Influence of Carboxylic Acids on Mechanical Properties of Thermoplastic Starch by Spray Drying

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Dedicated to my ***beloved parents***

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Abstract

The influence of carboxylic acids on the mechanical properties of TPS produced by spray drying have been investigated. Both malic acid and citric acid (polycarboxylic acids) were used as plasticizer. Starch was spray-dried from solution to prepare amorphous TPS dog bones by compression molding.

X-ray Diffraction (XRD) results showed that all the freshly solution spray dried TPS powder and dog-bones samples were amorphous irrespective of the amount of plasticizer added. Scanning Electron Microscope (SEM) was used to examine the morphology of solution spray dried TPS powder. No noticeable difference was observed on the morphology between the samples. Particles were spherical and homogenous surface was observed. The FT-IR analysis indicated the interaction of plasticizers with starch chains by hydrogen bonding. In TGA analysis, apart from moisture loss at 100^{o}C, samples were thermally stable up to 170^{o}C temperature. Tensile testing showed that Malic Acid plasticized samples exhibited a more elastic behavior as compared to Citric Acid plasticized samples. Whereas, the quantity of the plasticizers and tensile strength of TPS dog-bones was inversely proportional to each other.

Keywords: Biodegradable; Thermoplastic Starch; Biopolymers; Plasticizer

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Abbreviations

ATR	Attenuated Total Reflection
CA	Citric Acid
CAPS	Citric Acid Plasticized Starch
DS	Degree of Substitution
DTGA	Differential Thermal Gravimetric Analysis
EP	Extra Pure
FTIR	Fourier Transform Infrared Spectroscopy
GS	Glutinous Starch
HLB	Hydrophilic-Lipophilic Balance
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	Malic Acid
MAPS	Malic Acid Plasticized Starch
OSA	2-(2'-Octenyl) Succinic Acid
PCL	Poly ε-Caprolactone
PE	Polyethylene
PEA	Poly-Esteramide
PGS	Pregelatinized Glutinous Starch
PHA	Poly(β-Hydroxyalkonoates)
PLA	Poly-Lactic Acid
PP	Polypropylene

PS	Polystyrene
PVA	Polyvinyl Alcohol
PVOH	Polyvinyl Alcohol
PUR	Polyurethane
RH	Relative Humidity
RPM	Rotations Per Minute
SEM	Scanning Electron Microscopy
Tg	Glass Transition Temperature
TGA	Thermo-Gravimetric Analysis
TPS	Thermoplastic Starch
XRD	X-ray Diffraction

Chapter 1 - Introduction

In recent years, research has been focused on bio-degradable materials to replace petroleum based plastics in a cost effective manner [1]. Starch is a renewable, cheap and abundantly available biopolymer [2]. The inter-molecular forces and hydrogen bonds in starch resist it to be processed as a thermoplastic material. Hence, a plasticizer in addition with water is required to have a deformable thermoplastic material called Thermoplastic Starches (TPS). Plasticizer lowers the Glass Transition Temperature (Tg) of TPS, enhances its flexibility and stability to process below decomposition temperature [3].

TPS are very promising among the bio-based materials available for the production of biodegradable plastic. TPS have some limitations to be used for commercial applications i.e. bad mechanical properties and water sensitivity [4]. Starch absorbs water under higher relative humidity. TPS have been processed through extrusion [5], casting [6], injection molding [7], compression molding [8], blow molding [9] but its hygroscopic and hydrophilic nature has caused problems [10].

Different plasticizers had been used to overcome this problem e.g. glycerol, sorbitol, urea, formamide, glycerol etc. [11-13]. Biodegradation must be enhanced in the field of plastic packaging to achieve greener environment. Already performed methods must be applied in more cost effective manner by innovative strategies.

This chapter gives a general overview on the properties of starch, carboxylic acid as plasticizers and the applications of starch with emphasis on thermoplastic starch (TPS). Starch is processed as thermoplastic polymer by the use of plasticizers. Starch can also be formulated with other polymers. This chapter highlights the techniques to produce TPS and also introduces “spray-drying” as a process to generate the dry plasticized starch.

1.1 Starch

Starch is a natural polymer based on glucose that usually is a potential candidate for the biodegradable polymer in future. The extraction of starch is done from various plant tissues in the granular form having the size range of 1-100 microns [14] whereas the size and shape of granules are dependent on their sources [15]. The granules are found in chloroplast of green leaves. It is also found in the amyloplasts of storage organs like tuber or seed. These granules do not dissolve in cold water but if the outer membrane is broken then swelling takes place and they form a gel. On the other hand, if the water is warm, the diffusion of soluble part of starch from the wall of granule takes place and remaining granules swell and burst [16].

Starch plays an important role in human nutrition. The nutritional value of starch mainly depends on the physical structure, composition, and processing [15]. Common sources for starches are potato, cassava, and corn. It is a very useful, cost effective and natural polymer. Moreover, its physical and chemical properties can be enhanced by chemical and enzymatic modification [17]. Hence, starch gets much attention in food research and used as thickening agent in sauces, desserts, custards, and as a sweetener in drinks or confectionery. Besides, starch also plays an important role in the non-food applications. It is used in the paper or board sizing, as an adhesive in paper, textiles and packaging industries [4].

1.1.1 Properties of Starch

Starch primarily contains two polysaccharides that are amylose and amylopectin whereas ratios of both of them vary and is dependent on the starch source. In the starch granules, lipids and proteins are also found in a small quantity [18].

Amylose is a linear chain of D-glucose units connected by α-1,-4 bonds. The amylose chain length varies with each source or plant species. Its range generally lies between 10^2 to 10^4 glucose units. Amylopectin has shorter chains of α-1, 4 linked D-glucose units which are branched by α-1, 6 binds. Its chain length ranges between 10^4 - 10^5 glucose units [19].

The relative percentages of amylose and amylopectin in cereal endosperm starches usually lie between 18 to 28% of amylose and 72 to 82% of amylopectin. Whereas, this range differs in some mutant genotype maize, rice, and barley i.e. 70% of amylose [20].

Starch does not dissolve in cold water but it binds water because of its hygroscopic nature. The hydrogen bonding inside the starch granules vanishes when it is subjected to warm water. Granular swelling and gelatinization takes place [21].

Physically, most of the native starches having the crystallinity range of 20 – 40% come under the category of semi-crystalline. The amorphous part of the starch consists of amylose and branching points of amylopectin. Fundamental crystalline parts of granular starch are the short branched chains [10].

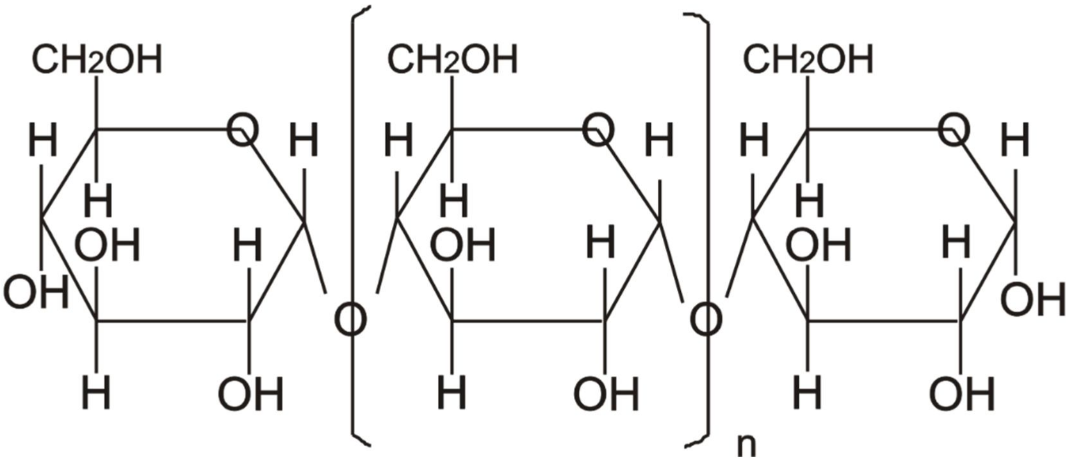


Figure 1.1 Chemical Structure of Starch

1.2 Thermoplastic Starch (TPS)

Native starch is not suitable for numerous applications because of its brittleness and hydrophilic behavior. Additionally, thermal process-ability is poor as the melting point of starch is greater than thermal decomposition temperature [22]. It can be transformed into a thermoplastic material by adding plasticizers such as water, sorbitol, glycol, glycerol etc. in combination with temperature and shear. In past few years, ample attention has been shown towards biodegradable plastic stuffs like shopping bags, trash bags, planting pots and dinner utensils [23]. In thermal processing of starch-based polymers, multiple chemical and physical reactions are involved such as water diffusion [24], granule expansion [18], gelatinization [25], decomposition [26], melting [24], and crystallization [27].

1.2.1 Thermoplastic Starch/Polymer Blends

Because of the rapid rise in the oil prices and other environmental concerns, biodegradable polymers became the center of attention in the research and development [28]. The basic idea of the research was to produce a plastic from renewable and biodegradable resources that must meet the market needs. As the pure starch is brittle and have bad mechanical characteristics, hence, it is blended with synthetic polymers [18].

Blending plays a key role in the modification of polymers properties. It does not need any special equipment or technique and is economical as well [29]. A compatible blend is obtained when two or more polymers are mixed together and the preferred properties are improved. The basic function of TPS blending is to enhance the water resistant and mechanical properties. TPS blends are hydrophilic in nature and water is used as a plasticizer [18].

Starch is either continuous or dispersed phase in TPS blends. It depends on starch/second-polymer ratio and on processing parameters. Blend properties are analyzed by the interfacial interactions between starch and the other components [10, 30].

1.2.2 Blends with biodegradable polymers

Blends have been produced with biodegradable polymers in order to produce biodegradable starch-based composites. Usually, starch is blended with components like polyvinyl alcohol (PVA), aliphatic polyesters and biopolymers. Most commonly used polyesters are poly(β-hydroxyalkonoates) (PHA), poly(ε-caprolactone) and poly-lactide (PLA). Completely biodegradable products are obtained by these blends that are cost effective as well [29].

1.3 Classification of Plasticizer

In polymer industries, plasticizers can be termed as internal or external. The internal plasticizers are the inherent phase of polymer molecules and are the product part that reacts with original polymer and is co-polymerized into a polymer structure [31]. Internal plasticizer has usually a bulky structure, so it provides enough room to move fluently to stop polymer from coming close together. That is why, polymers become soft when the glass transition temperature (Tg) is decreased. This results in the decrease in elastic modulus as well [32].

External plasticizers are added to the polymers and are considered as a low volatile substance [33]. Plasticizer molecules and polymer chains do interact with each other but they are not bonded chemically by primary bonds, so may easily lost by evaporation, extraction or migration [10].

The classification of plasticizers may also be done as primary and secondary [34]. In primary plasticizers, polymer is soluble at high concentration. Polymer is gelled by the plasticizer at a rapid rate and does not exude from plasticized material. Whereas, in secondary plasticizers, compatibility with polymers in quite limited and they have less gelation capacity as well. Hence, they are blended with the primary plasticizers so that the properties of the product can be enhanced and cost can be reduced [35].

1.3.1 Plasticizers for TPS Blends

As decomposition temperature of starch is greater than its melting point, hence a plasticizer or gelatinization agent is required to do thermally processing of starch-based blends [36]. In thermal processing, various plasticizers and additives were used for starch gelatinization. The processing conditions or the thermal/mechanical characteristics of final material are found by the quantity and class of plasticizers being used [4]. Most commonly used plasticizer during thermal processing is water. But the mechanical properties of TPS containing only water are poor. As a result, retrogradation occurs rapidly and practical applications become limited [25].

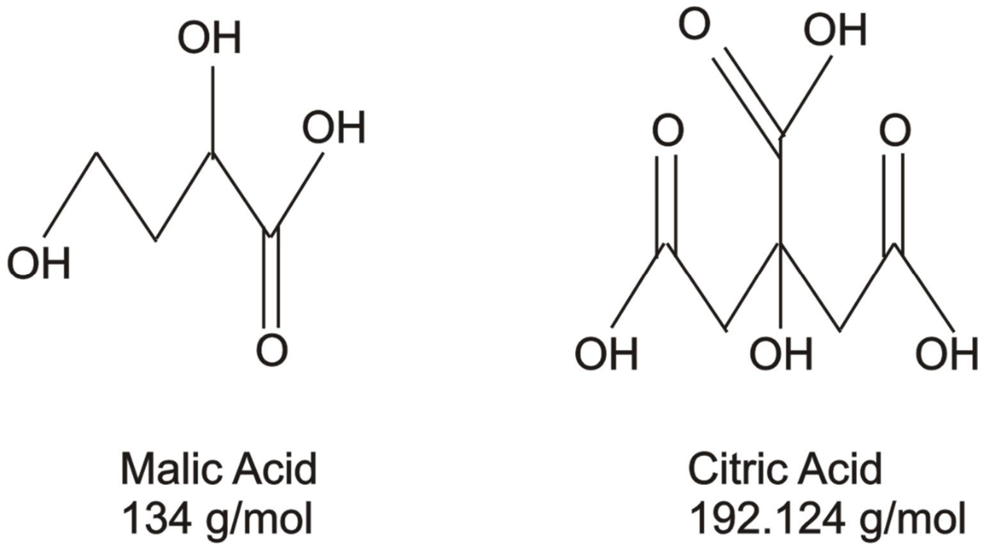
In order to improve such issues, several other plasticizers were evaluated such as urea [37], glycerol [38], sorbitol [13], formamide [39], amino acids [40], citric acid [41], and glycol [42]. Among these plasticizers, glycerol is the one that is used most commonly because of high boiling point, abundantly available and economical [43]. The interaction of plasticizers and starch is very specific. Plasticizers interact with starch chains by hydrogen bonding in a wide range of temperature. As the temperature goes higher, interactions increases due to the formation of hydrogen bonds. The material acts just like a rubber as its mobility rises and viscosity decreases [44]. The ability to form hydrogen bond between starch and plasticizers molecules rises in order of: urea > fomamide > acetamide > polyol [11]. Carboxylic acids have also been used to resist the retrogradation of starch. Ability to decrease viscosity and to improve mechanical characteristics of TPS has made carboxylic acids a better option as plasticizers for TPS [45].

1.4 Carboxylic Acids – Citric Acid and Malic Acid

The chemical modification of starch is a very broad field involving various reactions and products [46]. Usually these modifications are performed in aqueous media where starch swells. TPS has got much attention in the past decade as it is both renewable and biodegradable. But the main issue is its water sensitivity i.e. hydrophilic nature [47]. TPS can be processed with several processes such as extrusion, blow molding, injection molding, compression molding, and spray drying. In order to increase the fluidity of molten TPS, carboxylic acids are also being used to decrease the viscosity of TPS by controlling the starch macromolecules [48].

Citric acid (CA) is used in the modification of TPS during melt processing. The addition of CA to renewable materials is the focus in recent research. CA is a natural polycarboxylic acid found in fruits like lemon and lime. It acts as a plasticizer and inhibits the recrystallization of starch [48]. It can enhance both mechanical and barrier properties of the blends dramatically. Due to its biodegradable and renewable nature, it is included in several food products like jams and soft drinks. CA cross-links with polysaccharide like starch granules [49], starch nanoparticles [50], TPS [51], chitosan [52] and hydroxypropyl cellulose [53].

Malic acid (MA) is also a naturally occurring substance present in fruits and plants. It is referred as apple acid because apple is its richest source. It is usually blended with several food acids, sweeteners, flavors, and sugars to make a unique tastes in food and beverages. MA is being used as a plasticizer in biodegradable food packaging films [44]. Usually MA is a tough anti-retrogradation agent because it resists starch recrystallization and enhance esterification. Strong hydrogen bonding, cross-linking and grafting has been found between malic acid and starch [54]. MA controls the swelling of products based on starch. Moreover, malic acid plasticized films are highly flexible as well [10].



Malic Acid
134 g/mol

Citric Acid
192.124 g/mol

Figure 1.2 Chemical Structure of plasticizers used in preparation of TPS

1.5 Importance

Plastics have a wide range of applications; hence, their usage is increasing rapidly [55]. It has long shelf life properties and allows resistance to chemical or enzymatic reactions. But it cannot be degraded by natural phenomena. It takes hundreds of years to degrade a few grams of plastic naturally. So it is generating environmental problems by staying as waste [56].

Polyethylene bags are being used very commonly along with trash bags, bubble or candy wrappers, clear plastics, styrofoam cups, zip lock bags etc. All these are damaging the environmental health. Burning and burying are the two very common methods used for the treatment of waste but both of these are not suitable for the destruction of plastic. Burying does not destroy the plastic because it is non-biodegradable and burning emits toxic gases in the atmosphere [57].

Food packaging is gaining much importance as the awareness on sustainability has increased [58]. Sustainability can be achieved on various levels. For the level of raw materials, both the emission of carbon dioxide and the dependency on fossil resources can be minimized by the use of recycled and renewable resources. On the level of production, efficient (energy efficiencies, cost efficiencies) adjustments can be made [59]. Water management can be another level [60]. After all these levels, the next need is to reuse or recycle the used material. One of the options is to use biodegradable materials. It can contribute to minimize the municipal waste issues [61]. The biodegradable packaging will not only make the environment healthier but also will be economical [62]. Hence the production of biodegradable packaging is very important to keep the atmosphere clean and make the environment greener.

The basic functions of packaging and their applications are summarized in Table 1.1.

Table 1.1 Functions of packaging materials

Function	Applications	Example	Reference
Protection	Impact resistant packaging	Egg packs/boxes	[63]
Increase in product life	Different barriers, Making the atmosphere inert, Reduction in handling	Containing food items in a very protective atmosphere.	[8]
Tamper – evidence	Sealing the containers	Metal can lids - removable	[63, 64]
Handling of product	Containers, Small items packed in clusters.	Box, Bottle, Bag, Tray	[63, 65, 66]
Advertisement or information	Written statements/pictures	Labels, Printing	[63, 65, 67]
Barrier	Avoiding contact of environment or atmosphere with the product	Packaging in multi-layer form	[63, 65]

1.6 Techniques

Several techniques are used to produce bio-plastics from starch. The commonly used techniques are extrusion [5], casting [6], compression molding [8], spray drying [68] and injection molding [7]. The processing of starch is not easy to control as of conventional polymers. The reason behind this is the unsatisfactory properties of starch such as high viscosity, phase transitions, retrogradation, water evaporation, etc.

These issues can be tackled by adopting proper formulation and suitable processing conditions.

Typical techniques used for TPS modifications are as follows:

1.6.1 Extrusion

It is the most commonly applied technique to produce starch-based materials. Extrusion involves several steps; mixing, kneading, shearing, heating, cooling, shaping, and forming [69]. Material is made into a semi-solid mass by compression and it is then passed from an opening. Extrusion has a residence time of 10 to 60 seconds approximately, whereas, the temperature can reach up to 200^{o}C. It is used as a chemical reactor when used for starch modification [5].

Extrusion is being used in a wide range of processing parameters; it can deal with the high viscosity polymers in the deficiency of solvents. It allows to control the residence time and also offers the function of multiple-injection [70]. Extrusion of starch is also being used in the food industries for the last few decades and has got much consideration to produce biodegradable TPS [71].

1.6.2 Film Casting

Film casting involves four fundamental stages i.e. preparation of solution, gelatinization, casting and drying [72]. It is widely used in starch processes [18]. Starch with plasticizer are mixed in water and passed to Brabender viscograph cup where the solution is heated to 95^{o}C [10]. Blending of mixture is performed for about 10 minutes. By using the plasticizer, the processing of starch becomes easier and mechanical strength of TPS films are enhanced. Most widely used plasticizers are sorbitol and glycerol as they form more flexible films [73]. Other plasticizers like glucose, sugar, sucrose, xylose, urea, fructose etc. are also being investigated [12, 13, 37, 73]. The plasticized films have generally lower strength, hence, blending with other materials is done to sort out this problem. Commonly used blends are soluble starch and cellulose acetate [74].

1.6.3 Compression Molding

Starch-based products are being manufactured by compression molding as well [42]. Usually manufacturing of foamed containers are investigated by this technique. Three basic stages are involved in compression molding; gelatinization, expanding, and drying [18]. The two important stages of compression molding are gelatinization and ejection of product from the mold. Several gelatinization and mold agents are used in order to protect starch from sticking with the mold. Most commonly used agents are magnesium stearate and stearic acid [75].

1.6.4 Injection Molding

It is being widely used for the manufacturing of plastic parts [76]. In this technique, the required product is achieved by applying pressure to the molten polymers and passing it through an evacuated cavity. It is a cyclic process consisting of four fundamental processing steps; filling, packing, cooling, and ejection [7].

In injection molding, firstly, hot polymer melt is fed into a mold cavity. This step is known as filling step. Then the packing of the molten polymer into the cavity takes place to control the shrinkage caused due to solidification of polymer. This step is called post filling step. After that, cooling step starts where mold is cooled till it becomes rigid. Last step is ejection in which mold is opened to eject the part out of it [77].

1.6.5 Spray Drying

It is fast drying method that generates amorphous and semi-amorphous particulates from the droplets of liquid solution [68]. Pre-gelatinized starch is created by spray drying with no loss of granular integrity. This process is usually used in pharmaceutical and food industries. Various properties can be enhanced by spray drying like size and morphology of particle, solvent residual amount, crystallinity etc. [78]. It provides the control of the particle size and is characterized by high reliability and reproducibility. Feed is sprayed into the cylindrical chamber for drying. The solid particles are obtained quickly from the droplets where hot air is applied for the evaporation of the solvent. Direct contact of droplets and gas is made for both mass and heat transfer. The cooled gas is separated after drying. The spray dryers are categorized on the basis of height to diameter ratio of drying chamber, atomizer type, and air flow type [79].

TPS-based material are very sensitive to water. In the production of coating and packaging materials from TPS blends, starch recrystallization is the basic issue.

Recrystallization is simulated due to the water and it causes loss in mechanical characteristics like tensile strength or flexibility [80].

The plasticizers used are usually hydrophilic and extrusion may not be done without adding water. Hence, retrogradation is caused by the combination of plasticizers and water. It results in undesired changes in the properties of the final product [22].

Spray drying process of TPS blends from starch water dispersions and solution is under investigation for the past few years. It is believed that the problem discussed can be solved and the activity of the plasticizer during manufacturing can also be maintained by spray drying. Spray drying is considered as an interesting process to produce amorphous product [78].

Chapter 2 – Literature Study

This chapter complies the scientific work has been done on biodegradable food packaging, preparation of TPS with different plasticizers and its modifications. Literature survey, on the subject matter, is presented systematically.

2.1 Modification of Starch

The native starch has a restricted range of applications because of its unfavorable characteristics such as retrogradation, uncontrolled or high viscosity, brittleness, and cold water insolubility [4]. Hence native starch is modified both chemically and physically in order to improve such characteristics [17]. Following are the methods used for the modification of native starch.

2.1.1 Cross-Linking

The most important modification in the starch industry is cross-linking. The stronger covalent bonds take the place of weaker hydrogen bonding of starch chains [81]. Mostly, glucose units of starch consist of two secondary and one primary hydroxyl group that reacts certainly with numerous compounds like acid anhydrides, ethylenic, oraganic chloro, and epoxy compounds [82]. As the cross-linking is more permanent in nature, thus a few of it can generate positive effects. When the number of cross-links increases, it become more resistant to gelatinization. The cross-linked starch derivatives are more soluble in water and are highly stable as well [83]. These are used in numerous sectors like paper, textiles, food, and adhesive industry.

Lim *et al.* [84] enhanced the thermal stability and barrier characteristics of pure polyvinyl alcohol (PVA) by preparing five different cross-linked polyvinyl alcohol/boric acid (PVA/BA) hybrid films from a solution blending method. Barrier properties, transparency, thermal stability, and mechanical properties were investigated as a function of BA content. It was noticed that the physical properties of PVA/BA hybrid films were dependent on the chemical structure and morphology of the films originating from the amount of BA and change in degree of cross-linking. By increasing BA content, PVA crystallites size and amount were decreased, but the cross-linking density was increased, showing compact packing of molecules.

Moreover, by increasing BA content, glass transition temperature and thermal stability were also enhanced and the oxygen transmission rate (OTR) of pure PVA was decreased. In addition, water resistant pressure and tensile strength were also increased by increasing BA content. Each hybrid film showed good transparency. These properties of the cross-linked PVA/BA hybrid films showed that they are the potential candidates for packaging materials.

Tripathi *et al.* [85] prepared an antimicrobial film by blending chitosan (CS) and polyvinyl alcohol (PVA) with a cross-linker i.e. glutaraldehyde. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to investigate the miscibility and morphology of the films. The microbiological screening demonstrated the antimicrobial nature of the film against food pathogenic bacteria viz. Escherichia coli, Bacillus subtilis, and Staphylococcus aureus. The results indicated that the film may be a promising material for food packaging.

Yussof *et al.* [86] investigated the effect of cross-linking and concluded that when the cross linking is increased, the peak viscosities of pasting and susceptibility of enzyme to α-amylase and glucoamylase of starch were decreased. Moreover, Cross linking lowered the light transmittance, solubility and swelling volume of starch pastes.

2.1.2 Stabilization

The basic purpose of stabilization is to avoid recrystallization and to lift the tolerance of starch to the fluctuating temperature. It also enhances the shelf life of starch materials [87]. During stabilization, the bulky groups are substituted onto the starch to resist the linear, dispersed fragments to retrograde [29]. The number of substituted groups gives the idea about the value of stabilization. Moreover, number of substituents per hundred anhydroglucose units determines the degree of substitution (DS) [88].

Park and Goins [89] studied the covalent bonding between 2-(2'-octenyl) succinic acid (OSA) and starch. For free OSA, starch was removed from aqueous dispersion by precipitation with methanol and the acidified supernatant was extracted. Esterified OSA was hydrolyzed in an alkaline solution for total OSA. OSA after derivatization with ethereal diazomethane was quantified

The polyhydroxyl groups present in the chain make native starch hydrophilic in nature [90]. It does not has enough affinity for hydrophobic compounds but by the help of chemical modifications, the lipophilic character of starch can be improved significantly [91].

Olivier *et al.* [92] did structural and compositional investigation of thermoplastic blends prepared from native potato starch. Various amounts of allylurea were adapted to achieve possible radiochemical routes for the preparation of physically stable materials. The physical stabilization of starch blends were studied by electron beam grafting.

Gomand *et al.* [93] annealed potato starches with different amylopectin/amylose ratios at stepwise temperature increment. By the small-angle X-ray scattering experiments, it was concluded that the lamellar starch crystals stabilize more upon annealing.

2.1.3 Esterification

In esterification, ester groups take the place of some hydroxyl groups. By doing this, the thermal stability and gelatinization temperature can be enhanced. Moreover, it is also performed to decrease retrogradation [94]. 150 years back, synthesis of starch was initiated with production of acetylated starch by acetic anhydride as an acetylating agent. Various starch esters are available like starch nitrates, starch sulfates, starch fatty acid [95], and starch alkenyl succinates [10], and starch phosphates [96]. Depending upon the degree of substitution (DS), starch acetates are found in three forms. The products of low DS are used in textile industries or as food additives [10]. The medium DS products are soluble in water whereas high DS starch acetates are inorganic solvents. Starch acetylation made possible to produce polymers with a range of hydrophobicities. Esterification makes starch more hydrophobic in comparison with the native starch [97].

Different methods are being applied in order to make starch esters. On commercial scale, water is used as a solvent. Acetic anhydride is used as a reactant and an alkaline base (like sodium acetate and sodium hydroxide) is used as a catalyst [46]. For the food and non-food applications, fatty acid starch esters are generally used. They are very useful as a substitutes for oil based polymers in the packaging industries [98].

Wang *et al.* [99] did esterification for starch modification. They studied the morphology, thermal stability, and mechanical properties of starch/natural rubber composite. The results indicated that the crystal structure of starch in the composite vanished after esterification.

Zuo *et al.* [100] investigated the dry method esterification of starch and studied its influence on degradation properties of starch/PLA composite. Results showed that degradation of esterified starch/PLA was less than that of native starch/PLA.

2.1.4 Pregelatinization

Certain starches require cooking to generate their required characteristics. Pregelatinization was developed to eliminate this cooking requirement. It is applied to native or modified starches to get a wide range of cold thickening starches [101].

In the process of spray cooking, starch slurry (through a special nozzle) enters in a heating chamber. After that atomization takes place. At the same moment, hot steam (through the same or another nozzle) is injected into the chamber in order to cook the starch. As a result, uniform gelatinized starch is formed with minimum heat and shear damage [102].

In the process of drum drying, cooked sheets of starch are produced from starch slurry. Starch is then grounded to the required particle size [103]. When drum dried flakes are grounded to required size, lower viscosities are achieved.

The solvent based methods generate starches that are cold water swellable. Pregelainized starches are basically being dealt as a thickening agent for puddings, sauces, baby foods, and pie fillings [104].

Peerapattana *et al.* [105] worked on the modification of glutinous rice starch (GS) as a sustained release agent for the tablet preparation. The modification of GS slurry was done physically by heating. It was then dried by spray drying. The pregelatinized GS (PGS) was obtained in powder form. It was found that the higher the composition ratio of PGS, slower will be the release of the drug.

Ohwoavworhua and Osinowo [106] studied the pregelatinization of starch. It was noticed that pregelatinized starch preparation takes a lot of time to dry. To overcome this problem, acetone precipitation of gelatinized starch was performed. Two important methods, cold and hot precipitations, were performed and the results indicated that acetone treated pregelatinized starch retained good powder properties.

In conclusion, it seems obvious that each modification has its own potential to enhance the properties of starch for its better use in food packaging field. By these specific modification of starch, characteristics are continuously being improved that find increasing use in wide variety of packaging applications, leading to a significant value addition. Eventually biodegradable packaging will find larger and more receptive markets in future. It can be predicted that new ventures in starch modifications and their diverse applications and effects on food packaging will continue to be of great importance.

2.2 Thermoplastic Starch/Polymer Blends

Blending is very important in modifying the specific characteristics of polymers. Two or more polymers are blended to improve the properties of a polymer system like water resistivity and mechanical behavior. Various blends are being used depending upon their effects on the desired properties.

Polyethylene is chemically resistant and is not effected by acid/base or the salt. Other characteristics of PE that has turned it widespread are electrical insulation, toughness, flexibility and low cost [107-109]. Masoomi *et al.* [110] prepared low-density polyethylene/linear low-density polyethylene/thermoplastic starch (LDPE/LLDPE/ TPS) films to obtain environmentally friendly materials consisting of high TPS content with desired packaging properties. Blending was performed in a twin-screw extruder followed by a process called blowing. Blending of LDPE/LLPDE (70/30 wt/wt) with 5 to 20 wt% of TPS and 3 wt% of PE grafted maleic anhydride was performed. SEM results showed good dispersion of TPS in PE matrices. Differential scanning calorimetry analysis indicated that starch had more pronounced effect on crystallization of LLDPE than LDPE. The desired mechanical properties of packaging applications were achieved when 15 wt% starch was added. TPS/PE blends are very much suitable for food packaging due to their high toughness and flexibility properties.

Polystyrene is available in the form of grades that vary in impact strength between brittle and very tough. They are mostly used in containers, aircraft kit, vending cups [111], syringes (disposable), light fittings and coils due to their low cost coupling and ease of processing [112]. Pimentel *et al.* [113] investigated the recycled PS blends with TPS and concluded that by adding TPS, Tg lowers. Mihai *et al.* [12] fabricated extruded foams from TPS/PS blends. Glycerol acted as a plasticizer. The results indicated that the viscosity of TPS was reduced by the addition of glycerol content, so, the viscosity ratio between TPS and PS phase increases.

The electrical and insulating properties of Poly Propylene are very impressive. It is resistant to numerous chemicals that includes dilute and concentrated acids, bases, esters, alcohols, aldehydes, ketones etc. at high temperature. Kaseem *et al.* [114] melt blended PP with TPS using a single screw extrusion process and molded using injection molding process to study the mechanical and rheological properties of TPS/PP blends. Glycerol was used as a plasticizer. The rheological properties indicated that the viscosity of TPS was reduced by increasing the glycerol content in TPS and the mechanical results indicated that strain at break of blends was less than that of PP; Young’s modulus of the blends was higher than that of PP. TPS/PP have high crystallinity that helps to enhance its tensile strength, hardness and stiffness that are important factors in food packaging.

Poly-lactic Acid is an aliphatic polyester that is derived from corn beets and sugar [115]. It is degraded to non-toxic compounds in landfills. Mihai *et al.* [12] worked on TPS/PLA blends and made the comparison between the effect of two plasticizers i.e. glycerol and sorbitol. The granules of starch were plasticized by glycerol, sorbitol and with the mixture of both. It was noticed that sorbitol plasticized blends have higher modulus and tensile strength as compared with the other plasticized blends. Due to its low price and availability as compared to other biopolymers, PLA is widely used in food packaging. The resulting TPS/PLA film material offers very good moisture barrier properties. In addition, it can withstand the rigors of injection molding and vacuum- or blow-forming processes. PLA is currently being utilized in the generation of loose-fill packaging, food packaging, and in disposable food service tableware items as well.

The chain structure of Polyvinyl Alcohol is atactic. OH group is small in size that lets it fit in the crystal lattice. Polyvinyl alcohol is being used in paper, textile treatments [116] and wet-strength adhesives [117]. Zhou *et al.* [118] studied the effect of complex plasticizer (mixture of urea and glycerol) on the starch/polyvinyl alcohol blends. The work showed that the complex plasticizer formed stronger hydrogen bonds with water and starch/polyvinyl alcohol molecules than the single plasticizer. Moreover, the hydrogen bonding was more stable as well when compared to that of single plasticizer. So the blends prepared with complex plasticizers had better mechanical properties. When PVOH was blended with TPS, the development of surface cracks are prevented because both polymers are polar substances consisting of hydroxyl groups in their chemical structure, these polar hydroxyl groups tend to build intermolecular and intramolecular hydrogen bonds that enhance the compatibility between TPS and PVOH in the blends. The improved mechanical characteristics and compatibility play a vital role in building strength in food packaging films.

Poly ε-Caprolactone is linear polyester derived by polymerization of lactone (seven membered). It is a biodegradable and non-toxic polymer. PCL is used in controlled release applications such as in long term drug delivery [119]. Averous *et al.* [120] worked on Thermoplastic Starch/Poly ε-Caprolactone blends by using two techniques i.e. extrusion and injection molding. Glycerol was used as plasticizer. Thermal, hydrophobic, and mechanical properties were studied. By the presence of Poly ε-Caprolactone, hydrophobicity was enhanced. Elongation at break for all TPS/PCL blends reduced inversely with Poly ε-Caprolactone content because of the phase separation and non-miscibility between these two.

Polyesteramide is a thermoplastic that has good biodegradability and technical performance [121]. Averous *et al.* [120] worked on the Thermoplastic Starch/Polyesteramide blends prepared by extrusion. After pelletization, granules were injection molded to make test specimens. The results indicated that the weaknesses of pure TPS i.e. low mechanical strength, shrinkage, and sensitivity of moisture were overcome by adding polyesteramide. A wide range of mechanical behavior was obtained by the several combinations between Thermoplastic Starch formulations and Polyesteramide. This type of blend is an interesting approach to generate cheaper biodegradable material.

2.3 Importance of biodegradable packaging materials

Over the past several years, there are many bio-based materials which have gathered attentions in food packaging because of their specific innovative functions.

Biodegradable packaging plays a vital role in the packaging industry because of increasing awareness of consumers and importance of using environmental friendly, biodegradable packaging materials instead of non-biodegradable ones [122]. At the moment, starch based polymers, PLA, and PHA are dominating the biodegradable packaging market and will be growing at a healthy rate in the next five to ten years [123].

Biodegradable packaging takes much less time to break down after being discarded. It gets absorbed in the earth, and there will no longer be tons of plastic dominating our landfills. It is made from a completely renewable resource that includes trees, plants, grass, and all organic materials that decompose. Biodegradable packaging materials need less than half the energy to produce than their non-biodegradable counterparts [124]. Consumers are demanding for better features and convenience in packaging products. Besides new biodegradable packaging material development, increasing awareness of environmental issues, and the adoption of new regulatory requirements are going to be the key growth drivers for the future biodegradable packaging business.

Chapter 3 – Aim of Project

The production of packaging materials based on biodegradable materials has gained much attention in the last few years. Starch has become the most promising option among the tested classes of synthetic and natural materials because it is found abundantly in various renewable resources [125]. Starch was plasticized with water in combination of other plasticizers of low molecular weight that can be interacted with backbone of starch by hydrogen bonding resulting in thermoplastic starch (TPS) [18].

The basic issue of using TPS to produce packaging materials is starch retrogradation that ends in the loss of mechanical characteristics like tensile strengths and brittleness [80]. Numerous studies have been under observation regarding interaction of plasticizers and starch, and on finding out the way to reduce or delay retrogradation. Retrogradation occurs due to the combination of water and plasticizers (by the recombination of amylose and amylopectin) [126].

CA and MA are used in the modification of TPS during melt processing. They are natural polycarboxylic acids that act as a plasticizer and inhibit the recrystallization of starch [48]. Both can enhance mechanical and barrier properties of the blends significantly [45]. Strong hydrogen bonding, cross-linking and grafting has been found between carboxylic acid and starch [54]. MA controls the swelling of starch products and can produce are highly flexible packaging films as well [10].

Various techniques are being used in order to produce bioplastic from starch. The most commonly used plastic manufacturing techniques are: extrusion, casting, compression molding, and injection molding. Each mentioned TPS system is made in presence of plasticizer-water combinations. Water and plasticizer combined together cause retrogradation that results in changing in the properties of the final product. To overcome this problem, it is necessary to operate in such way that disturbing effect of water is tackled as well as the plasticizer activity should also be maintained. That is the why, spray drying of TPS blends from starch-water dispersions and solutions have been investigated. This technology is under a lot of observation nowadays and is considered as an important route to generate amorphous material [78].

In food packaging material, various properties are essential to be controlled in a desired manner. Effect of relative humidity on retrogradation and mechanical properties plays an important role in food packaging as retrogradation must be resisted in order to maintain the mechanical strength of packaging material. There must be a proper balance between strength and flexibility of a packaging material. However the low retrogradation increases the moisture absorption so various pathways should be developed to decease the effect of moisture and acquire better mechanical properties.

Objectives

1. To investigate the effect of carboxylic acid plasticizers on mechanical properties of biodegradable films.
2. To study the effect of quantity of plasticizer on mechanical properties.
3. To find new materials for biodegradable food packaging application to improve the quality with respect to environmental health.

The purpose of this work was to identify the drivers and obstacles for carboxylic acid and TPS to be processed as a food packaging material, various ratios of starch and water with carboxylic acids, i.e. Malic acid and Citric acid (as plasticizers), were studied and performed by spray drying. TPS blends were prepared by spray drying and TPS dog-bones were prepared via compression molding of spray dried powder. Malic acid and citric acid were taken as plasticizers to investigate the characteristics of TPS. Mainly, the focus was on mechanical properties of TPS dog-bones. The obtained starch powder as well as dog-bones were characterized. The equipment settings and parameters used during spray drying were constant. Moisture contents, crystallinity, morphology, thermal properties, and powder recovery were compared in terms of plasticizers and their quantities. Effect of relative humidity on retrogradation and mechanical properties were analyzed by X-ray Diffraction (XRD) and mechanical tester. Thermal properties and morphology of TPS were studied by Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy (FTIR) was also used to study the interaction of starch and additives.

Chapter 4 – Materials and Methods

In this chapter, materials and methods are discussed that are used for the production of TPS powder and dog-bones.

4.1 Materials

The materials used in this study are starch (soluble EP), malic acid (EP), and citric acid (anhydrous, 99.5 % EP). The details of materials and their suppliers are given in Table 4.1.

Table 4.1 Materials descriptions, and suppliers

Description	**Supplier**
Starch, soluble EP	Daejung Korea
Malic acid (extra pure)	Scharlau Spain
Citric acid (anhydrous, 99.5 % EP)	Daejung Korea

4.2 Sample Preparation

The preparation of aqueous solution was done using 15% (w/w) of soluble starch. Three different ratios i.e. 10%, 20%, and 30% of each carboxylic acid (malic acid and citric acid) were used as plasticizer. All of the six solutions were heated at 95^{o}C with a stirring rate of 600 RPM for 25 minutes. Samples compositions, codes, ratios, are mentioned in table 4.2.

Table 4.2 Samples' codes, compositions, and ratios used

Code	**Sample**	**Starch % (w/v)**	**Plasticizer % (w/w based on starch)**
US	Untreated Starch	-	-
SD.S	Spray Dried Starch	15	0
30MAPS	30% Malic Acid Plasticized Starch	15	30
20MAPS	20% Malic Acid Plasticized Starch	15	20
10MAPS	10% Malic Acid Plasticized Starch	15	10
30CAPS	30% Citric Acid Plasticized Starch	15	30
20CAPS	20% Citric Acid Plasticized Starch	15	20
10CAPS	10% Citric Acid Plasticized Starch	15	10

4.3 Preparation of TPS Powder

The obtained samples were fed to a spray dryer (Shanghai Sunyitech Co. Ltd, SP – 1500). The outlet temperature of the spray dryer was controlled by combination of inlet temperature, wriggle pump speed, and fan speed [127]. The fan speed was set at 60 Hz and the wriggle pump speed was 750 ml. The inlet and outlet temperature was 140^{o}C and 80^{o}C respectively. The powder was collected from sample collector and any remaining powder in cyclone was discarded.

4.4 Preparation of TPS Dog-Bones

TPS dog-bones (63.5 mm x 9.5 mm x 1.8 mm) [ASTM-D638] were obtained by compression molding of TPS powder. Progressive pressure was applied up to 10 bars after that pressure of 25 bars was applied for 5 minutes to compress the sample. The molding temperature was 140°C for all the samples. At lower temperature, no powder flow was seen but significant degradation of material was observed at temperature higher than 150°C.

4.5 Thermogravimetric and Differential Thermalgravimetric Analysis (TGA/DTGA)

Thermal properties of TPS were analyzed by TGA. Usually, it is used to ascertain specific properties of a material that exhibits either mass loss or gain because of oxidation, decomposition, or loss of volatiles such as moisture. Whereas, DTGA is a method to analyze the changes in a sample in form of endothermic or exothermic peak.

Open pan TGA was performed. 25 mg of each sample was tested. The temperature range was 25°C to 750°C with a heating rate of 25°C/min. The derivative of the weight loss curve was determined by software – Origin 8.1, yielding DTGA-curve. The decomposition temperature (T_{dec}) was determined by the method applied by Soliman *et al.* [26].

4.6 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR (PerkinElmer, Spectrum^{TM} 100) was performed to evaluate the structural changes that occurred due to solution spray drying and plasticization. Moreover, FT-IR gives the insight of the interactions of plasticizer with the starch molecules. Spectra was recorded by FT-IR spectrometer equipped with an attenuated total reflection (ATR) unit. The resolution was 4 cm^{-1} for each spectrum. All analysis were done at ambient temperature.

4.7 X-Ray Diffraction (XRD)

XRD is done to analyze the crystalline structure of a specimen by the interaction of X-Rays with the specimen at various angles on different planes. Different peaks are generated and the location of the peaks are found by applying Bragg's law with the help of Miller indices.

XRD (STOE – Germany, $\theta - \theta$) was performed for both TPS powder and dog-bones. Cu radiation with wavelength of 1.5418Á was considered to record diffractograms from 5^o 2θ to 40^o 2θ at 40 mA and 40kV. Step size was 0.02^o 2θ with a scan speed of 2 s/step. Powder was analyzed by using the sample holder.

4.8 Scanning Electron Microscopy (SEM)

A SEM is kind of electron microscope that generates images of a specimen by scanning it with a focused beam of electrons. The interaction of electrons with atoms takes place in the specimen resulting in numerous signals that are detected as they contain the information regarding specimen’s topography and composition.

The morphology of the spray dried particles was studied by the SEM micrographs. A Scanning Electron Microscope (JSM-64900) was used. Before analysis, a thin palladium/platinum conductive layer was used to cover the samples. The layer was created by sputter coater.

4.9 Moisture Uptake

Moisture uptake was studied by storing starch dog-bones (63.5 mm x 9.5 mm x 1.8mm) at relative humidity level 50% (35.64% of $CaCl_2$ solution).

Moisture uptake of the dog-bones stored at 50% RH was gravimetrically analyzed. Calculations were performed daily for the first seven days. Then, weekly calculations were done up to 56 days. Moisture uptake of the dog-bones was determined by using the equation 4.1 [128].

$$\text{Moisture uptake} = \frac{\text{weight (day, n)} - \text{weight (day, 0)}}{\text{weight (day, 0)}} \,.\, 100\% \qquad \text{(Eq. 4.1)}$$

where,

day, n = day of measurement

day, 0 = day at which film was prepared

4.10 Mechanical Testing

A tensile tester (Shimadzu, M129607) was used to measure mechanical characteristics of TPS dog-bones. The crosshead speed was set at 10 mm/min. Each specimen was conditioned at Relative Humidity = 50% for 24 hours before measurement. For the validity of the research, minimum of 5 specimens were tested for every sample.

4.11 Powder Recovery / Yield

For all processing operations, powder recovery is an important consideration. According to Hanus *et al.* [129], yield is “the ratio of the actual amount of solid powder product to the maximum amount of powder achievable”. The yield was measured as the ratio of quantity of product obtained to the quantity of starch and additive used as an input material (Equation 4.2).

$$\text{Yield} = \frac{weight\ (product)}{weight\ (starch) + weight\ (plasticizer)} \ .\ 100\ \% \qquad \text{(Eq. 4.2)}$$

Chapter 5 – Results and Discussion

In this chapter, results obtained from various analytical techniques are presented and critically discussed.

5.1 XRD Analysis

X-ray diffraction patterns of native starch and TPS powders obtained after spray drying are shown in Figure 5.1 and 5.2 respectively. The XRD showed native starch possesses a semi-crystalline structure. It was specified by broad crystalline peaks at $2\Theta = 15.04^{o}$, 17.23^{o}, and 23^{o} (Figure 5.1) [18, 37]. These peaks relate to B- and V-type crystallinity [130]. B-type crystallinity is related to the higher brittle behavior. In order to create flexible dog-bones, the elimination of these crystal elements is required [131].

Whereas, all the freshly spray dried powder samples appeared amorphous irrespective of the amount of plasticizer used. Hence, no crystalline peaks were noticed (Figure 5.2). The B- and V-type crystalline peaks in the native starch were completely absent after spray drying. Plasticizer interfered the intra and inter-molecular hydrogen bonds in between starch chains, hence resisted the retrogradation during the processing step. Moreover, retrogradation was inhibited during spray drying operation due to the high drying rate and low moisture content. Short drying spans attained in spray drying did not allow starch chains to reallocate into crystal lattices [39].

All the freshly prepared TPS dog-bones (Day 1) were hazy and amorphous (Figure 5.3). Moreover, compression molding did not cause retrogradation. XRD analysis of the dog-bones stored at 50% RH showed slight retrogradation during 7 days (Figure 5.4). It was noticed that the degree of retrogradation was more in dog-bones having larger quantity of plasticizers as both plasticizers were hydrophobic. The structure of citric acid is more crystalline as compared to malic acid. Hence, it resisted moisture more than malic acid. Results showed that 10% and 20% plasticized samples of both malic and citric acid inhibited better retrogradation as compared to 30% plasticized samples. Moreover, citric acid plasticized TPS samples executed better performance and stopped retrogradation as compared to malic acid plasticized TPS samples.

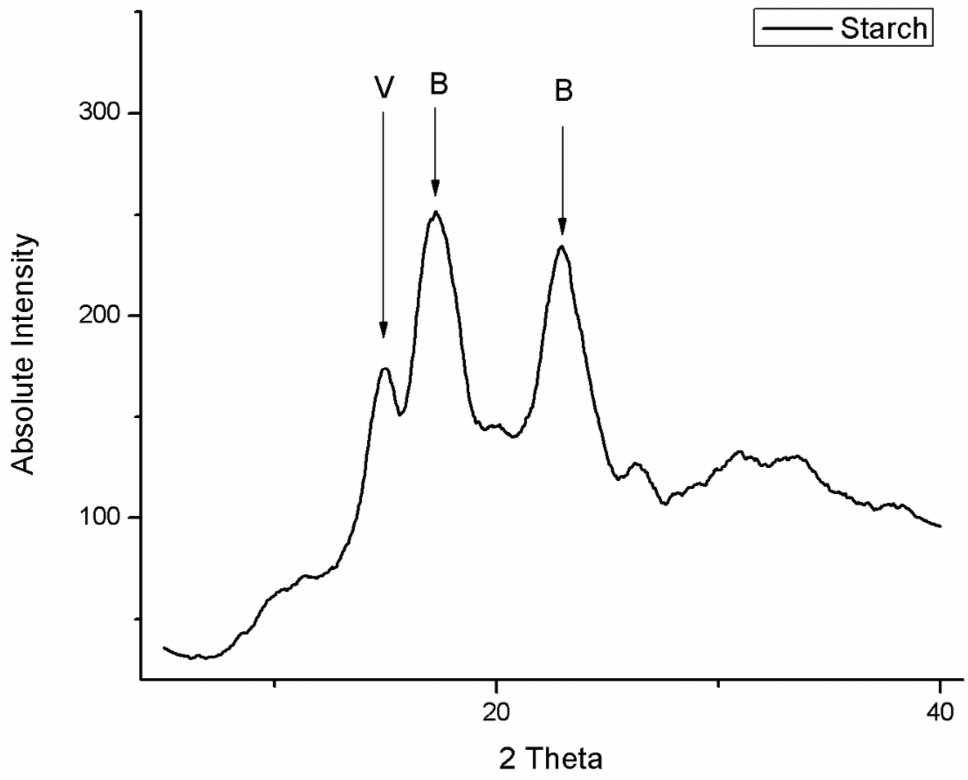


Figure 5.1 X-ray Diffractogram of Native Starch

Comparison of this result with those available in literature concluded that malic and citric acid plasticized samples were transparent like tartaric acid, phthalic acid, succinic aicd, oxalic acid, glycerol, urea, and formamide plasticized TPS samples whereas asparagine and isoleucine plasticized TPS samples were hazy and non-transparent (Table 5.1). Spray dried starch and co-plasticized samples were slightly hazy and mat. Moreover, carboxylic acids plasticized TPS samples controlled crystallinity much better like urea, glycerol and acetamide plasticized TPS samples. Carboxylic acids controlled crystallinity even when used with other co-plasticizers [10, 132, 133]. The crystallinity of the spray dried TPS samples was compared with the TPS samples prepared from solution casting. It was found that the samples prepared by spray drying via compression molding exhibited no crystal structures but sample obtained by solution casting showed slight crystallinity. Hence, rate of retrogradation and ultimate equilibrium crystallinity levels are less for the samples prepared by spray drying as compared to those via solution casting. More efficient drying in spray drying is the main reason behind better control over rate of retrogradation and crystallinity as it lowers the initial moisture from plasticized starch samples and reduces the mobility of starch chains occurred by plasticization of water [37].

Rui *et al.* [133] studied the casted polyvinyl alcohol (PVA)/starch blends at about 140^{o}C. The blend was plasticized with glycerol and citric acid with various ratios. XRD analysis of TPS sample were performed and indicated that most of the peaks in the blends were found just like of native materials Intensity of the peak at 19.3^{o} was decreased due to the presence of citric acid but the samples were still crystalline.

Table 5.1 Comparison of XRD results with the literature.

Plasticized TPS Samples	Re-crystallization Control	Transparency	References
Malic Acid	Controlled	Transparent	[10, 132, 133]
Citric Acid	Controlled	Transparent	
Tartaric Acid	Controlled	Transparent	
Phthalic Acid	Controlled	Transparent	
Oxalic Acid	Controlled	Transparent	
Urea	Controlled	Transparent	
Glycerol	Controlled	Transparent	
Acetamide	Controlled	Transparent	
Formamide	Controlled	Transparent	
Isoleucine	Not Controlled	Hazy, Non-Transparent	
Asparagine	Not Controlled	Hazy, Non-Transparent	

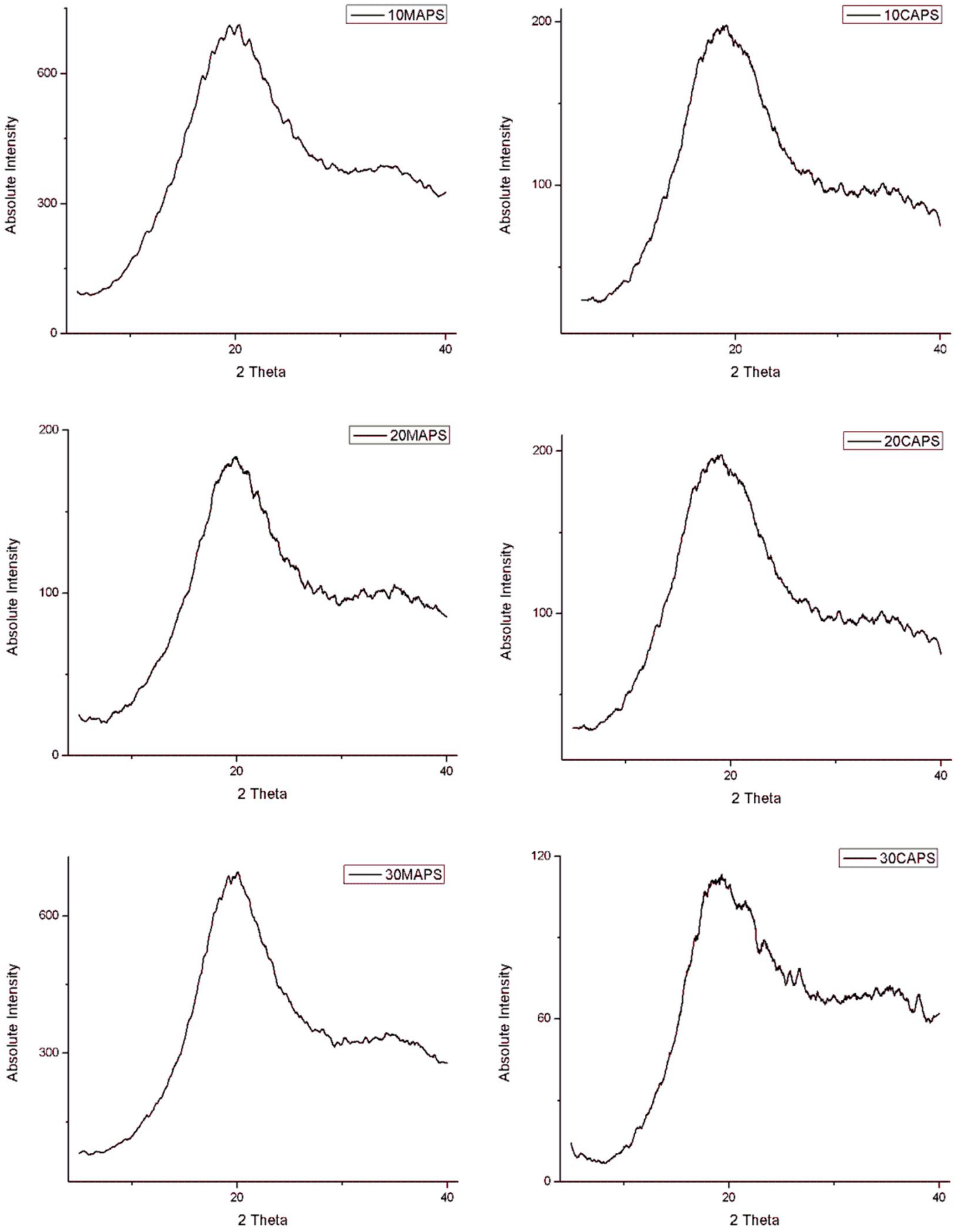


Figure 5.2 X-ray Diffractograms of the freshly produced powders after spray drying

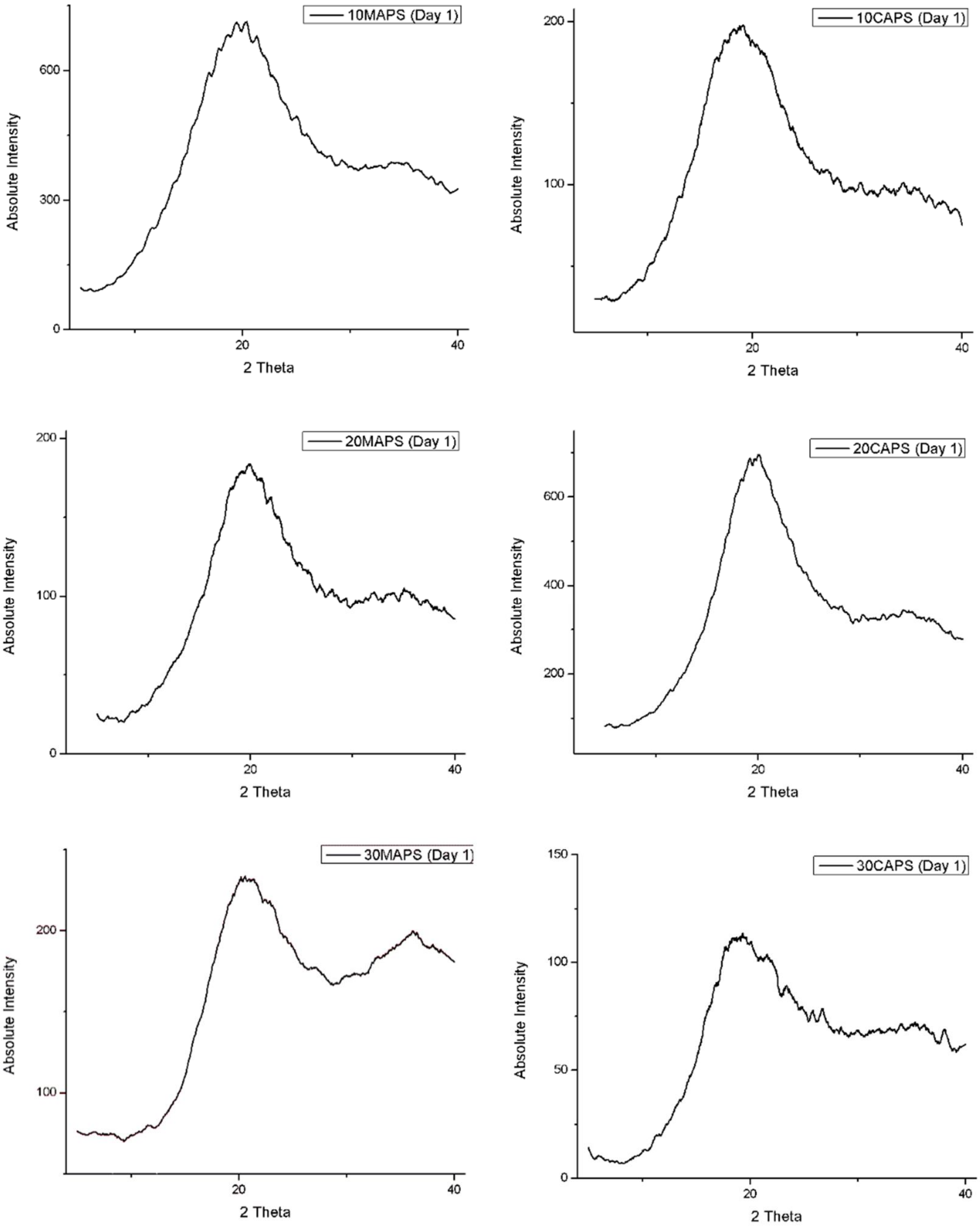


Figure 5.3 X-ray Diffractograms of freshly prepared TPS Dog-bones

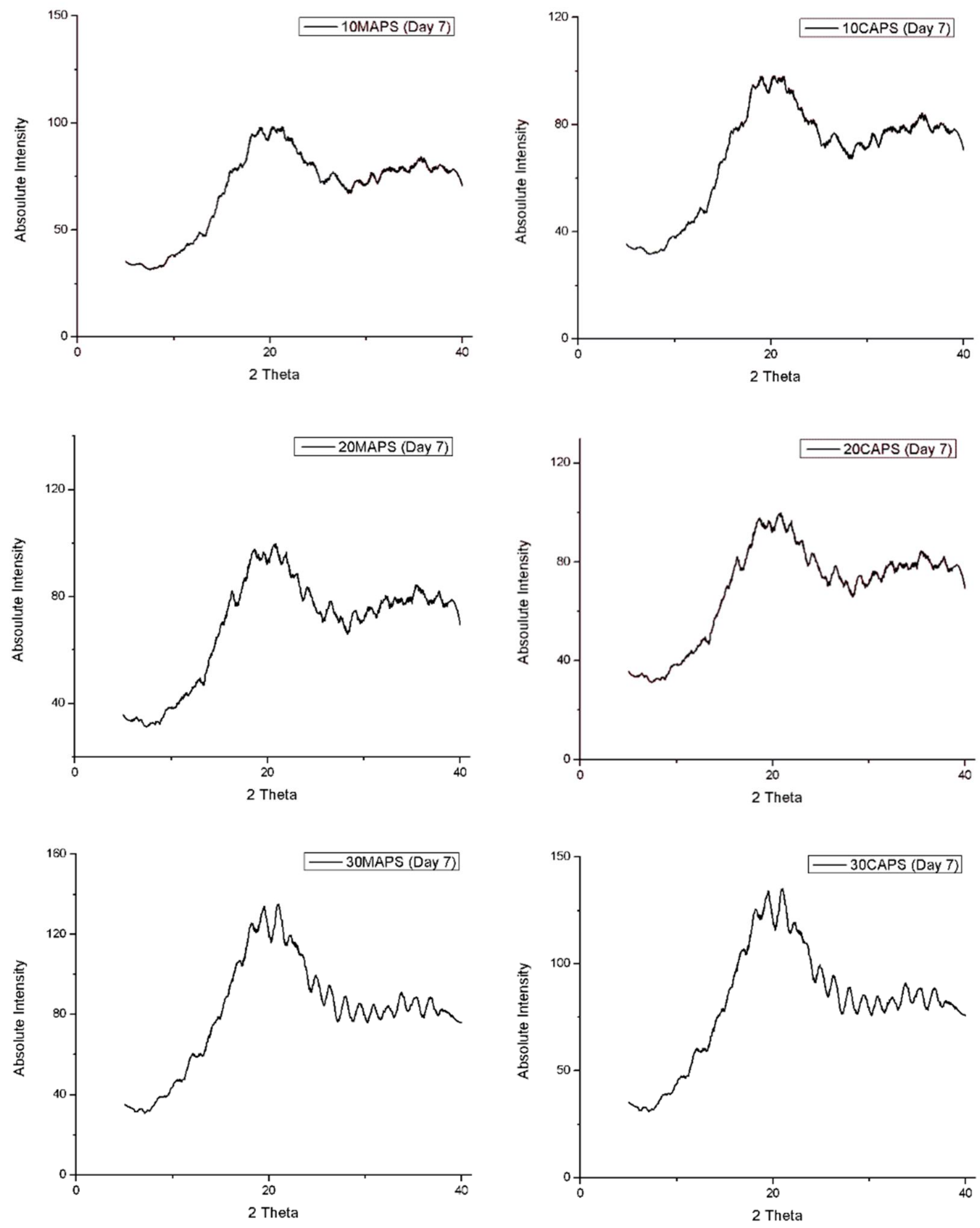


Figure 5.4 X-ray Diffractograms of the Dog-bones (after Day 7) at 50% RH

5.2 TGA and DTGA Analysis

Thermal properties of the TPS powders were investigated by both TGA (Figure 5.5 and 5.6). TGA of feedstock material was also done to take as a reference sample (Figure 5.5). It showed typical thermal behavior, moisture loss up to 110^{o}C (labeled ‘a’), followed by degradation of starch from 300^{o}C. Complete decomposition was observed above 350^{o}C (labeled ‘c’). Similar behavior was observed for TGA of malic acid and citric acid showing region ‘a’ for moisture loss and region ‘c’ for complete decomposition.

Apart from moisture loss at 100^{o}C, all plasticized TPS samples showed thermal stability up to 170^{o}C temperature. Depending upon the composition of the formulations, the curve was divided into 3 or 4 identifiable regions. From 100^{o}C to 110^{o}C (labeled ‘a’), loss of water was observed in all samples. The TGA analysis is not that simple as the results cannot be converted directly into absolute features of material under observation. Starch degradation started at 300^{o}C (labeled ‘b’) followed by char production above 350^{o}C (labeled ‘c’). The formulated systems indicate a fourth region from 180^{o}C to 300^{o}C (labeled ‘b1’) that was related to the plasticizers decomposition or to specific unidentified degradative interactions of starch with plasticizer. Whereas, main degradation zone for starch is observed in region ‘b2’.

The addition of plasticizer molecules decreased the decomposition temperature and an extra bend in DTGA curve appeared (labeled ‘b1’). For both malic acid and citric acid, decomposition temperatures, i.e. $T_{dec,b1}$, and $T_{dec,b2}$ were decreased by increasing the quantity of plasticizer. That indicated more homogeneous blending and interactions between starch and plasticizer (Figure 5.6 and Table 5.2).

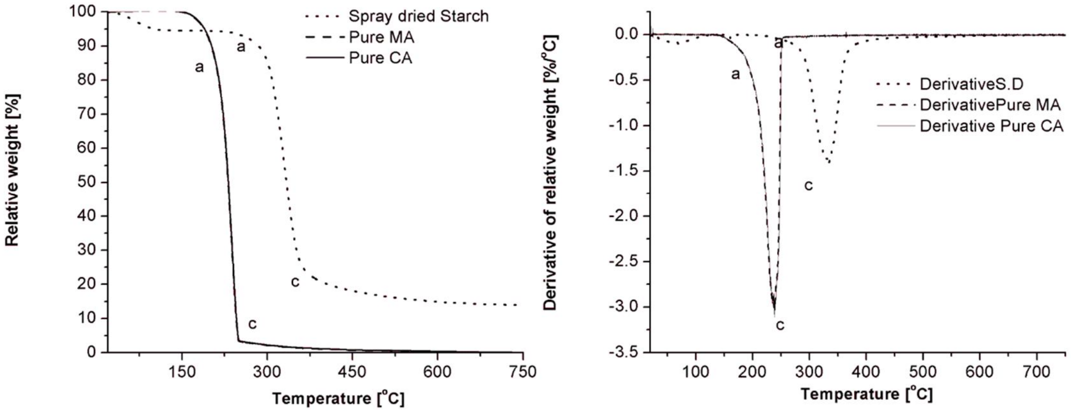


Figure 5.5 TGA and DTGA curve of spray dried starch and pure plasticizers

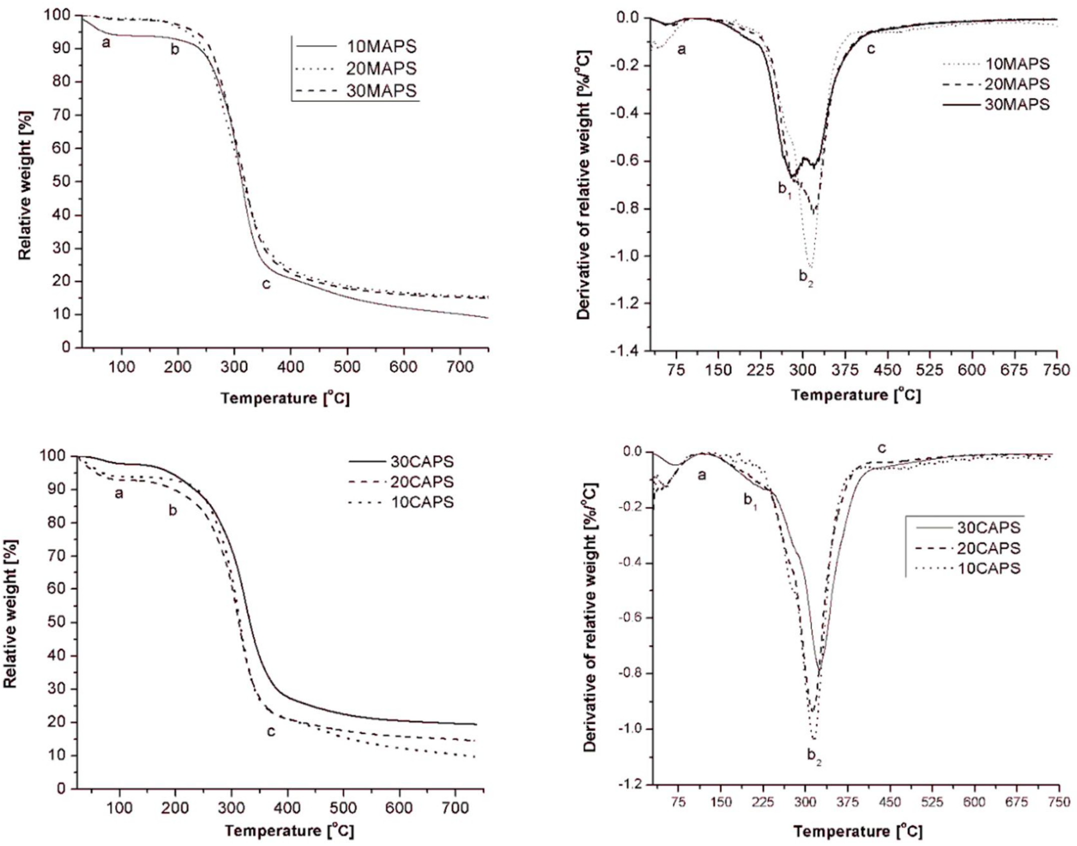


Figure 5.6 TGA and DTGA curves of solution spray dried amorphous TPS plasticized powder samples

Table 5.2 Thermal Properties of the Studied Samples

Samples	**Onset, T_{dec} (°C)**	**Peak, $T_{dec,b1}$ (°C)**	**$T_{dec,b2}$ (°C)**
SD.S	292	-	331
30MAPS	230	279	313
20MAPS	253	285	315
10MAPS	271	292	318
30CAPS	229	242	314
20CAPS	242	249	317
10CAPS	256	258	319

The comparison of this work with the literature showed that both malic acid and citric acid were quite different from other commonly used plasticizers i.e. tartaric acid, succinic acid, phthalic acid, oxalic acid, glycerol, urea, formamide (Table 5.3). Carboxylic acids seemed to form more homogeneous blending with starch matrix [48, 134]. Starch plasticized with malic acid or citric acid were non-swelling due to the better cross-linking between starch and both of the carboxylic acids [135]. TGA and DTGA analysis can be used to find out the role of carboxylic acid plasticizers in the formulated TPS samples. Comparing malic acid with other commonly used plasticizers (citric acid, tartaric acid, succinic acid, phthalic acid, oxalic acid, formamide, glycerol) showed that malic acid formed a distinct phase or even new composition during drying and mixing operations indicating better stability of malic acid plasticized TPS samples. When carboxylic acids were used with other co-plasticizers, the rate of weight loss was reduced by the addition of malic acid and citric acid. Stability of formulations was affected by varying the quantity of the carboxylic acid plasticizers. By increasing the quantity of carboxylic acid component in the co-plasticizers, thermal stability was improved because cross-linking is not resisted and carbonization is also enhanced by increasing the quantity of carboxylic acids [48, 132-135]. Hence, improved thermal stability of TPS samples can be explained by stronger hydrogen bonding and potentially covalent bonding i.e. esterification and cross-linking by malic and citric acid.

Rui Shi *et al.* [133] worked on the casted polyvinyl alcohol (PVA)/starch blend at about 140^{o}C. Various ratios of glycerol and citric acid were applied as plasticizers. TGA analysis indicated that better thermal stability of PVA/Starch blend was achieved when plasticized with citric acid as compared with glycerol plasticized PVA/Starch blends.

Table 5.3 Comparison of Thermal behavior with literature

Plasticized TPS Samples	Thermal Stability	References
Malic Acid	Improved	[10, 48, 132-135]
Citric Acid	Improved	
Tartaric Acid	Improved	
Phthalic Acid	Improved	
Succinic Acid	Improved	
Oxalic Acid	Improved	
Urea	Improved	
Formamide	Improved	
Acetamide	Improved	
Glycerol	Deteriorated	

5.3 FT-IR Analysis

FT-IR analysis were performed to understand the interactions of starch with plasticizer (Table 5.4, Figure 5.7 and 5.8). A shift in the absorption bands was the indication of interactions. Untreated starch spectrum was used as a reference sample to describe the absorption bands for the formulated samples. A red-shift occurred for starch stretching vibrations of O-H, C-O, and C=O due to hydrogen bond vibrations [10]. Moreover, bond elongations also occurred because of hydrogen bond interactions resulting in lower stretching vibrations [136, 137]. The peaks at 3427-3390 cm^{-1} were attributed to O-H stretching [39]. C-H stretching was indicated by the peaks at 2928-2921 cm^{-1} [39]. The bands at 1027-1021 cm^{-1} were attributed to C-O bond stretching [37, 39].

The absorption bands 1021 and 1022 were clearly visible indicating low crystallinity of the samples [138].

All spectra indicated shifts towards fingerprint region of starch, showing interaction of starch and plasticizers. A red shift was visible upon increasing the quantities of plasticizers (not in all cases). This was because the number of hydroxyl and carboxyl groups increased as the citric acid or malic acid quantity was increased. So hydrogen bonding interactions were increased by increasing the plasticizer content (30% > 20 % > 10%).

The comparison of this work with the ones available in literature (Table 5.5) indicated that malic and citric acid mixed plasticized TPS samples showed carbonyl absorption bands at 1729-1723 cm^{-1} i.e. esterification of starch and cellulose samples [133, 134]. A red shift observed by the increase in the quantity of carboxylic acids indicates improved hydrogen bond interactions. Carboxylic acids showed an increase in hydrogen bond interactions when their quantity was increased even when being used with other co-plasticizers. Similar results were obtained for malic acid plasticized TPS sample when it was compared with glycerol plasticized TPS sample. Isoleucine plasticized TPS samples showed a blue shift (not in every case) that indicates low interactions between starch molecules and plasticizer [39].

Pushpadass *et al*. [139] studied the effect of extrusion temperature and plasticizers on functional and physical characteristics of starch samples. Improved interactions of plasticizers with starch also lowered the glass transition temperature. Nevertheless, molar ratios of starch to plasticizer cannot be ruled out in interpreting the spectra. It was investigated that hydrogen bond interactions of starch within the blends was in an inverse relation with molecular size of the plasticizer. Hence, based on FTIR analysis, it can be concluded that stronger hydrogen bonding interactions with starch was formed by smaller molecules.

Table 5.4 FT-IR Absorption Bands of the Studied Samples

	Wave Number (cm^{-1})				
Samples	**3427-3390 (O-H stretching)**	**2928-2921 (C-H stretching)**	**1729-1632 (presence of carbonyl group)**	**1410-1384 (C-O-H bending)**	**1027-1021 (C-O bond stretching)**
US	3427	2921	-	1384	1022
10CAPS	3408	2926	1728	1408	1022
10MAPS	3390	2927	1728	1408	1022
20CAPS	3391	2928	1723	1398	1021
20MAPS	3419	2927	1729	1410	1025
30CAPS	3414	2928	1729	1404	1021
30MAPS	3397	2926	1729	1395	1027

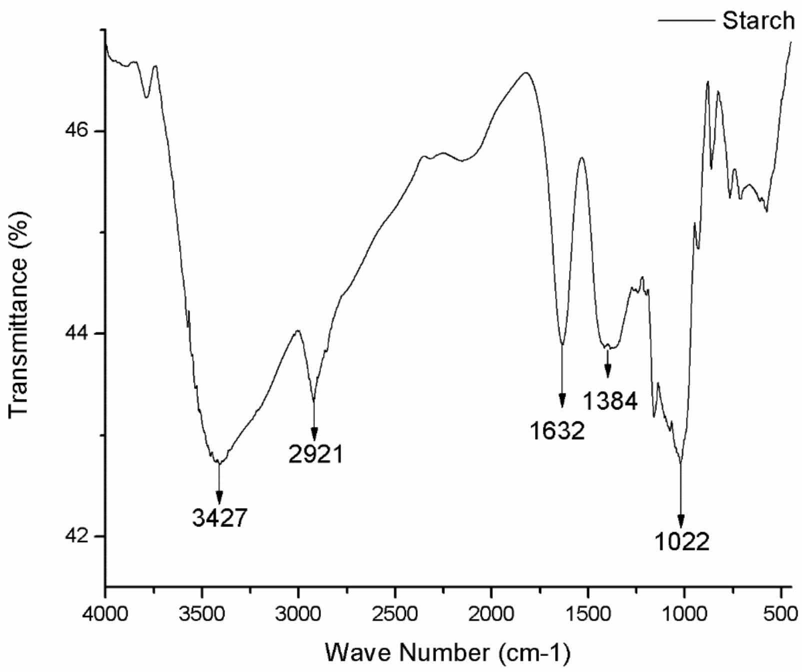


Figure 5.7 FT-IR Analysis of Untreated Starch

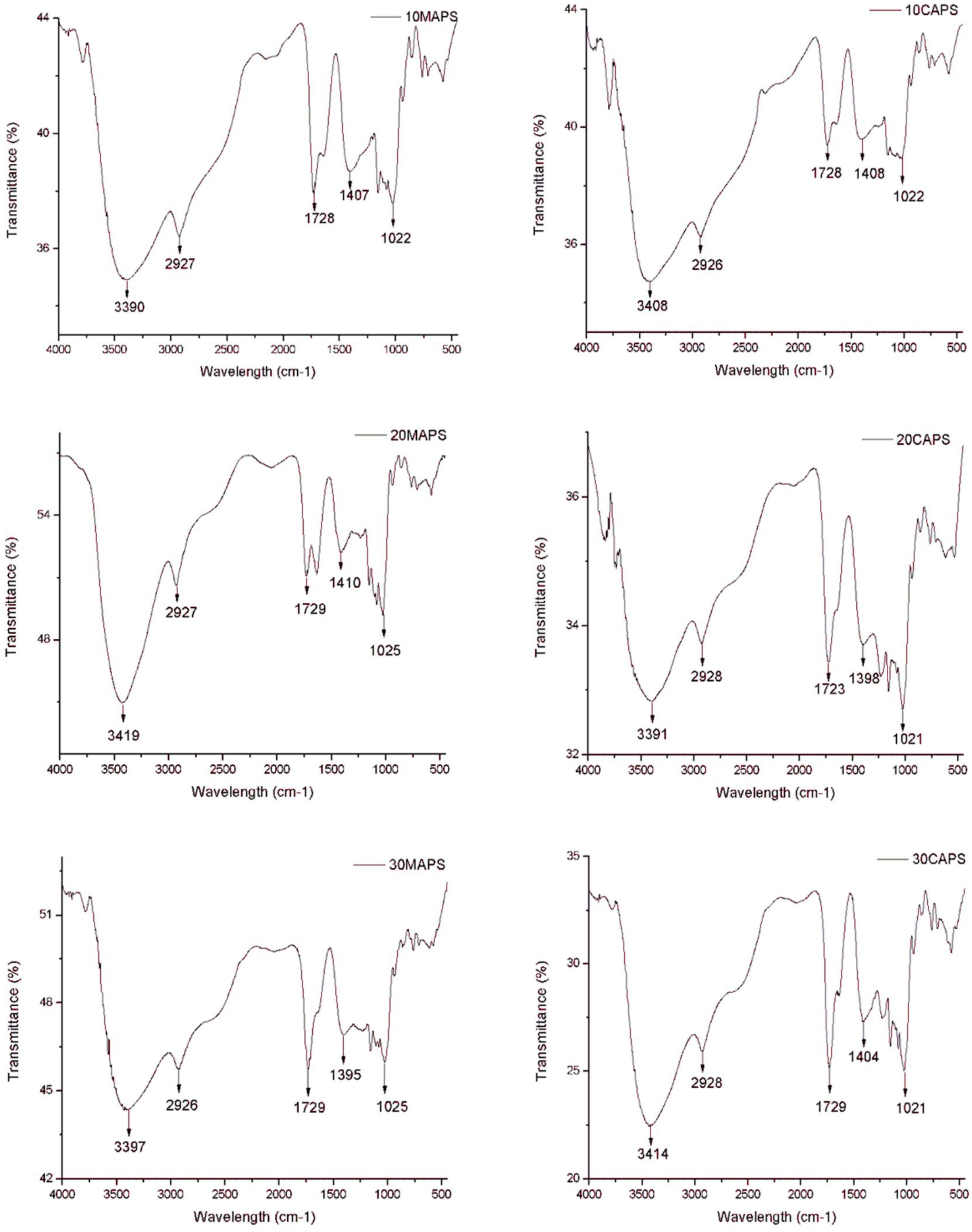


Figure 5.8 FT-IR Analysis of solution spray dried amorphous TPS powder plasticized samples

Table 5.5 Comparison of FTIR data with literature

Plasticized TPS Samples	Starch – Plasticizer Interactions	Absorption Bands Shift	References
Malic Acid	Stronger	Red Shift	[10, 39, 133, 134, 139]
Citric Acid	Stronger	Red Shift	
Tartaric Acid	Stronger	Red Shift	
Succinic Acid	Stronger	Red Shift	
Phthalic Acid	Stronger	Red Shift	
Oxalic Acid	Stronger	Red Shift	
Urea	Stronger	Red Shift	
Formamide	Stronger	Red Shift	
Asparagine	Stronger	Red Shift	
Glycerol	Strong	Red Shift	
Acetamide	Strong	Red Shift	
Isoleucine	Weak	Blue Shift	

5.4 Powder Recovery

Powder recovery is an important factor in every processing method. In spray drying, yield is reduced because of the powder deposition on walls of drying chamber. A low yield reduces efficiency of a process [129]. During spray drying, the factors that affect the powder recovery are: solution properties, operating parameters, type and amount of plasticizer being used. All operating parameters were kept constant for all the samples but the nature and quantity of the plasticizers were varied. Mainly, loss was expected because of the deposition of powder on the wall of the spray dryer. Spray dried starch was taken as a reference sample and indicated maximum powder recovery of 78 ± 1%. Powder recovery of the spray dried TPS samples are shown in Figure 5.9 and Table 5.6. The formulated samples showed the powder recovered in each of the formulated sample in order 10% plasticized starch > 20% plasticized starch > 30% plasticized starch (by using equation 4.2) indicating a significant decrease in powder recovery by increasing the quantity of plasticizers in both of the cases.

The major losses usually occurred because of powder stickiness to walls of the drying chamber of a spray dryer. Glass transition temperature (Tg) is one of the most important parameter that effects stickiness. When the inlet temperature is higher than the Tg, the particles adopt sticky or rubbery state [140]. In this study, the samples did not indicate a Tg and process temperature was less than initial temperature of each of the formulations resulting in high powder recovery. The comparison of this work with the literature showed that the losses increased in the order spray dried starch > citric acid plasticized starch > malic acid plasticized starch > tartaric acid plasticized starch > glycerol plasticized starch > urea plasticized starch [10, 44, 141].

Table 5.6 Powder recovery/yield of formulated samples

Sample	**Powder Recovery (%)**
SD.S	78 ± 1
30MAPS	63 ± 2
20MAPS	66 ± 2
10MAPS	68 ± 1
30CAPS	64 ± 2
20CAPS	67 ± 1
10CAPS	69 ± 1

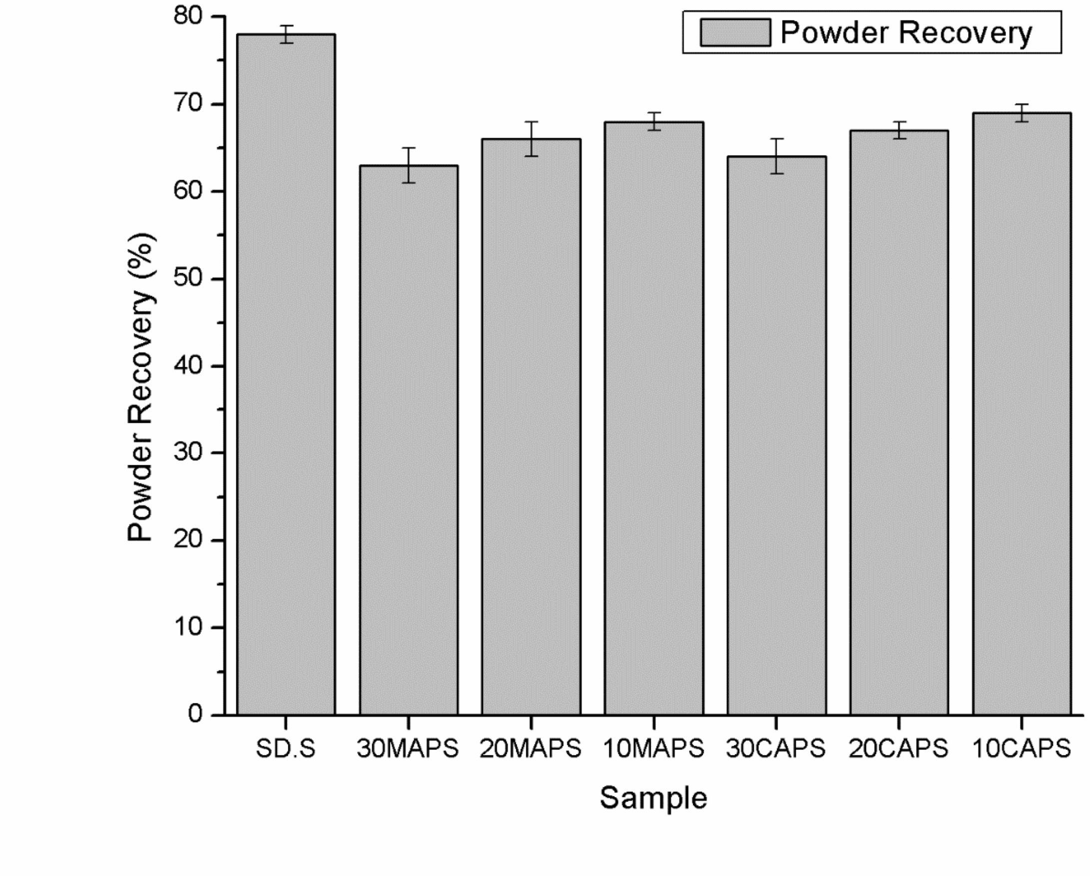


Figure 5.9 Powder Recovery/Yield after Spray Drying of plasticized TPS samples

5.5 Powder Morphology

SEM was used to examine the surface morphology of TPS powder. Morphology of untreated starch is shown in figure 5.10. Untreated starch exhibited oval and spherical shaped particles of irregular sizes. Homogeneous surface of the particles was observed. There was a visible difference in the morphology of the particles after spray drying. Figure 5.11 showed the morphology of plasticized spray dried TPS powders. Particles were spherical in nature but shriveled and deformed that are typical for spray dried powders due to fast drying [142]. Surface of the droplets was initially covered by a skin formed during spray drying, leaving the remaining liquid trapped inside. By further drying, particle size was reduced because of liquid diffusion through the dried surface. Hence, the surface of the particles was shriveled and deformed. All the solution spray dried TPS samples showed a similar appearance (Figure 5.11). There was not any noticeable difference observed on the morphology of the particles.

Quantity of plasticizer did not visibly change the morphology of particles. No phase separation was observed from SEM. The surface of the particle was homogeneous and smooth. Moreover, any difference in the combination of plasticizer or its nature did not cause noticeable differences in morphology.

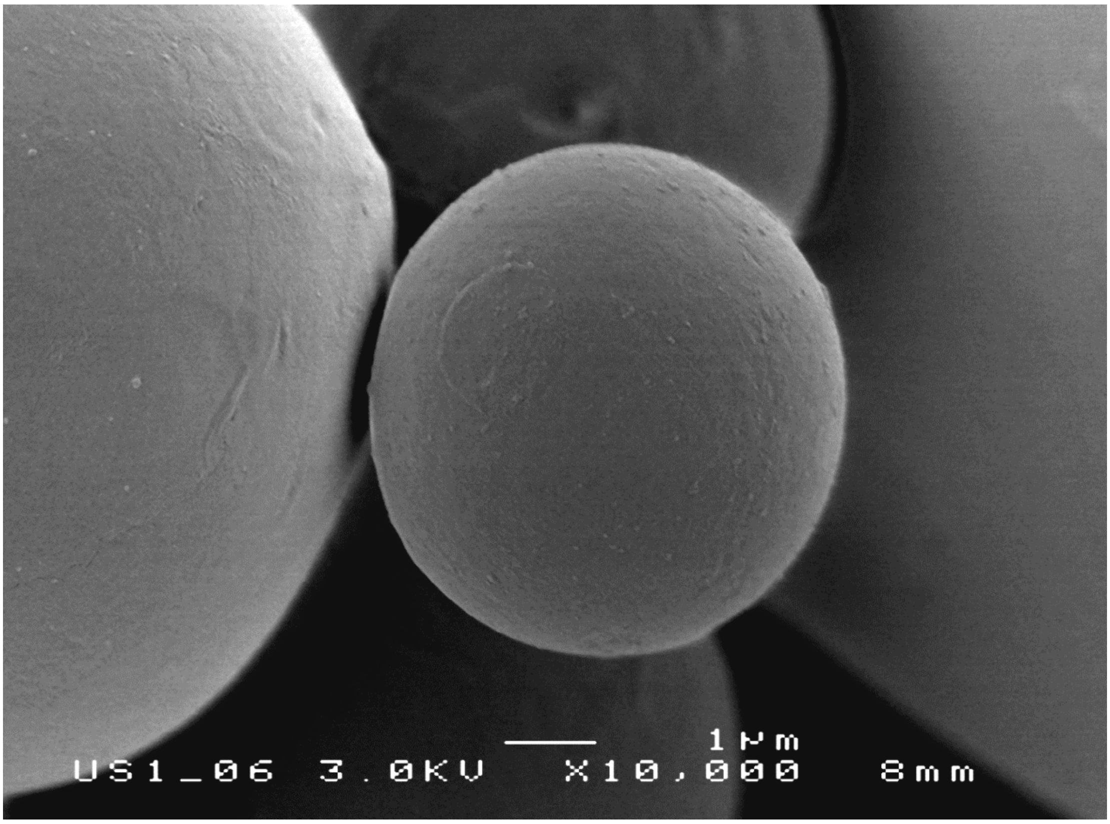


Figure 5.10 SEM Micrograph of Untreated Starch

The comparison of this work with the literature showed that malic acid, citric acid, tartaric acid, phthalic acid, succinic acid, oxalic acid, glycerol, urea and mixed plasticized samples displayed similar morphology when compared with spray dried starch except isoleucine (Table 5.7). Similar results were observed when malic acid was used in combination of a co-plasticizer like urea, glycerol, or maltodextrin. On the other side, isoleucine plasticized TPS sample gave a different appearance (Hollow Particles). It was expected that carboxylic acids are more compatible with moisture-rich starch droplets during the drying phase [143, 144].

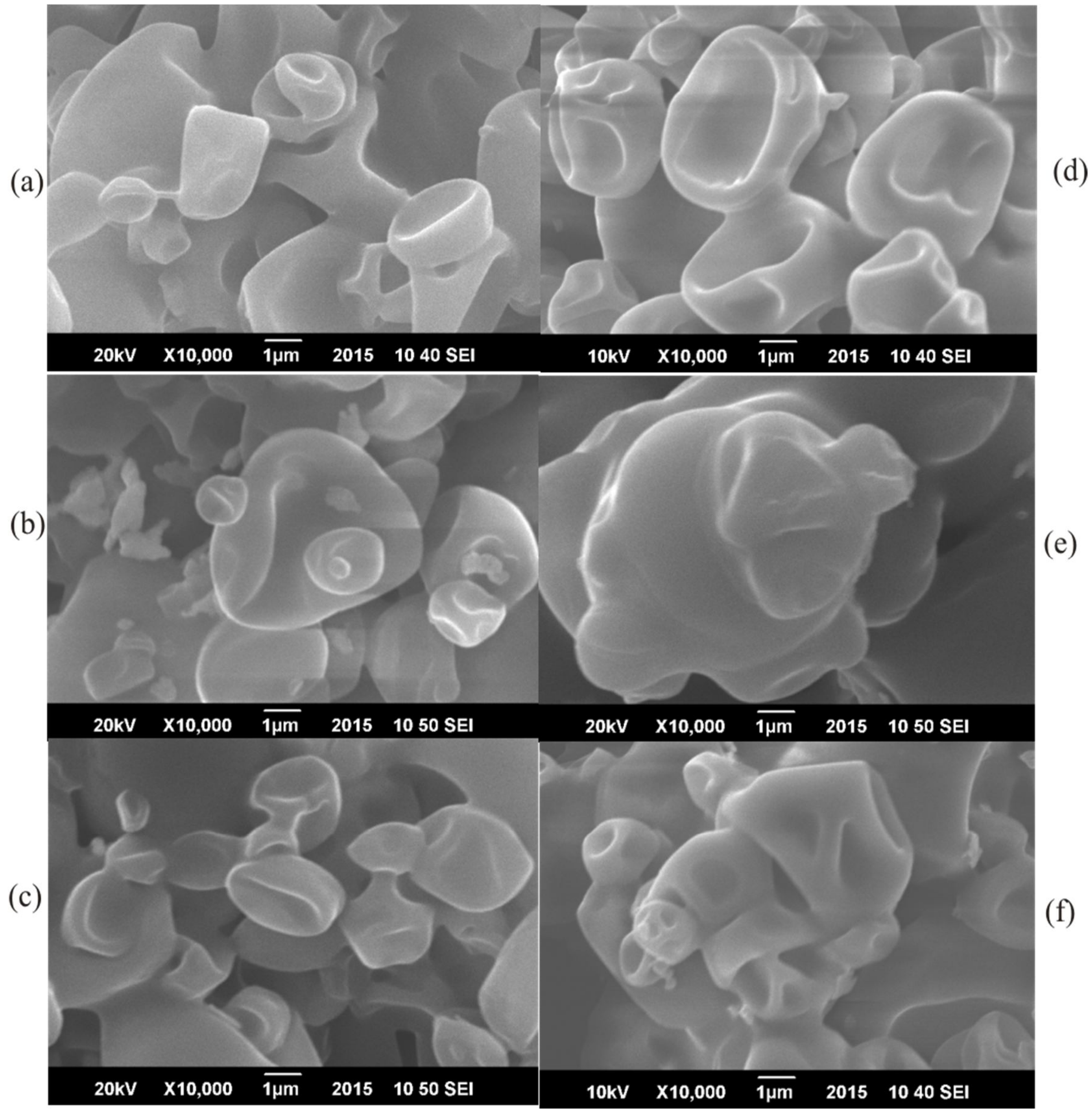


Figure 5.11 SEM Micrographs of spray dried TPS plasticized powders (a) 10MAPS, (b) 20MAPS, (c) 30 MAPS, (d) 10CAPS, (e) 20CAPS, (f) 30CAPS

Table 5.7 Comparison of SEM results with literature

Plasticized TPS Samples	Homogeneity	Surface	References
Malic Acid	Homogeneous	Shriveled and Deformed	[10, 143, 144]
Citric Acid	Homogeneous	Shriveled and Deformed	
Tartaric Acid	Homogeneous	Shriveled and Deformed	
Phthalic Acid	Homogeneous	Shriveled and Deformed	
Succinic Acid	Homogeneous	Shriveled and Deformed	
Oxalic Acid	Homogeneous	Shriveled and Deformed	
Urea	Homogeneous	Shriveled and Deformed	
Glycerol	Homogeneous	Shriveled and Deformed	
Asparagine	Homogeneous	Shriveled and Deformed	
Maltodextrin	Homogeneous	Shriveled and Deformed	
Acetamide	Homogeneous	Shriveled and Deformed	
Isoleucine	Less Homogeneous	Hollow	

5.6 Moisture Uptake

The moisture absorption data recorded at 50% RH were the valid indication for the specific behavior of malic acid comparative to citric acid formulations. Figure 5.12 showed the overview of the moisture uptake data for both MAPS and CAPS dog-bones. Moisture uptake calculations were performed on daily basis for the first seven days. After that, weekly measurements were taken till the 56th day. As both plasticizers were hydrophobic so they absorbed moisture throughout 56 days. The structure of citric acid was more crystalline as compared to malic acid, hence, resisted moisture uptake. In terms of quantity of the plasticizers, both MAPS and CAPS showed similar behavior as expected. As the quantity of the plasticizer was increased, the moisture uptake was also increased.

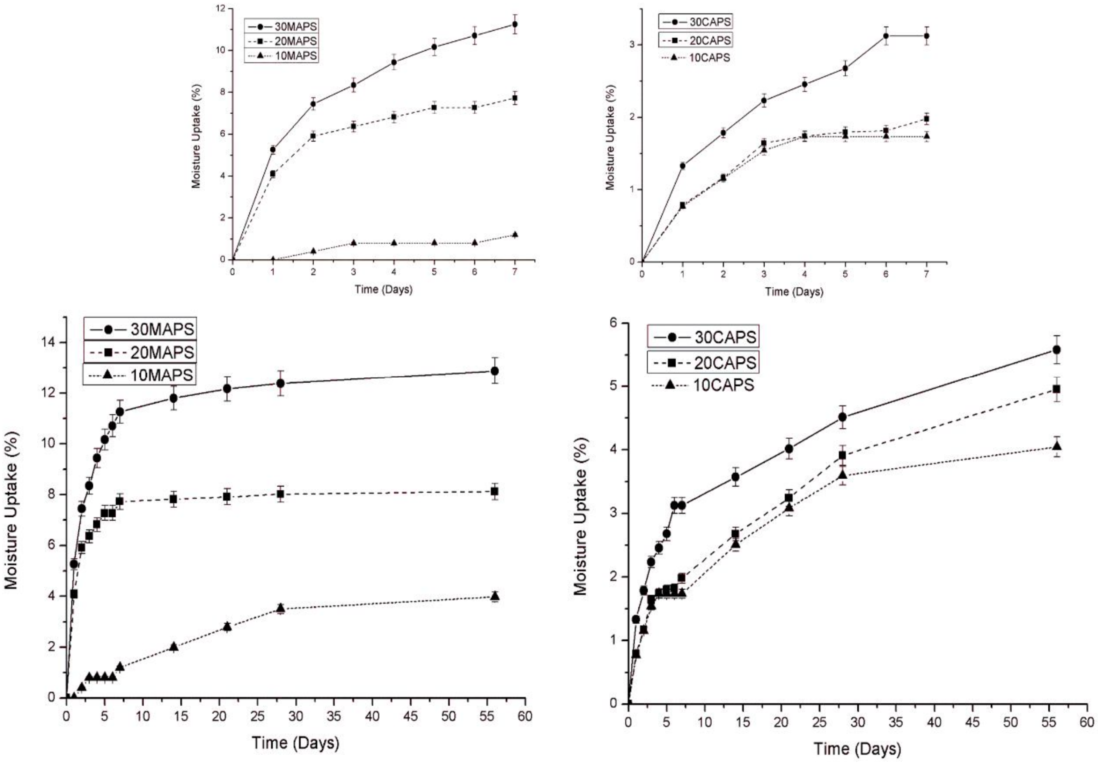


Figure 5.12 Moisture Uptake Curves at 50% RH for malic and citric acid plasticized TPS dog-bones

By comparing this data with literature, it can be seen that carboxylic acids i.e. malic and citric acid, like all other plasticized TPS samples (tartaric acid, succinic acid, oxalic acid, phthalic acid, asparagine, acetamide, formamide, glycerol, urea, maltose, maltodextrin plasticized TPS samples), gained moisture and indicated an increase in final relative weights and crystallinity (Table 5.8). Both malic and citric acid resisted moisture uptake more than tartaric acid, succinic acid, oxalic acid, phthalic acid, maltose, acetamide, formamide, glycerol and urea plasticized TPS samples. TPS samples were observed as brittle upon storage whereas malic acid, citric acid, and mixed plasticized TPS samples did not show any significant increase in crystallinity at 50% of relative humidity over time. They indicated slight retrogradation and samples remained flexible. A very low water uptake and hence low increment in the weight was observed after 56 days at RH 50%. This was attributed to limited chain movement and retrogradation [132].

Table 5.8 Comparison of Moisture Uptake with literature

Plasticized TPS Samples	Moisture Uptake Control	References
Malic Acid	Better	[10, 132]
Citric Acid	Better	
Urea	Good	
Tartaric Acid	Good	
Succinic Acid	Good	
Phthalic Acid	Good	
Oxalic Acid	Good	
Formamide	Good	
Asparagine	Good	
Glycerol	Good	
Acetamide	Good	
Isoleucine	Good	

5.7 Mechanical Properties

Mechanical properties play a key role in the evaluation of strengths and ability of TPS material to bear external disturbances. Mechanical behavior of TPS dog-bones is shown in Figure 5.13 and 5.14. The mechanical behavior of all the plasticized TPS dog-bones were assessed after equilibration at 50% RH for 24 hours. Native starch samples were not analyzed due to its rigid and brittle behavior. MAPS showed more flexible behavior than CAPS. The flexibility of TPS plasticized dog-bones increased in order of 30MAPS > 20MAPS > 10 MAPS and 30CAPS > 20CAPS > 10CAPS (Figure 5.13). Similarly, the flexibility of all the plasticized TPS samples were increased in order of Day 1 < Day 7 < Day 14. This was attributed to increase in moisture uptake, as the quantity of plasticizer increased. Increase in the hydrogen bond capability per molecule of plasticizer increased the strain at break but decreased the crystallinity and tensile strength of TPS dog-bones. Tensile strength was directly affected by water uptake and retrogradation. Citric acid has more crystalline structure than malic acid. Hence, MAPS tend to absorb more moisture and had low tensile strength as compared to CAPS. In comparison with the quantity of the plasticizers, tensile strength showed the order 10MAPS > 20MAPS > 30MAPS and 10CAPS > 20CAPS > 30CAPS (Figure 5.14). In term of days, the tensile strength of each sample was decreased in the order Day 1 > Day 7 > Day 14. This was due to increase in moisture uptake with time.

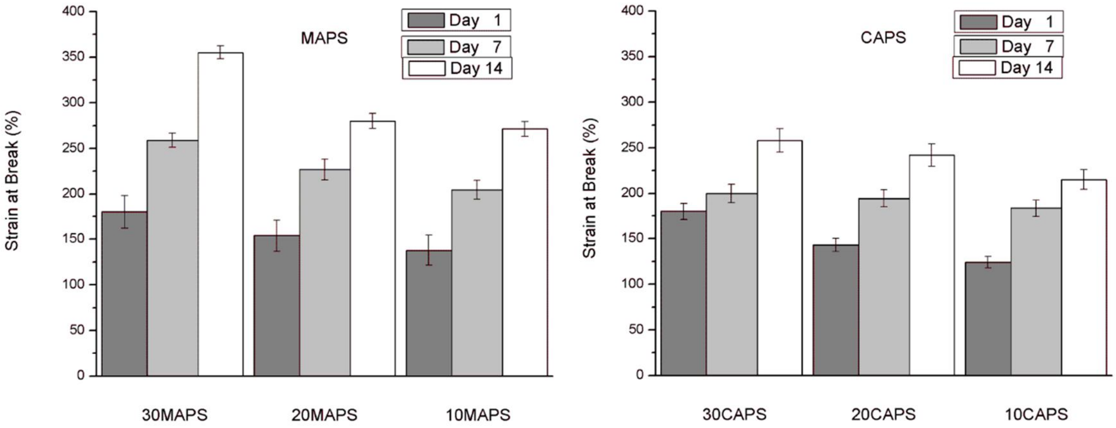


Figure 5.13 Strain at Break (%) of TPS Dog-bones at 50% RH

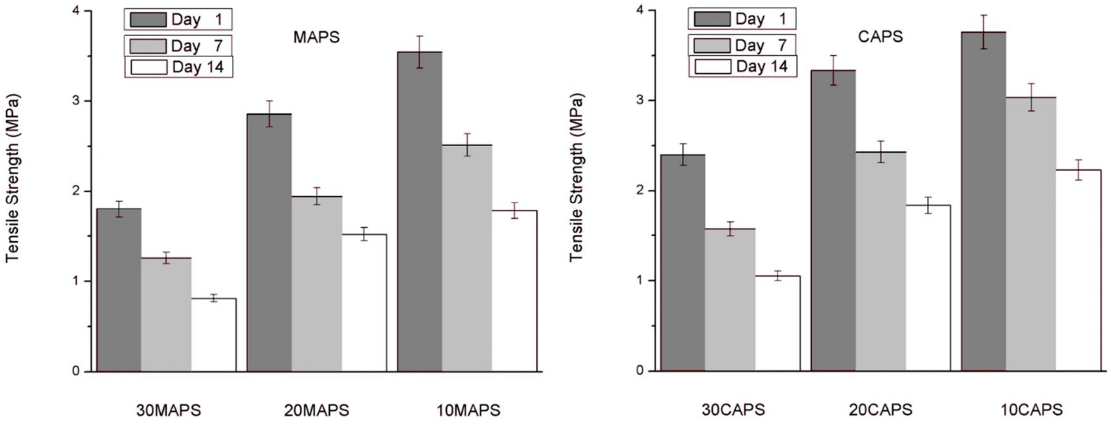


Figure 5.14 Tensile Strengths of TPS Dog-bones at 50% RH

Comparison of this work with the literature showed that both carboxylic acids plasticized TPS samples have higher flexibility than tartaric acid, succinic acid, phthalic acid, oxalic acid, urea, glycerol, formamide, acetamide plasticized TPS samples. Flexibility of prepared plasticized TPS samples increased in following order: isoleucine < asparagine < citric < malic acid – maltodextrin, malic acid – glycerol, malic acid – urea (Table 5.9). The increase in the hydrogen bond capabilities per molecule reduced the crystallinity and tensile strength but increases the level of strain. High hydrogen bonding functionalities increased the capability of the plasticizer to disrupt starch inter and intra-molecular hydrogen bonds and to gain moisture. So the mobility of starch chain and thus flexibility was improved. Moreover, carboxylic acids plasticized TPS samples showed higher structural integrity upon storage reasoning increase in strain [10, 132, 145].

Table 5.9 Comparison of Mechanical Properties with literature

Plasticized TPS Samples	Strength	Flexibility	References
Malic Acid	Higher	Higher	[10, 132, 145]
Citric Acid	Higher	Higher	
Tartaric Acid	Higher	High	
Succinic Acid	Higher	High	
Oxalic Acid	Higher	High	
Phthalic Acid	Higher	High	
Urea	Higher	High	
Formamide	Higher	High	
Acetamide	Higher	High	
Glycerol	Higher	High	
Asparagine	Higher	High	
Isoleucine	High	High	

Chapter 6 – Conclusions and Recommendations

6.1 Conclusions

The objectives of this thesis were to study the effect of carboxylic acid plasticizers on mechanical properties of biodegradable dog-bones, to study the effect of quantity of plasticizer on mechanical properties and to find out new materials in food packaging techniques in order to improve the quality of packaging with respect to the environmental health.

X-ray diffraction showed that all freshly prepared powders were amorphous. The freshly prepared dog-bones did not show any sign of recrystallization. Signs of recrystallization were noticed when XRD of dog-bones were performed on day 7. Thermal properties of the TPS powders were investigated by TGA. Apart from moisture loss at 100^{o}C, all the samples were thermally stable up to 170^{o}C temperature. A phase between 300^{o}C to 350^{o}C was the characteristic for starch degradation that was followed by char production above the temperature of 350^{o}C. The formulated systems indicated a fourth region at 180^{o}C that is related to the plasticizer decomposition or to unidentified degradative interactions between starch and the plasticizer. The addition of plasticizer molecules decreased the decomposition temperature. For both malic acid and citric acid, the decomposition temperatures were decreased by increasing their quantity that indicate more homogeneous blending and interaction of starch and plasticizers. Thermo-gravimetric analysis also showed similarities in each sample result. FTIR spectra for the formulated samples were line with literature and absorption at 1021 and 1022 cm^{-1} were clearly visible indicating low crystallinity of the samples. All spectra showed shifts towards fingerprint region of starch, indicating interaction of plasticizers and starch. A red shift was visible upon increasing the quantity of plasticizer. So hydrogen bonding interactions were enhanced by adding the plasticizer content. No noticeable difference was observed on the morphology between the samples. The amount of plasticizer did not noticeably influence the morphology of particles. Moreover, any difference in the combination of plasticizer or its nature did not cause visible differences in morphology.

Malic acid plasticized starch dog-bones showed slightly more flexibility as compared to citric acid plasticized starch dog-bones. The flexibility was increased but the tensile strength was decreased when the results of dog-bones (day 1 to day 14) were compared. Two common points in both cases were noticed: Firstly, the tensile strength was decreased as the quantity of the plasticizers were increased. Secondly, flexibility was increased as the quantity of the plasticizers were increased and brittleness was increased as the quantity of the plasticizers were decreased.

6.2 Recommendations

This work opens the gates to numerous new directions of research. TPS was used with plasticizers to produce biodegradable food packaging material by spray drying.

- The spray drying technique applied to produce TPS blends is underdeveloped but it is considered as an important route to generate amorphous materials, especially for native starches, to produce small particles. Cost is also the main issue in spray drying.
- Particle size distribution may also be performed as it determines the transport and flow of powder equipment, and its compaction and segregation behavior.
- Plasticizers are the important additives and performance enhancers of polymers. They can vary the properties of biodegradable polymers, hence, are considered as an opportunity to enhance the characteristics of bio-based plastics. Starch based plastics have represented a major section of the biodegradable polymer marker. On commercial scale, the success of TPS polymers is widely affected by the source, cost, quality, safety, and functionality of plasticizers.
- PLA/TPS blend should also be tried and compared keeping same parameters and conditions as this blend have improved performance with respect to degradation rate, thermal and mechanical properties. PS/TPS blend should also be used in spray drying especially with glycerol as thermal degradation can be controlled. Amphiphilic plasticizers should also be analyzed and compared with co-plasticizers as well because of its better flow ability, extensibility, and plasticization.
- Carboxylic acids showed intensive interactions to control the retrogradation significantly. At the same time, lack of retrogradation leads to higher moisture absorption. Hence, other pathways are needed to be developed in order to reduce

the moisture effect so that better mechanical properties of food packaging can be achieved and maintained.

Chapter 7 – References

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