><td></td></tr>
<tr><td>HDPE
(Roumeli et al., 2015)</td><td>HF
(10-50%),
PE-G-MA
(1-5%)</td><td>Melt Mixing</td><td colspan="3">HDPE
EM= 1340 MPa
TS= 28.3 MPa
EAB= 946%
IS= 624.7 J/m</td><td colspan="4">50%HDPE/50%HF
EM= 3010 MPa
TS= 19.5 MPa
EAB= 0.8 %
IS= 74.3 J/m</td><td colspan="3">45%HDPE/50%HF/5%MA
EM= 2961 MPa
TS= 25.4 MPa
EAB= 1 %
IS= 82 J/m</td><td>Packaging</td></tr>
<tr><td>LDPE, WS
(Tajeddin, 2015)</td><td>MAPE
(7% -10%)
PEG (7%-10%)</td><td>Extrusion</td><td colspan="1">100% LDPE
TS = 3.245 MPa</td><td colspan="2">70 LDPE + 30%WS+ 7%MAPE
TS=3.0 MPa</td><td colspan="2">60%LDPE + 40%WS+ 7%MAPE
TS= 2.881 MPa</td><td colspan="2">60%LDPE + 40%WS+ 10%MAPE
TS= 3.20 MPa</td><td colspan="2">50%LDPE + 50%WS+ 10%MAPE
TS= 3.123 MPa</td><td colspan="1">40%LDPE + 60%WS+ 10%MAPE
TS= 2.924 MPa</td><td>Packaging</td></tr>
</table>

HDPE, WSF, (PEG-MA) (Babaei et al., 2014)	AZD (0-4 Phr) Nanoclay (NC) (0-5 Phr)	Injection Molding	**60HDPE/40WSF/0NC/0AZD** TS= 18 MPa THS =1.3 % WAB =1.5% IS = 42 J/m	**60HDPE/40WSF/2NC/0AZD** TS= 22 MPa THS = 1.1% WAB =1.25% IS = 38 J/M	**60HDPE/40WSF/5NC/0 AZD** TS= 20 MPa THS = 1% WAB = 1.2%, IS = 36 J/m	**60HDPE/40WSF/0 NC/2AZD** TS= 18 MPa THS = 1.4% WAB = 1.4 % IS = 35J/m	**60HDPE/40WSF/0 NC/ 4 AZD** TS= 12 MPa THS = 1.5% WAB = 1.2%, IS =30 J/m	**60HDPE/40WSF/5NC/4 AZD** TS= 15 MPa THS = 1.3% WAB = 1.2%, IS = 28 J/m	Packaging
PP (Etaati et al., 2014)	HF (20-50 %), MAPP (0-5%), MAPOE (0-5%)	Injection	**70%PP/30%HF** TS= 28 MPa EM= 2.8 GPa SM at 40^{O}C= 10000 MPa		**65%PP/30%HF/5%MAPP** TS= 39.3 MPa EM= 3.3GPa SM at 40^{O}C = 13000 MPa		**65%PP/30%HF/5%MAPOE** TS= 38.50 MPa EM= 3 GPa SM at 40^{O}C = 14000 MPa		
HF, PP (Etaati et al., 2013)	MAPP		**PP** TS= 31.1 MPa	**70%PP/30%HF** TS=28 MPa	**70%PP/30%HF/5%MAPP** TS=39.3 MPa		**60%PP/40%HF** TS=28.1 MPa	**60%PP/40%HF/5%MAPP** TS=40.87 MPa	Automotive, Construction and Packaging
Recycled PP, HF (Bourmaud et al., 2011)		Injection	**Recycled PP After 1 Cycle** TS= 15.4 MPa EAB = 6.5% TM= 1193 MPa		**Recycled PP After 7 Cycles** TS= 14.8 MPa EAB = 8.9% TM= 1085 MPa		**70%Recycled PP/ 30% HF After 1 Cycle** TS= 29.7 MPa EAB= 2.70% TM= 4577 MPa	**70%Recycled PP/ 30% HF After 7 Cycles** TS= 25.9 MPa EAB = 3.7 % TM= 4239 MPa	

WS, HDPE, PO, PN (Zabihzadeh, 2011)	MAPE (0 % -2 %)	Injection	**65%HDPE/35%WS** WAB= 9.57% WDC= $8.658x10^{-13}\ m^2/S$ THS= 4.71%	**63% HDPE/35%WS/2% MAPE** WAB= 7.22% WDC= $5.433\ x10^{-13}\ m^2/S$ THS= 3.77%	**65% HDPE/35%PO** WAB= 3.85% WDC= $4.975\ x\ 10^{-13}\ m^2/S$ THS= 1.36%	**63% HDPE/35%PO/2% MAPE** WAB= 2.72 % WDC= $4.378\ x10^{-13}\ m^2/S$ THS= 0.91%	**65% HDPE/35%PN** WAB= 3.15% WDC= $4.678\ x10^{-13}\ m^2/S$ THS=1.26 %	**63% HDPE/35%PN/2%MAPE** WAB= 2.54% WDC= $4.124\ x10^{-13}\ m^2/S$ THS = 0.74%	Automotive, construction and packaging

2.1.6.3 Incorporation of pre-treated agro-waste in PE/PP composites

Arrakhiz et al., 2013 examined the mechanical and thermal stabilities of extruded low-density polyethylene/NaOH treated-Doum fiber composite. A 30 wt.% alfa fiber incorporated based polymer composite showed 145% enhancement in tensile modulus as compared to a pure polymer with a slight decrement in thermal stability for aerospace, packaging and construction applications.

Lu & Oza, 2013 elucidated the impacts of silane and NaOH treatment on hemp fiber in order to observe the thermo-mechanical stabilities of extruded hemp fiber-reinforced high-density polyethylene composites. Their results signified that treated-hemp fiber had higher thermal and mechanical stabilities as compared to native-hemp fiber-reinforced high-density polyethylene composite. The degradation temperatures at 50% weight loss for native-hemp fiber, NaOH treated-hemp fiber and silane treated-hemp fiber were 404.25^{O}C, 418.42 ^{O}C and 421.33^{O}C, respectively assuring better strong adhesion between treated-hemp fiber and polymer matrix for reinforcement applications.

Arrakhiz et al., 2012 synthesized polypropylene/ chemically modified alfa fiber composite film for aerospace and packaging applications. This study enlightens the effect of different pre-treatments such as alkali, etherification and esterification on the surface of alfa biomass and observed its impact on tensile and thermal characteristics of composites. The remarkable 35 % increment in tensile modulus with enhanced thermal stability was observed in etherified treated-alfa based polypropylene composites that assured the successful replacement of polymer with treated-fiber for aerospace and packaging applications.

Suhara Panthapulakkal & Sain, 2006 prepared environment-friendly fungal treated-natural fibers (wheat straw and corn stem) reinforced polypropylene composite films for automotive, construction and packaging industries and visualized the effect on tensile strength, flexural strength, tensile modulus, and flexural modulus to meet required characteristics of packaging film. As an outcome, the fungal treated-wheat straw based composite film had a remarkable improvement in mechanical properties as compared to pure polypropylene film assuring its application for several applications.

Czigány, 2006 studied the mechanical properties for basalt fiber, hemp fiber, glass fiber and carbon fiber-based polypropylene composites and compared tensile strength and bending strength of the prepared composites. The authors also examined the surface treatment of fiber in order to improve the interfacial interaction of fiber in a polypropylene matrix. The tensile and bending strengths of 30% carbon fiber-based composite signified remarkable mechanical stability as compared to other fiber incorporated composites.

Table 2.3 Literature review for pre-treated agro-waste incorporated polyethylene and polypropylene matrix for packaging applications.

Raw materials (Reference)	**Parameters**	**Pre-treatment**	**Method**	**Result**					**Applications**
PP (Madhusudhana et al., 2018)	HF (5-15%)	NaOH treatment of hemp fiber	Hand lay -up	**PP** TS at 10 mm thickness = 40 MPa FT at 10 mm thickness = 4.2$\text{MPa.m}^{0.5}$	**95%PP/5% Alkali treated-HF** TS at 10 mm thickness= 60 MPa FT at 10 mm thickness = 4.3 $\text{MPa.m}^{0.5}$	**85%PP/15% Alkali treated-HF** TS at 10 mm thickness= 44 MPa FT at 10 mm thickness = 3.95 $\text{MPa.m}^{0.5}$			Automobiles, military, construction, packaging, aerospace, railway coach
LDPE (Arrakhiz et al., 2013)	DF (5%-30%)	NaOH treatment of Doum fiber (TDF)	Extrusion	**LDPE** TS=12.75 MPa EAB = 240% YM= 200 MPa	**95%LDPE/ 5%TDF** TS=11.90 MPa EAB = 200% YM= 200 MPa	**85%LDPE/15%TDF** TS=10.75 MPa EAB = 180 % YM= 300 MPa	**70%LDPE/30%TDF** TS=10 MPa EAB = 140% YM= 500 MPa		
HDPE (Lu & Oza, 2013)	HF (20-50%)	Silane and NaOH treatment of hemp fiber	Extrusion	**50%HDPE/50%HF** Degradation temperature at 10 % weight loss= 317.5^{O}C Degradation temperature at 20 % weight loss= 343.5^{O}C Degradation temperature at 50 % weight loss= 404.25^{O}C SM at 50^{O}C = 775 MPa	**50%HDPE/50% NaOH treated-HF** Degradation temperature at 10% weight loss = 328.67^{O}C Degradation temperature at 20 % weight loss= 348.25^{O}C Degradation temperature at 50 % weight loss= 418.42^{O}C SM at 50^{O}C = 850 MPa	**50%HDPE/50% Silane treated-HF** Degradation temperature = 328.17^{O}C Degradation temperature at 20 % weight loss= 347.17^{O}C Degradation temperature at 50 % weight loss= 421.33^{O}C SM at 50^{O}C = 1200 MPa			
PP, AF (Arrakhiz et al., 2012)		Chemical treatment of AF	hot-press	**PP** YM= 700 MPa TS=35 MPa	**Raw-AF/PP** YM= 1000 MPa TS=31MPa	**Alkali treated-AF/PP** YM= 1200 MPa TS=31 MPa	**Esterified-AF/PP** YM= 1400 MPa TS=32 MPa	**Etherified-AF/PP** YM= 900 MPa TS=32 MPa	Aerospace and packaging

PP, WS, CS (Suhara Panthapulakkal & Sain, 2006)		Fungal treatment of WS	Compounding	**PP-1(Brabender)** TS=32 MPa FS=50 MPa TM= 1.1GPa FM=1.2 GPa	**PP-1+wheat straw fibers (Brabender)** TS=40 MPa FS=76 MPa TM= 3 GPa FM=3.3 GPa	**PP-2 (K-mixer)** TS= 30 MPa FS= 42 MPa TM= 1 GPa FM = 1.1 GPa	**PP-2+wheat straw fibers (K-mixer)** TS= 38 MPa FS= 58 MPa TM= 2.1 GPa FM =2.1 GPa	Automotive, construction and packaging

2.1.7 Response surface methodology study for optimization of inherent properties for packaging film

2.1.7.1 Response surface methodology

To optimize the parameters for achieving benchmark characteristics of packaging film, a large number of experimental tests are normally conducted. Moreover, to carry out such experiments, one condition needs to be optimized while fixing other required conditions constant. Thus, the traditional methods may not be able to provide collective enhancement of all essential factors. Moreover, they are time consuming and cost-intensive. Response surface methodology, an empirical design-based technique eliminates all limitations created by the usually adopted traditional methods and provides collective optimization of all key factors by simultaneously applying both the mathematical and statistical techniques. So, this technique is capable to optimize key factors when complex interactive behaviour of process factors exists in the system. In order to meet simultaneously optimize operating conditions, RSM proves out to be the best method for demonstrating the desirable conditions of the system.

RSM is an elegant way to predict a response as precisely as possible within the experimental zone where no experiments are carried out. Moreover, RSM is also reliable in terms of time and cost with high accuracy and proves its suitability by providing the adequacy between predicted output response and actual output response. These inherent characteristics of RSM technique encourage many researchers to employ this reliable model for the optimization of required properties according to industrial applications. Generally, two types of experimental designs are frequently used for the optimization of the process viz. Box-Behnken design and Central composite design.

2.1.7.2 Box-Behnken Design

Box-Behnken Design- Response surface methodology (BBD-RSM) is commonly used for the optimization of the system which is not working on a fractional factorial design. BBD provides lesser selected experimental runs in order to provide the surface response as compared to other response designs with simple factorial strategy. Thus, BBD is less expensive as compared to others for equivalent process factors. In this BBD, all points exist at the midpoint of the edge as well as center and need three levels for each factor. But there is no point that exists at the vertices of cube and this proves its unsuitability for consecutive experiments. Many types of research have been done using the Box-Behnken Design method.

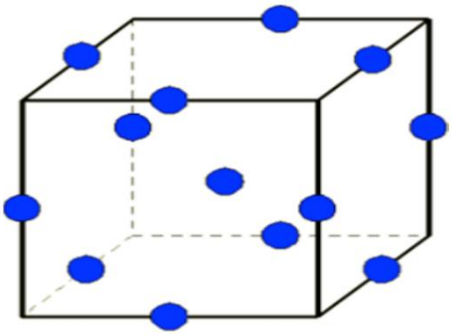

Figure 2.1 Generation of Box- Behnken Design (Ait-Amir, Pougnet, & El Hami, 2015).

Giteru et al., 2019 optimized polyvinyl alcohol/zein/chitosan/polyethylene glycol based edible film using BBD. In this paper, four process factors viz. ratio of zein:chitosan (w/w), polyvinyl alcohol (wt.%), polyethylene glycol (wt.%), and ethanol (v/v% in water) were examined for optimization of the output responses such as tensile strength, young modulus, elongation at break, solubility in water, optical test and water vapor permeability. Optimum film zein:chitosan (0.35:0.29)/ polyvinyl alcohol

(0.13)/polyethylene glycol (0.23)/ ethanol (60%) exhibited higher output responses and were found to be suitable for edible packaging film.

In this study, three independent variables, i.e. natural rubber (wt.%), Peroxide Luperox (phr), and coagent co-agent trimethylolpropane triacrylate (phr) were taken for the optimization of output responses such as tensile strength, impact strength and flex modulus. Optimized film at 15 wt. natural rubber, 4.2 phr luperox, 3 phr trimethylolpropane exhibited 28.1 MPa of tensile strength, 27.5 J/m of impact strength, 8679 MPa of flex modulus. These results assured the reliability of film for food packaging applications (Zhao et al., 2019).

BBD-RSM was employed to examine the impact of independent variables viz. maize starch (1-3g), agar (0.5-1 g), sorbital (0.5-1 ml), tween-80 (0.1-0.5 ml) for the optimization of edible film characteristics (water vapor permeability, thickness, solubility, oxygen permeability, moisture content, and transparency). Reported results showed the percentage contribution of sorbital and tween-80 had a remarkable impact on the properties of edible packaging film (Maran et al., 2013).

2.1.7.3 Central composite design

For a remarkable estimation of higher-order factors, central composite design- response surface methodology (CCD-RSM) optimizes the system with fractional factorial experiments. CCD-RSM design uses center points with axial points for fractional factorial experiments. Axial points help to evaluate extreme minimum and maximum values for every process factors in the experimental design. These characteristics increase RSM design flexibility and permit the designer to exactly know the impact of process factors on output while going beyond the levels of factors. The total number of experimental runs is calculated using the following equation:

$$N = 2^n + 2n + n_c \qquad (1)$$

where n is the number of independent variables, (n_c) is the number of replicates at central points and N is the total number of runs.

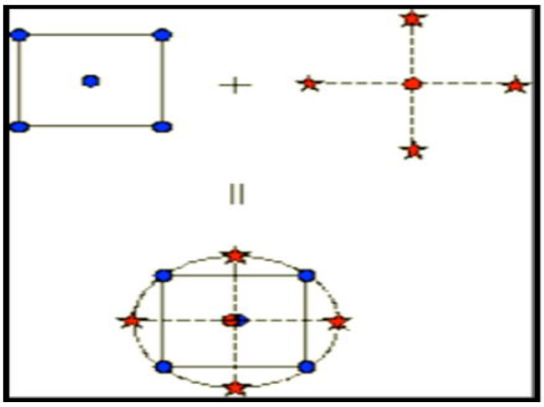

Figure 2.2 Generation of Central composite design (Ait-Amir et al., 2015).

Jancy et al., 2019 prepared PVA/ cellulose nanoparticles/feneel seed essential oil bio nanocomposite film and optimized the packaging film properties using response surface methodology. In this study, PVA, cellulose nanoparticles and essential oil were used as independent variables. Moreover, elongation at break, tensile strength, antioxidant activity and antimicrobial activity were used as responses for food packaging applications. The optimized compositions of independent variables such as 7% PVA, 5% cellulose nanoparticles, and 0.6ml/100ml essential oil provided 11.49 MPa tensile strength, 118.21% elongation limit, 42.81% antioxidant activity and 4.78 mm antimicrobial activity. These results suggested bio-composite film suitability for packaging applications.

Azarifar et al., 2019 demonstrated the influence of process factors viz. carboxymethyl cellulose (4-16%), chitin nanofiber (2-5 wt.%), ajowan (0.2-1 v/v%) on output responses (tensile strength, elongation at break, water vapor permeability, yellowness index) for optimization of active edible film using CCD-RSM technique. The optimized values of process factors such as carboxymethyl cellulose, chitin nanofiber, ajowan were 15.83 wt.%, 3 wt.%, 0.75 v/v%, respectively provided the benchmark output responses for active edible film applications.

Mustapha et al., 2019 investigated the microbial activity and biodegradability of Aspergillus niger/ turmeric oil film for paper packaging application using CCD-RSM method. In this study, the authors examined the effect of two independent variables namely the volume of turmeric oil and thickness of film on output responses. This study revealed that the turmeric oil inhibited the microorganism growth in the film preserving the shelf life of food.

Fakhri et al., 2018 synthesized nano clay incorporated polystyrene/zinc oxide composite film for food packaging application. In this study, CCD-RSM technique was applied to observe the effect of independent variables i.e. zinc oxide (0-2 wt.%), nano clay (0-7.01 wt.%) on mechanical and colour characteristics of packaging film. The values of independent variables (zinc oxide, nano clay) for synthesizing optimized film provided by CCD-RSM were 0.81 wt.% and 0.57 wt.%, respectively with 0.805 desirability assuring successful application of film for packaging application.

CCD-RSM technique was employed to examine the physical-mechanical properties of recycled polyethylene/polyethylene terephthalate film and observed the impact of maleic anhydride and glycidyl methacrylate compatibilizers on impact strength, elongation limit and yield strength of the packaging film. As an outcome of this study, it can be concluded that the compatibilizers have a significant effect on the physical-mechanical properties of recycled polyethylene/polyethylene terephthalate film for packaging applications (Uehara et al., 2015).

Espitia et al., 2014 optimized antimicrobial property of thyme essential oil incorporated apple skin polyphenols composite film using CCD-RSM technique. Optimal independent factors value i.e. 6.07% apple skin polyphenols and 3.1% thyme essential oil in composite showed excellent antimicrobial characteristics for potential food preservation applications.

Campos-Requena et al., 2014 used CCD-RSM technique for optimization of packaging film properties of montmorillonite incorporated polyethylene composite film. In this study, influence of four independent variables (clay concentration (wt.%), compatibilizer concentration wt.%), mixing temperature (^{O}C) and mixing time (min) on six packaging film properties viz. interlayer distance, decomposition temperature, melting temperature, young’s modulus, loss modulus and storage modulus was investigated. Response surface graphs helped to establish an optimum combination of independent variables in order to obtain the desired properties of film for packaging applications.

CCD-RSM was applied to elucidate the impacts of the concentrations of Na Montmorillonite and glycerol on output responses such as thickness, luminance, contact angle, tensile strength, elongation at break and transparency of starch based packaging film. Results encouraged increasing the use of clay with minimum plasticizer in composite preparation for obtaining a higher mechanically stable packaging film with least transparency (Heydari et al., 2013).

Table 2.4 Literature review for reinforcing agent in polymer matrix for packaging application using RSM.

Raw materials (Reference)	Design	Process factors	Output responses	Applications
PVA, EO (Fennel seed), Jack fruit (Jancy et al., 2020)	CCD-RSM	PVA (wt.%) Jack fruit (wt.%) EO (wt.%)	TS EAB Free radical scavenging Antimicrobial activity	Packaging
Zn, Cs, PVA, PEG (Giteru et al., 2019)	BBD-RSM	Zn:Cs(W/W) PVA(Wt.%) PEG (Wt.%) Ethanol (V/V% In Water)	TS YM EAB Solubility In Water Optical Test Water Vapor Permeability	Packaging
Natural Rubber, Peroxide Luperox, Trimethylolpropane Triacrylate (Zhao et al., 2019)	BBD-RSM	Natural Rubber (Wt.%) Peroxide Luperox (Phr) Coagent Trimethylolpropane Triacrylate (Phr)	TS IS FM	Packaging
Maize Starch ,Agar ,Sorbital, Tween-80 (Maran et al., 2013)	BBD-RSM	Maize Starch (G) Agar(G) Sorbital (Ml) Tween-80 (Ml)	WVP Thickness Solubility, Oxygen Permeability Moisture Content Transparency	Packaging
Carboxymethyl Cellulose , Chitin Nanofiber, Ajowan (Azarifar, Ghanbarzadeh, Khiabani, et al., 2019)	CCD-RSM	Carboxymethyl Cellulose (Wt.%) Chitin Nanofiber(Wt.%) Ajowan (V/V%)	TS EAB WVP Yellowness Index	Packaging
PE, Polyethylene Tere phthalate Film, Maleic Anhydride, Glycidyl Methacrylate (Uehara et al., 2015)	CCD-RSM	Polyethylene Terephthalate(%) Maleic Anhydride (Wt.%) Glycidyl Methacrylate (Wt.%)	IS EAB YS	Packaging
Apple Skin Polyphenols, Thyme Essential Oil (Espitia et al., 2014)	CCD-RSM	Apple Skin Polyphenols (%) Thyme Essential Oil (%)	EAB Elongation At Yield (%)	Packaging

Polyethylene, Montmorillonite (Campos-Requena et al., 2014)	CCD-RSM	Clay Concentration (Wt.%) Compatibilizer Concentration (Wt.%) Mixing Temperature (℃) Mixing Time (Min)	Interlayer Distance Decomposition Temperature Melting Temperature YM LS SM	Packaging
Corn Starch, Na-Montmorillonite and Glycerol (Heydari et al., 2013)	CCD-RSM	Na-Montmorillonite Glycerol	Thickness Luminance Contact Angle TS EAB Transparency	Packaging

2.2 Objectives

The detailed literature review shows that non-biodegradable polyethylene and polypropylene are frequent polymers commonly used for packaging applications. Thus, there is imperative scope to reduce polymer contributions towards packaging film applications worldwide. In order to produce valuable green packaging film based on abundantly available agro-waste, some pre-treatment techniques especially alkali treatment is necessary to make agro-waste suitable for polymer adhesion. Thus, a detailed study on the synthesis of polyethylene/polypropylene/alkali treated-agro-waste is necessary to produce green packaging film. In order to meet the requirements, the thesis has the following objectives:

- To observe the effect of alkali treatment of agro-waste for enhancing the suitability of agro-waste for polymer adhesion
- To optimize the process parameters (wt. of polyethylene, wt. of polypropylene, wt. of alkali treated-agro-waste) for composite packaging film based on polyethylene, polypropylene and treated-agro-waste
- To compare the properties of alkali treated-agro-waste based packaging film with native agro-waste based film, pure polymeric film and real packaging films at optimum conditions of process parameters