Influence of Amphiphilic Plasticizer on Thermoplastic Starch Films

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Certificate

This is to certify that work in this thesis has been carried out by **Mr. Israr Ahmed** and completed under my supervision from School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedicated to my ***beloved parents***

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Abstract

Different combinations of hydrophilic (malic acid and water) and amphiphilic (isoleucine and butyric acid) plasticizers were studied in the production of thermoplastic starch (TPS) powders and T-bones from corn starch. Spray drying was used to produce TPS powder followed by compression molding for development of T-bones. Amphiphilic plasticizers were used for better control over rate of moisture uptake and compatible mechanical properties in terms of tensile strength and elongation at break. All powder samples had an irregular and shrivelled morphology. In all combinations containing isoleucine, this additive exuded from the starch matrix and re-crystallized during spray drying, resulting in hollow particles. Rate of retrogradation and nature of freshly prepared powder were studied by XRD. Formulated samples inhibited the retrogradation of starch till 7th day and the nature of samples was amorphous due to spray drying except isoleucine plasticized and co-plasticized samples. FTIR was performed to investigate the better insight of the functional groups and interaction of plasticizers and starch matrix. Thermal stability was analyzed by TGA and DTGA curves of the samples. The crystallinity and moisture sensitivity of freshly prepared films depended on the amphiphilic plasticizer content in the plasticizer formulation. Increasing the content led to a decrease in moisture absorption. Isoleucine formulated films showed the best tensile strength, whereas malic acid-rich ones showed better strain at break values. At a relative humidity (RH) of 50%, the rate of retrogradation was low, but rate of it increased with increase in malic acid contents.

Keywords: Biodegradable; Thermoplastic Starch; Amphiphilic; Retrogradation

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Abbreviations

ATR	Attenuated Total Reflection
BU.PS	butyric Acid Plasticized
CA	Citric Acid
DS	Degree of Substitution
DTGA	Differential Thermal Gravimetric Analysis
EP	Extra Pure
FTIR	Fourier Transform Infrared Spectroscopy
HLB	Hydrophilic-Lipophilic Balance
IS.PS	Isoleucine Plasticized Starch
MA.PS	Malic Acid Plasticized Starch
MAIS.PS	Malic Acid Isoleucine Plasticized Starch
MABU.PS	Malic Acid Butyric Acid Plasticized Starch
PLA	Poly-Lactic Acid
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 a lot of research has been done on biodegradable materials to develop flexible packaging materials [1]. Biopolymers are considered to be the best materials for this purpose [2]. Starch is obtained from a natural resource which is naturally biodegradable and this combination of biodegradability with readily availability and cost reduction has been a source of attraction for the researchers and made it preferable over various classes of synthetic and natural materials tested [3].

1.1 Biopolymers

Generally the biopolymers may be categorized into three main types based on their genesis and production [4].

1.1.1 Type 1

Polymers instantly extracted from biomass. Proteins like gluten and casein and polysaccharides like cellulose and starch.

1.1.2 Type 2

Polymers extracted from renewable bio based monomers by typical chemical synthesis. A best example is polylactic acid (PA) which is a biopolyester polymerized from the monomers of lactic acid.

1.1.3 Type 3

Polymers synthesis by microorganisms or biologically modified bacteria. This class of biopolymers mainly consists of polyhydroxyalkonoates (PHA).

Different biological materials according to their origin is shown in Table 1.1 [5].

Table 1.1 List of biological materials

TYPE 1: Polymer directly extracted from biomass			
Polysaccharides			
Starch	Cellulose	Gums	Chitosan
Maize	Wood	Alignates	
Rice	Cotton	Guar	
Potato	Derivatives	Pectins	
Wheat		Locust Bean	
Derivatives		Derivatives	
Proteins			
Plant		Animal	
Soya		Casein	
Zein		Gelatine	
Gluten		Whey	
Lipids			
Crossed-linked tri-glycerides			
TYPE 2: Polymers synthesis from bio-derived monomers			
Polylactate		Other Polyesters	
TYPE 3: polymers produced directly by natural or genetically modified organisms			
PHA		Bacterial Cellulose	

1.2 Biopolymers in food packaging

In food packaging materials the designing and manufacturing is a multistage technique and involves various considerations to manage the final packaging with all the essential properties. The properties may include the moisture uptake, retrogradation, thermal properties and mechanical properties [6].

Development and commercial trials are taking place at increasing rate from cellulose based materials for food packaging. Starch based packaging trails are carried out in the developed countries, however there are some challenges which need to be addressed before it takes the place of conventional petroleum based commodity packaging materials [7].

1.3 Starch

Starch is considered to be a potential candidate to replace the petroleum based materials in near future. It is a natural glucose based material and is extracted from different plant tissues in granular form with particle size between 1-100 micron [8], and the morphology of the granule depends on the resource [3]. These granular particles are originated from the amyloplasts of tubers and seeds and chloroplasts of green leaves [9]. When these granules are treated with warm water, the starch soluble part starts entering the walls of the granule and the remaining poart of the granule swells to a limit where it burst. The granules are insoluble in cold water, however the swelling takes place if the outer surface of granule has been crushed by grinding which results in the formation of gel [10].

Potato, corn and cassava is the most important origin of starches [11]. Approximately 66 million tons of starch were produced worldwide in 2008 [12]. Starch is a beneficial and versatile polymer because of its readily availability and low cost. It also possesses unique physiochemical properties and can be modified through chemicals and enzymes. That is the reason of extensive attention for researchers in food packaging [13].

1.4 Importance of starch in packaging materials

Starch receive extensive attention in food packaging application because numerous amount of starch produced are used in the application of food and beverages industry [7, 13]. It is also directly used as thickener in custards, desserts and sauces and can also be applied as sweetener in drinks after enzymatic hydrolysis. Apart from this, starch is also considered a suitable material for non-food purposes like adhesive in paper, textile industry, fructose, polyols, antibiotics, cyclodextrins and in the processes of sizing of paper and board through different fermentation techniques [12].

1.5 Thermoplastic Starch (TPS)

The raw starch due to its hydrophilic behavior and brittleness makes it inappropriate for various applications. Furthermore the decomposition temperature is lower than the melting point of starch which makes it deficient in the thermal process ability of starch [14, 15]. Starch alone cannot be treated as thermoplastic starch (TPS) until a plasticizer in combination with high shear and elevated temperature is added [16, 17]. Common plasticizers used are glycerol, water, sorbitol, glycol etc [18]. A lot of research has been made in this field during the last decade and TPS has gained much attention to manufacture the biodegradable plastic materials such as shopping bags, planting pots, trash bags, diapers etc [19]. Multiple physical and chemical reactions like gelatinization, decomposition, granule expansion, melting and water diffusion occurs during thermal processing of starch [16, 18].

1.6 Different Techniques to make biodegradable films

Various techniques are used to manufacture bio based materials from starch. Typical techniques for plastic processing may include film casting, extrusion, compression molding, injection molding and spray drying [20]. These techniques are widely applied in the processing and production of conventional petroleum based plastics. However handling and controlling the starch is far more complex and difficult than that of traditional polymers. It is attributed to poor processing properties of starch like high viscosity, fast retrogradation, phase transition and water evaporation etc. However with appropriate formulations and adequate processing conditions, these properties can be overcome [21].

Common techniques used for TPS modifications are as follows:

1.6.1 Film casting

Film casting is one of the common technique used for starch processing and producing films [22-24]. It consists of four major steps which include solution making, gelatinization, casting and drying. The solid starch is mixed with plasticizers directly in water and heated to 95°C temperature. Then the mixture of starch and plasticizer is mixed for about 10 minutes. The blending is carried out in Brabender viscograph cup whose temperature depends on the plasticizer used in the mixture e.g. high temperatures are used if glycerol is used as plasticizer in the mixture. After the mixing flat acrylic or Teflon plates are used to hold the gelatinized suspensions. The plate is placed in oven at 40-75°C for 24 hrs. and are dried [21].

Plasticizers facilitate the starch processing and enhance the mechanical properties of TPS films. By adding suitable plasticizer the flexibility of the films may increase. Commonly plasticizers used are glycerol and sorbitol. Other plasticizers like malic acid is also been reported to increase the flexibility of films [24, 25] [26].

1.6.2 Extrusion

Extrusion is also a technique widely used to process starch. It consists of various unit operations like crushing, blending, shearing, heating, cooling, sizing and shaping. The extrusion temperature can kept upto 200^{o}C and the residence time is 10-60 seconds [27]. The material is entered through a hopper and solid material is converted into semi solid mass in compression zone of extruder. The mass is then passed through an opening to produce an extrudate of a desired shape. In the case of starch modification the extruder is used as chemical reactor [28].

Extrusion is widely used because of its suitable processing conditions like treating polymers with high viscosity without solvents, controlling the residence time and the operation of multiple injection [29]. The production of biodegradable TPS has triggered much attention and the usage of this technique in food packaging has also gained interest [30].

1.6.3 Compression Molding

Compression molding is also one of the technique widely used to manufacture the starch based plastics [31]. This technique consists of three major steps; gelatinization of starch, expansion and drying. The process of gelatinization and extracting the prepared sample from the mold are the two major steps of this method. Specific chemicals are used in the mixture of TPS like stearic acid and magnesium stearate to prevent the stickiness to the mold [21].

1.6.4 Injection Molding

Injection molding is also widely used method to produce starch based plastics [32]. In this method pressure is applied to the molten mass and passed it through a cavity or mold to obtain the final required product [33]. The four major steps like filling, packing, cooling and ejection makes it a continuous process [34].

In the filling step the molten mass is fed into a cavity or mold. In the second step of packing the molten polymer is packed in the mold to balance the shrinkage of material caused by the solidification of material. The mold is then cooled till the material shows rigidity in the cooling step. In the last step of ejection, the mold is opened to remove the required part [35].

1.6.5 Spray Drying

Spray drying is also one of the technique to produce the TPS material. It is and a well-known unit operation. In this technique semi amorphous or amorphous particulates are produced from liquid solution. It is regarded as a fast drying technique with low moisture contents in the particulates [36].

This method is majorly used in food and pharmaceutical industries. Different properties like solvent residual amount, morphology and crystallinity of the material can be enhanced and the granular integrity is maintained through this technique. A heating zone in the form of cylindrical chamber is used for drying. Heated air is used in the chamber and the feed is sprayed which results in the solid particles without the solvent. Heat and mass transfer both occurs due to the direct contact of liquid and gas [37].

The spray driers are classified on three important parameters [38]:

- The ratio of height to diameter of the drying chamber
- The type of air flow
- Type of atomizer

1.7 Why Spray Drying?

One of the major challenges that need to be addressed before producing TPS films for coatings and packaging materials is the recrystallization i.e. the retrogradation of starch.

Starch shows sensitivity towards water, as it triggers the recrystallization which effect the mechanical properties in terms of flexibility and tensile strength [39].

The use of conventional techniques for the production of TPS films for packaging purpose have some specific challenges, including [21]:

- Various physical and chemical reactions can take place during the process.
- The complex rheological behavior of TPS makes it difficult to treat and handle especially when an additive is mixed in the formulation.
- Unwanted bubble in starch based products can be formed which can alter the mechanical properties of the films.

Moreover the combination of water and plasticizers exhibits the recrystallization due to the recombination of amylopectin and amylose, which results in poor mechanical properties of the required product [16].

Spray drying is the process which is found to prevent this disturbing effect of water and keep the activity of plasticizer during the production process. It is considered to an alternate thermal route to produce dry amorphous starch based polymer blends. This process is under developed but has a lot of potential to manufacture amorphous particulates and improve the properties of TPS blends [37].

1.8 Importance of Plasticizers

Plasticizers are low molecular weight nonvolatile compounds and are extensively used in polymer industries as additives. The main purpose is to lower the glass transition temperature (Tg), reduction in Tg will help to enhance the process ability and elongation of polymers. A plasticizer is define as "a substance or material incorporated into a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility" by IUPAC (International Union of Pure and Applied Chemistry) [2].

The Plasticizers can be categorized as internal and external. The internal plasticizer become a part of the polymer, reacts with the original portion of polymer or co-polymerized with the structure where they cannot be separated easily. Whereas the external plasticizer are not chemically bonded with the structure and therefore can easily be separated by extraction, evaporation or migration [40]. Starch based blends cannot be thermally processed without a plasticizer, as the decomposition temperature is higher than that of the melting temperature. Various plasticizers are analyzed and developed to process starch thermally [14].

1.9 Plasticizers

Various plasticizers were analyzed and investigated to improve the properties and the performance of material. The most common plasticizer used in thermal processing of starch is water, but water alone in TPS leads poor mechanical properties like brittleness and stiffness which results in fast retrogradation and reduce other applications [21].

Other common plasticizers for TPS blends include glycol, urea, formamide, sorbitol, critric acid, glycol, organic acid and amino acid [19, 41-43]. Glycerol is widely used after water because of its low cost, readily availability and high boiling point [18]. The starch plasticizer interaction can be very peculiar, as the hydrogen bonding takes place with the starch backbone in a wide temperature range. The H-bond formation takes place as the temperature increases. As a result the material exhibits a rubbery behavior with an increase in mobility of matrix and decrease in the viscosity [2]. Plasticizers including amide groups were also investigated for TPS plasticization. The use of amino acid results in decrease of starch retrogradation. The main properties of TPS blends i.e. retrogradation and mechanical properties largely depends on the hydrogen bond forming abilities of between the starch matrix and plasticizers [42]. The hydrophilic nature and plasticizer concentration mainly affect the moisture affinity of TPS blends e.g. glycerol plasticized films absorb more water than those of sorbitol plasticized films [22].

1.10 Amphiphilic Plasticizer

An amphiphilic plasticizer is the additive which possesses both hydrophilic and lipophilic properties. Various amphiphiles were reported in literature which includes tween 60, linoleic acid and zein to produce TPS blends. The addition of these amphiphilic plasticizer in the formulation of TPS blends results in [44]:

- Improved extensibility
- Enhanced processability and plasticization

- Decrease rigidity, stiffness and strength.
- Enhanced flowability.

In this context an amphiphilic plasticizer with low molecular weight, considerable high solubility and high boiling point will be analyzed. The thermal properties, mechanical properties, degree of crystallinity of films, the relative weight change and the retro gradation at 50% relative humidity of the produced films will be evaluated.

Chapter 2 – Literature Study

The purpose of this survey is to discuss all the research and developments being done in formulation of thermoplastic starch films. Starch is a potential candidate to substitute the synthetic polymer for packaging materials to some extents. However there are some challenges that need to be addressed before it take the place of conventional products used for the packaging. Figure 2.1 shows the overall research carried out for the last two decades on thermoplastic starch used for packaging. However the Water susceptibility, low degradation temperature of starch and poor mechanical properties stop its way to replace the synthetic polymers. To overcome these problems different combinations of plasticizers are used for better mechanical properties and biodegradability of the desired product. The starch is plasticized with different plasticizers under shear and heat using conventional processing methods like extrusion and injection molding.

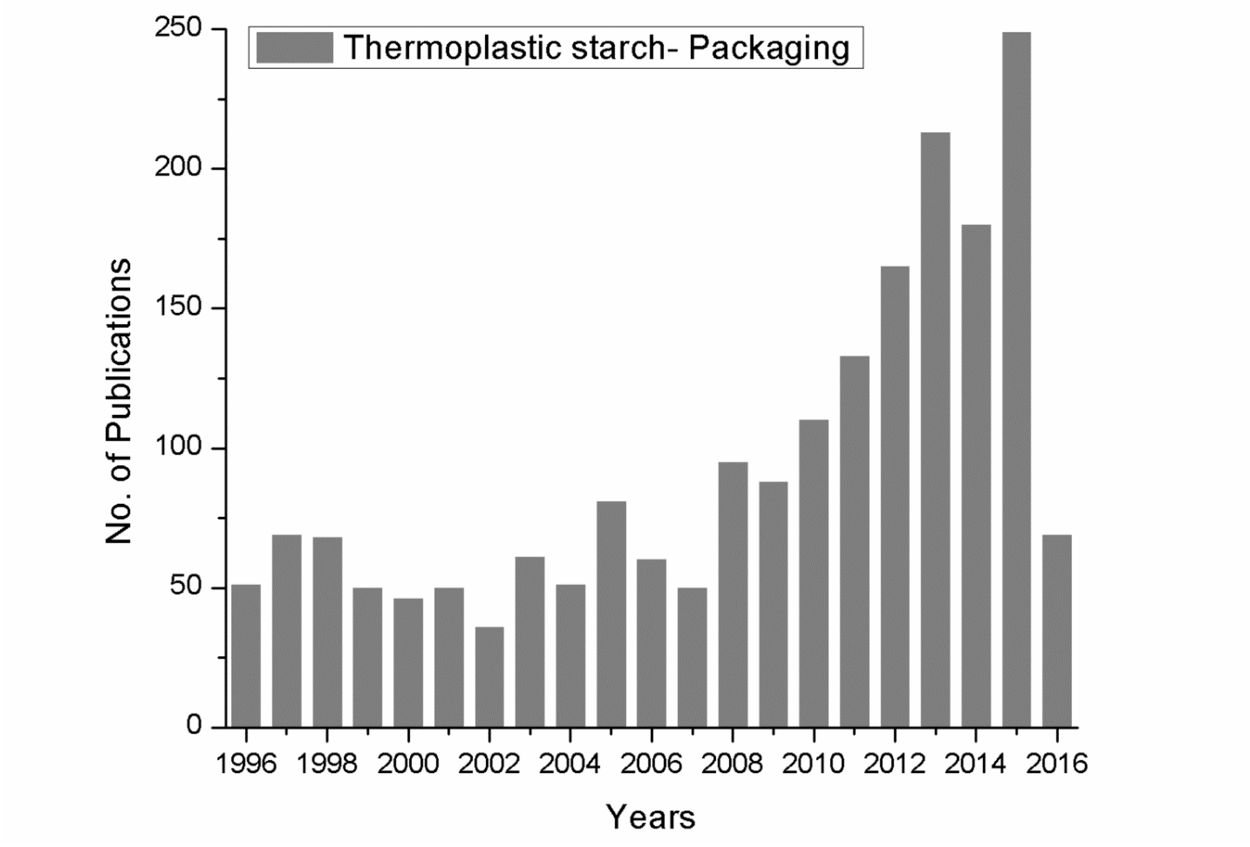


Figure 2.1: Research in the field of thermoplastic starch for packaging material

Niazi et al [45] reported the role of plasticizers in spray dried starch. The films were prepared by compression molding of solution spray dry (SSD) by using glycerol and urea. It was found that urea was more effective plasticizer than glycerol because of its small molecular structure and more interaction with the amylopectin fractions which results in lower glass transition temperature, lower tensile strength, low degree of retrogradation and high elongation. Although glycerol is also a good plasticizer but it did not showed good interaction with the amylopectin fraction rather it stays outside or at the interface of the amylopectin structure which promotes the retrogradation in the humid conditions.

In another work Niazi, Zijlstra [46] reported malic acid as plasticizer for thermoplastic starch. Some more selected plasticizers were used to formulate TPS films i.e. malic acid, isoleucine, asparagine and combinations of glycerol and urea with malic acid. The powder obtained in SSD and the films of malic and asparagine with co plasticized starch were amorphous. The films containing malic acid were transparent while the films containing asparagine were marginally mat. The powder and the films which comprises of isoleucine formed crystal structure associated to isoleucine were not transparent. It was investigated that 15% malic acid with urea plasticized starch film overcome the retro gradation for 56 days at relative humidity 100%. Isoleucine was isolated during the SSD process because of the low interaction with the starch. Tg was only recorded for the films containing asparagine and all the films were stable at 160^{o}C.

Yokesahachart et al [43] reported the effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with poly (lactic acid). Polylactic acid (PLA) was blended with TPS. Three amphiphilic molecules i.e. linoleic acid, tween 60 and zein were used and mixed in blend to analyze the characteristics and tensile properties of TPS. The technique used for the production of TPS was twin screw extruder and water and glycerol were used as plasticizers. The addition of amphiphiles enhanced the processability and plasticization, facilitated melting and reduce Tg and Tm of TPS materials which is helpful in further converting processes. The rigidity, tensile strength and stiffness of TPS materials decrease with the addition of amphiphiles. Zein plasticized starch was 2-3 times rigid and 5 times stronger than that of linoleic acid plasticized starch and tween plasticized starch while the latter two showed two time more extensibility than the first one. The rigidity and tensile strength were enhanced 1-30 times by blending it with 30-70% w/w of PLA. By increasing PLA content in TPS-PLA blends the modulus and tensile strength also increased.

Olivato et al [46] reported the effect of malic acid (MA), citric acid (CA) and tartaric acid (TA) in starch/polybutylene adipate co-terephthalate blown films by investigating structural, barrier and mechanical properties of the films in various relative humidities. The films obtained by using higher concentrations of CA and TA (1.5wt %) enhanced the tensile strength (6.7 MPa and 6.8 MPa respectively), decreased the water vapor permeability and enhanced homogenous structure. MA was lacking in efficiency because of its compatibilising effect. The elongation of the films was also affected by changing the relative humidity. No side reactions took place due to addition of additive and the examined results were associated to esterification reaction and hydrolysis of starch resulting in films with attractive properties.

Xiaofei Ma et al [47] reported the influence of plasticizer containing amide groups on the properties of TPS. Urea, acetamide and formamide with glycerol as a reference were used in this literature. FTIR spectroscopy was used to investigate the interaction of hydrogen bond between the plasticizer and the starch. The oxygen of both C-O-C and C-O-H group in starch has the tendency to form hydrogen bond with these plasticizers. The order urea > formamaide > acetamide > polyols reported to have hydrogen bond forming abilities. By using X-ray diffractrometry the retrogradation of acetamide, formamaide, and urea plasticized starch is analysed at three different relative humidities i.e. RH=0%, 50% and 100%. Formamide and urea showed resistance towards retrogradation. The mechanical properties of urea plasticized starch showed poor flexibility but good breaking stress. Whereas the formamide plasticized starch showed the opposite reults to that of urea plalsticized starch. The hydrogen bond between the plasticizer and starch is considered to be the important factor in evaluating the properties of TPS. On the contrary the plasticizer play an important role in water resistance of TPS. The higher the plasticizer absorbed water the maximum was the water resistance of TPS.

Erik Olsson [48] reported the influence of citric acid and curing on moisture sorption, diffusion and permeability of starch films. Solution casting was used to produce starch films containing citric acid with different amounts and the films were analysed in different curing temperatures and compared with glycerol plasticized films. Controlled moisture generator was used to test the films by measuring the water sorption and diffusion coefficient and calculate the water vapor permeability. By comparing it with glycerol plasticized films the films containing increasing amounts of citric acid resulted in low water vapor permeability, diffusion coefficient and equilibrium moisture content. It was also reported that the above characteristics were reduced by curing the films in 30 pph citric acid at 150°C in high relative humidity.

Jin Hui Yang [49] reported a novel plasticizer for the production of TPS. In this context a novel plasticizer was synthesized to produce thermoplastic starch from corn starch. Stable and strong hydrogen bond of ethylenebisformamide with starch molecules was shown in FTIR when compared to native corn starch. The A-style crystallinity was also destructed in native corn starch by using this plasticizer shown by XRD. SEM showed that the granules were transferred to a homogenous system. The mechanical properties were also investigated by the plasticized starch at relative humidity of RH=33% for one week, which resulted in the elongation to 264%.

Narendra reddy et al [50] reported the cross linking of starch through citric acid and enhanced the tensile strength, improve the thermal stability and decrease the starch films dissolution in formic acid and water. Starch has restricted its application because of poor mechanical properties and water absorption. Cross linking could improve the starch properties however current cross linking techniques were either toxic or expensive. In this context citric acid was used to improve the strength and stability by cross linking approach. The cross-linked films showed 150% higher strength than those of non-crossed linked. Crossed linked films with 5% citric acid lose 35% weight when kept in formic acid at 150°C for 5 hrs. Whereas the films having non crossed linking dissolved immediately.

Yachuan Zhang [51] reported the crystallization of high amylose starch by the addition of plasticizers at low and intermediate concentrations. Monosaccharides and polyols i.e.

glycerol, sorbitol, ethylene glycol, fructose, glucose and mannos were used to plasticized pea starch films at 0% to 25% (w/w, plasticized/starch). The films were stored at 50°C relative humidity for 14 days. The increase in concentration of plasticizer increased the crystallinity of films and decrease the water vapor permeability, moisture content and elongation of the films. It also showed that plasticizers added above 20% decreased the crystallinity of the films, resulted in the plasticization effect.

B. Adikari [52] reported the effect of plasticizers on the moisture migration behavior of low amylose starch films during drying. In this context the competitive and synergistic interaction between the plasticizers in low amylose TPS that either reduced or enhanced the effective moisture diffusivities and the water migration fluxes. Plasticizers like glycerol and xylitol was used in starch either separately or in a combination of 1:1. It was found that xylitol plasticized films were higher in moisture diffusivities and water migration than glycerol plasticized films. The films containing both plasticizers in low concentration reduced the moisture migration fluxes and the moisture diffusivities. On the other hand with high concentration of plasticizers at 15% or above enhanced the moisture diffusivities and moisture migration fluxes. Glycerol was found to be stronger in terms of the above properties than xylitol.

Niazi et al [53] reported crosslinking of oxidized thermoplastic starch films. Malic and Citric acid and glycerol as a co-plasticized were used to prepare thermoplastic starch films. They were surface cross-linked and the films were soaked in sodium benzoate aqueous solution and were exposed to UV irradiation. Despite of varying combination and plasticizers, all the films produced by SSD technology were amorphous. Malic acid and citric acid plasticized TPS blends were better than those of glycerol plasticized and co plasticized blends in terms of their better hydrogen bonding interaction and better thermal stability. The strength of the films was improved by UV cross linking. The cross linking of TPS films were investigated to be more efficient when they were soaked in the solution of sodium benzoate. However the cross-linking decreases the solubility and swelling of the prepared films. The films were analyzed in RH50% and RH100% and it was observed that the films conditioned in RH50% had lower degree of swelling and better strength. Low swelling and high strength of cross-linked films of citric acid plasticized and co plasticized were observed as compared to those of cross linked films of malic acid plasticized and co plasticized. It has been reported that carboxylic acids like citric and malic acid acted different than most of the common plasticizers used like urea and glycerol as they show deep interaction and lower the retro gradation significantly especially malic acid. However the low retro gradation increases the moisture absorption so various pathways should be developed to decease the effect of moisture and acquire better mechanical properties.

Chapter 3 – Aim of Project

3.1 Selection of biopolymer

Starch is extracted from various agriculture products and its alteration and growth into technical and consumer goods and the applications of these goods is considered to the oldest branch of chemical industry. Presently, worldwide production of starch and the starch products are reported to be 70 million ton per year. Starch and its derivatives present in commercial products are almost found in every chemical industry [47].

Starch is obtained from a natural resource which is naturally biodegradable and this combination of biodegradability with readily availability and cost reduction has been a source of attraction for the researchers and made it most suitable over various classes of synthetic and natural materials tested [13]. The main constituents of starch i.e. amylose and amylopectin can be extracted in a range of various blend ratios [48]. Water is added to starch in combination with other low molecular plasticizers that interacts through hydrogen bonding with the starch backbones and results in the formation of TPS [21].

3.2 Importance of the project

The increased activity to pollute the environment and high oil prices pushed the researchers to replace the petroleum based commodity plastics to biodegradable plastics in cost effective way and with better mechanical properties [2]. The retrogradation occurs due to the recombination of the amylose and amylopectin through the use of plasticizers and water thus resulting in the recrystallization[48].

The main drawback of using the TPS as packaging material is the retrogradation of starch which results in poor mechanical properties like tensile properties and brittleness. Numerous studies have been reported on the interaction between the starch plasticizer and co-plasticizers to establish a method to reduce retrogradation [49].

3.3 Selection of plasticizer

In order to overcome this disturbing effect of retrogradation, lot of attention has been paid to the plasticizers and the techniques to produce TPS which would reduce the effect of water on TPS. Moisture uptake from the environment also enhances the rate of retrogradation of TPS. If a plasticizer with a capability to resist moisture from the environment is used in the formulation of TPS T-bones then it would greatly reduce the retrogradation effect on the TPS T-bones, which would ultimately result in better mechanical properties as well.

An amphiphilic plasticizer is the additive which possesses both hydrophilic and lipophilic properties. The amphilphiles usually interacts with water molecule through hydrogen bonding. As the carbon chain increases the solubility of acid in water decreases as the dispersion forces becomes much stronger and dipole forces becomes less important [50]. Moreover the boiling point of the plasticizer should be high than that of processing temperature i.e. 140°C.

In light of the above context three main properties were considered for the selection of the plasticizer

- Short chain molecule
- Considerable solubility in water
- High boiling point

Two amphiphilic plasticizers were studied in this context i.e. isoleucine and butyric acid. The aim was to process and facilitate the starch with water through its polar property and resist the moisture uptake through its non-polar property. It is expected that, through reducing the moisture uptake of the TPS T-bones, the rate of retrogradation would decreased which probably will result in improved mechanical properties.

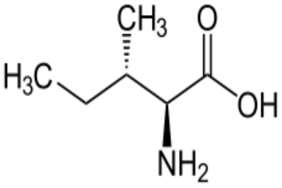
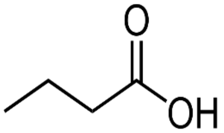
Isoleucine	**Butyric acid**
	

Figure 3.1: Structure of Amphiphilic plasticizers

Another co-plasticizer i.e. malic acid is used in the formulation of TPS with isoleucine and butyric acid in order to maintain the balance between the strength and flexibility of TPS T-bones. Moreover malic acid is also a strong anti retrogradation agent which inhibits the retrogrdadtion of starch and increase the esterification. Strong hydrogen bond, grafting and cross-linking has also been found between starch and malic acid. It also controls swelling of the products and increase the flexibility as well [26].

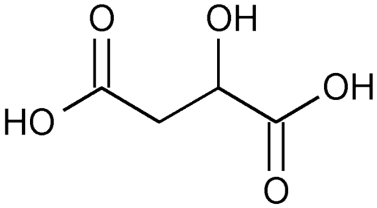


Figure 3.2: Structure of Malic acid

3.4 Selection of Spray Drying

The most common techniques to produce bio based plastics from starch are extrusion, injection molding, casting and compression molding. The production of TPS through these techniques involves water in the operation. The plasticizer and water combined results in the retrogradation of starch and disturb the properties of TPS. To maintain the plasticizer effect and to deal with the disturbing effect of water a new thermal route is preferred in this study which is spray drying process. Various blends of TPS from starch water dispersion and solutions were performed. This technique is underdeveloped but a lot of attention is being paid since it produced amorphous particles and considered as fast drying process with low moisture content [37].

3.5 Important properties of TPS T-bones

Various properties should be controlled in order to get biodegradable food packaging material. The moisture absorption in relative humidity enhance the retrogradation thus effecting the mechanical properties [51]. In this study the effect of moisture uptake by TPS T-bones was greatly reduced by using an amphiphilic plasticizer which resulted in the reduction of retrogradation and improved mechanical properties. However there must be a proper balance between strength and flexibility [45]. As the isoleucine plasticized films were reported to be brittle in nature, a co-plasticizer i.e. malic acid was also used in the formulation with isoleucine and butyric acid to enhance the flexibility of the TPS T-bones.

3.6 Objectives

- To reduce the moisture uptake of thermoplastic starch (TPS) T-bones by using an amphiphilic plasticizer.
- To control the rate of retrogradation and enhance the mechanical strength of the TPS T-bones.
- To investigate the effect of co-plasticizer on the properties of thermoplastic starch T-bones.

Chapter 4 – Materials and Methods

This chapter includes the materials and methods used to produce the TPS powder and the T-bones.

4.1 Materials

The materials used in this research are corn starch (soluble EP), L-Isoleucine, Isobutyric acid and malic acid (EP). The following table (4.1) gives the details of materials and their suppliers.

Table 4.1 Materials descriptions, makers, and suppliers

Description	Supplier
Starch, soluble EP	Daejung Korea
L-Isoleucine	Daejung Korea
Isobutyric acid	Daejung Korea
Malic acid (extra pure)	Daejung Korea

4.2 Sample Preparation

The samples were prepared from aqueous solution using 15% (w/v) of corn starch and 30% (w/w and w/v) of plasticizer based on dry starch. Different ratios (w/w, w/v based on starch) of amphiphilic plasticizer i.e. 30%, 15%, 10% and 5% of each isoleucine and butyric acid were used as a plasticizer where as 30%, 25%, 20% and 15% of co-plasticizer i.e. malic acid was used in combination of amphiphilic plasticizers to maintain the plasticizer quantity to 30% based on starch. Heating plate was used to heat the solution at 95^{o}C for 25 minutes and stirred by a mechanical stirrer at a rate of 600 rpm. Samples names and corresponding description are mentioned in table (4.2).

Table 4.2 Sample names and description.

Samples	Description
U.S	Untreated starch
S.D	Spray dried starch
30MA.PS	30% Malic acid plasticized starch
30IS.PS	30% Isoleucine plasticized starch
25MA5IS.PS	25% Malic acid and 5% Isoleucine plasticized starch
20MA10IS.PS	20% Malic acid and 10% Isoleucine plasticized starch
15MA15IS.PS	15% Malic acid and 15% Isoleucine plasticized starch
30BUPS	30% Butyric acid plasticized starch
25MA5BU.PS	25% Malic acid and 5% Butyric acid plasticized starch
20MA10BU.PS	20% Malic acid and 10% Butyric acid plasticized starch
15MA15BU.PS	15% Malic acid and 15% Butyric plasticized starch

4.3 Preparation of TPS powder

A mini spray drier (Shanghai Sunyitech Co. Ltd, SP – 1500) with a (0.7mm) dia nozzle was used to process the obtained solution for production of dry powder. The dry powder with different combination of plasticizers was then converted into TPS T-bones by compression molding technique. The operating conditions of spray dryer was controlled i.e. the inlet temperature, outlet temperature, wriggle pump speed and the fan speed. The wriggle pump speed was set at 750 ml and the fan speed was at 60 Hz. The inlet and outlet temperature was 140^{o}C and 80^{o}C respectively. The dried powder was collected at the bottom of the spray drier in sample collector. The waste powder in cyclone was discarded.

4.4 Preparation of T-bones

T-bones (63.5 X 9.53 X 1.8 mm) were prepared from TPS powder through compression molding technique. The molding temperature for all the samples were kept at 140^{o}C and progressive pressure of 25 bars was applied for 5 minutes to compress the sample. At low temperature there was no significance flow of the powder but degradation of the sample was observed at temperature higher than 150°C.

4.5 Thermogravimetric and Differential Thermalgravimetric Analysis (TGA/DTGA)

TGA of freshly produced formulation was performed in an open pan. The temperature range was 25°C to 800°C with a heating rate of 15°C/min and 5-10 mg of each sample was tested. Origin 8.1 software was used to determine the derivative of weight loss curve. The decomposition temperature was also measured according to the method used by Soliman *et al.* [52].

The ascertain specific properties of TPS like mass loss or gain because of oxidation, decomposition or loss of volatiles such as moisture of material is analyzed by TGA. Whereas DTGA is done to evaluate the changes in material in the form of endothermic or exothermic peak.

4.6 Fourier Transform Infrared Spectroscopy (FT-IR)

The freshly prepared samples were analyzed by Fourier transform infrared FT-IR (PerkinElmer, Spectrum^{TM} 100). It provides the intrinsic interaction between the starch molecules and the plasticizers and the structural changes that occurred during the plasticization and the spray drying process. The FT-IR spectrometer recorded the spectra with an Attenuated Total Reflection (ATR) unit and 32 consecutive scans were carried out at rate of 4 cm^{-1} resolution for each spectrum. Ambient temperature was used for all the analysis.

4.7 X-Ray Diffraction (XRD)

XRD was performed to measure the crystallinity of the samples by the interaction with X-Rays at different angles on various planes. Many peaks were generated and the position of peaks were found by Bragg's law with the help of Miller indices.

XRD (STOE – Germany, θ-θ) was carried out for both freshly produced TPS powder and T-bones. Cu radiations with wavelength of 1.5418Ǻ were used at angle of 5° 2Ө to 40°

2ϴ. 0.02^o step size of 2ϴ was maintained at scan speed of 2 s/step. The operation was carried out at 40 kV and 40 mA.

4.8 Scanning Electron Microscopy (SEM)

Spray dried powder morphology were studies by a Scanning Electron Microscope (JSM-64900). Accelerating voltage applied was 20.00 kV for the measurements. The probe current and the energy ranges were 1.0000 nA and 0-20 keV respectively. A thin palladium/platinum conductive layer was used to cover the samples. The layer was made by sputter coater.

4.9 Moisture Uptake

A relative humidity i.e. RH=50 (35.64% of $CaCl_2$ solution) was used in order to store the TPS T-bones (63.5 X 9.53 X 1.8 mm) to measure the moisture uptake. The moisture uptake of TPS T-bones kept at RH=50% were analyzed gravimetrically. Measurements were carried out daily for the first week. After that weekly calculations were performed up to 56 days. The moisture uptake of TPS T-bones were calculated using the following equation [53].

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

Where, Day, n = day of measurement,

Day, o = day at which film was prepared

4.10 Mechanical Testing

Tensile tester (Shimadzu, M129607) was used to measure mechanical properties of TPS T-bones. The cross head speed was maintained at 10mm/min. Samples were kept in relative humidity RH=50% for 24 hours before testing. At least 5 TPS T-bones of each sample was tested for the validity of research.

4.11 Powder Yield

The yield is defined as “the ratio of the actual amount of solid powder product to the maximum amount of powder achievable” [54].

Powder yield is one of the important consideration for all processing operations. The yield was measure as the ratio of quantity of product obtained to the quantity of starch and additive used as an input material (Equation 4.2).

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

Chapter 5 – Results and Discussion

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

5.1 Moisture Uptake

The moisture absorption data was recorded at 50% relative humidity and the specific behavior of all plasticized and co-plasticized T-bones were analyzed and compared. The calculations were performed on daily basis for the first seven days. After that weekly calculations were taken till 56th day.

Isoleucine and butyric acid are amphiphilic in nature with structure containing both polar and non-polar parts. The non-polar part which is typically considered the hydrocarbon chain tends to resists the moisture. And the polar part which include a hydroxyl group participate in hydrogen bonding with starch matrix. At RH 50% a minimum percentage of moisture absorption was observed in amphiphilic plasticized T-bones. Malic acid on the other is hydrophilic in nature with two hydroxyl groups in the structure absorb moisture throughout 56 days than amphiphilic plasticized TPS T-bones shown in figure (5.1).

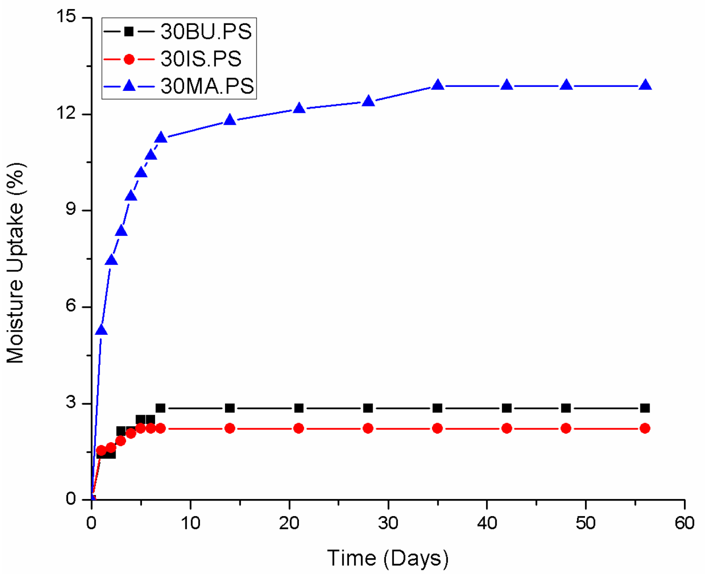


Figure 5.1 Moisture Uptake Curves at 50% RH for butyric acid, Isoleucine and malic acid plasticized TPS T-bones.

The 30% butyric acid plasticized (30BU.PS) T-bones were too hazy and gritty. The gritty nature of 30BU.PS was reduced by the addition of co-plasticizer i.e. malic acid. The films containing malic acid was reported to have flexible nature and high strain at break [26, 46].

In mixed plasticized formulations the moisture absorption is reduced to a high extent by using amphiphilic plasticizer i.e. butyric acid and Isoleucine, however the trend in the T-bones having malic acid as co-plasticizer showed relatively high moisture absorption. This may be due to the addition of malic acid in the formulation. The moisture absorption increased as the quantity of malic acid increased as shown in the figure (5.2).

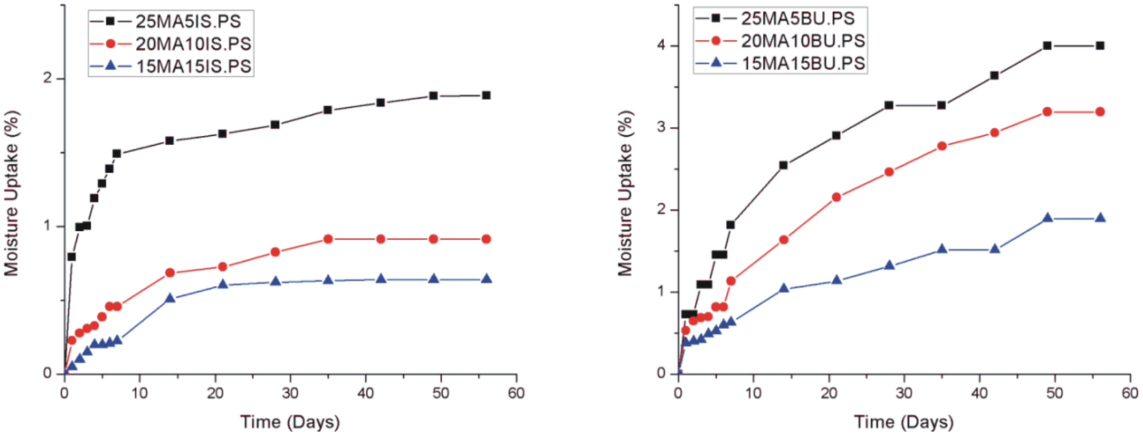


Figure 5.2 Moisture Uptake Curves at 50% RH for isoleucine and butyric acid co-plasticized TPS T-bones.

The T-bones with 30 % isoleucine plasticized was regarded to be the most efficient plasticizer in reducing the moisture uptake as shown in the figure (5.1). This is due to the high crystalline nature and amphiphilic property of the plasticizer. The T-bones obtained using 30IS.PS were also hazy, mate and brittle. However the brittleness kept on decreasing on increasing the quantity of co-plasticizer i.e. malic acid. The moisture absorption also increased when the quantity of malic acid increased.

When observed the calculations for the first week, the moisture absorption rate was high throughout the first week in both the formulations containing co-plasticizer as shown in figure (5.3).

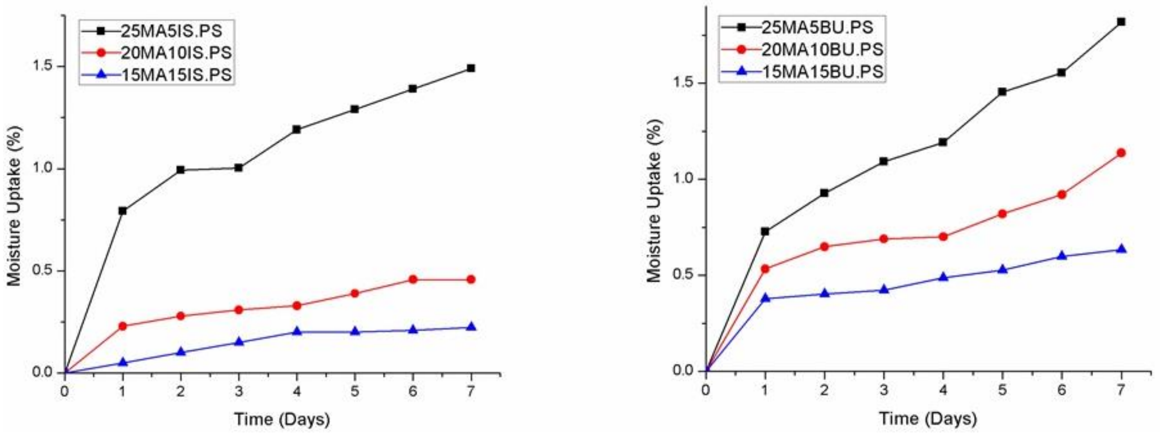


Figure 5.3 Moisture Uptake Curves at 50% RH for butyric acid and isoleucine co-plasticized TPS T-bones for 1st week.

The moisture absorption rate was more pronounced during the first week in both plasticized and co-plasticized formulations because of major arrangements of molecules occurred in conjunction with initial wetting [51].

When both the co-plasticized formulations were compared, the T-bones containing isoleucine tends to resist more moisture than that containing butyric acid as shown in figure (5.2-5.3). That is because the more crystalline nature and hydrophobic part of isoleucine. The moisture uptake of the T-bones containing 15% isoleucine and 15% malic acid i.e. 15MA15IS.PS absorb the lowest moisture among the formulations. The order of moisture uptake was malic acid > butyric acid > isoleucine. The isoleucine resists high amount of moisture in 50% relative humidity.

By comparing this data with literature table (5.1) isoleucine and butyric acid plasticized TPS samples resisted moisture uptake more than glycerol, urea, malic and citric acid plasticized TPS samples [45, 55]. It is because of their brittle and crystalline nature. The miscibility of isoleucine is also very low in water that resulted in low hydrogen interactions with starch. Also due to its crystalline nature, it crystallizes in the process. That is why the TPS samples including isoleucine remained crystalline due to its crystalline domains. The reason of resisting moisture in isoleucine and butyric acid plasticized TPS samples was because of their amphiphilic property i.e. the non-polar part which repelled moisture in humid conditions. However butyric acid plasticized T-bones were too hazy and gritty. Malic acid on the other hand was hydrophilic in nature absorbed moisture almost more than citric acid, glycerol, and urea. Morever, as showed in literature due to its strong anti retrogradation and flexible nature it was used as a co-plasticizer. Malic acid mixed plasticized with glycerol and urea absorb more moisture than malic acid mixed plasticized with isoleucine and butyric acid [55]. A very low moisture uptake and hence a low increment in the weight was recorded for 56 days at relative humidity of 50%.

Table 5.1 Comparison of Moisture Uptake with literature

Plasticized TPS Samples	**Moisture Uptake**	**References**
Malic Acid	High	This work
Isoleucine	Low	
Butyric Acid	Low	
Malic & Butyric Acid	Low	
Malic Acid & Isoleucine	Low	
Glycerol	High	[45, 46, 55]
Urea	High	
Asparagine	Low	
Citric Acid	High	
Malic Acid & Glycerol	High	
Malic Acid & Urea	High	
Citric Acid & Glycerol	High	

5.2 Crystallinity of freshly prepared Thermoplastic Starch Powder

XRD was performed in order to analyze the crystallinity of freshly prepared TPS powder after spray drying. Figure (5.4) shows the X-ray diffraction patterns of raw starch. The raw starch possessed a semi crystalline structure. Broad crystalline peaks at 2Θ = 15.04°, 17.23°, and 23° were observed as shown in figure (5.4). These peaks gave an account of B- and V- type crystallinity [56, 57].

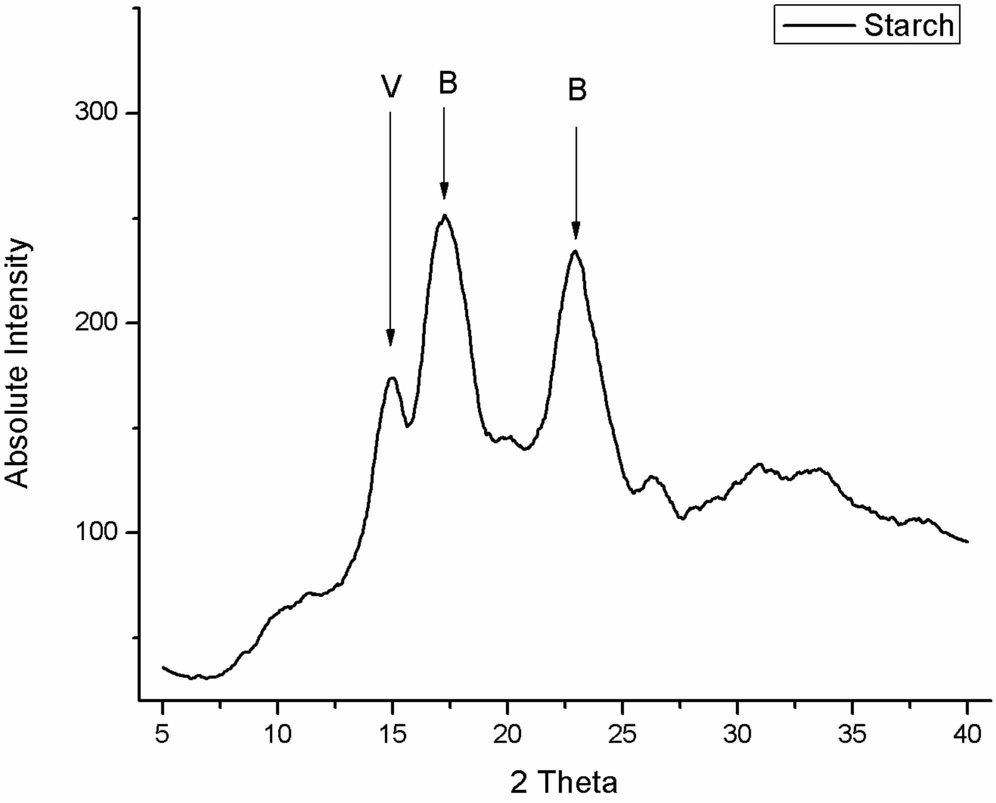


Figure 5.4 X-ray Diffractogram of Raw Starch

The B- type crystallinity should be eliminated in order to obtain flexible TPS T-bones. Crystallinity should be reduced, as it describes the high brittleness of TPS T-bones [58]. All the formulated plasticized and co-plasticized TPS solutions were passed through a spray dryer and white powder samples were collected. Malic acid and butyric acid plasticized and co-plasticized powder samples were amorphous and no sharp crystalline peaks were observed figure (5.5-5.6). However the isoleucine plasticized and co-plasticized powder samples indicated crystalline peaks. These peaks were attributed to the crystalline domains of isoleucine present in the samples as shown in figure (5.6).

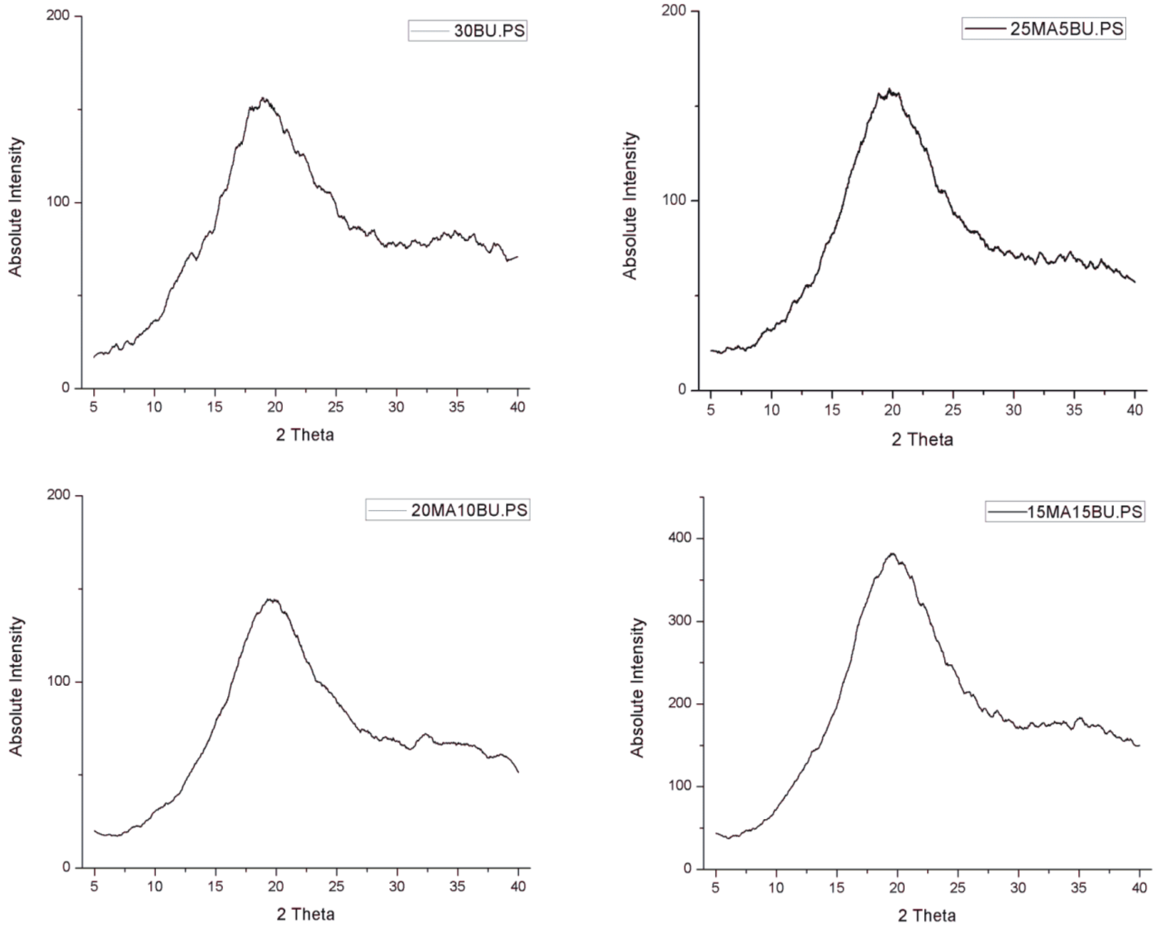


Figure 5.5 X-ray Diffractograms of the freshly produced butyric acid plasticized and co-plasticized TPS powder after spray drying

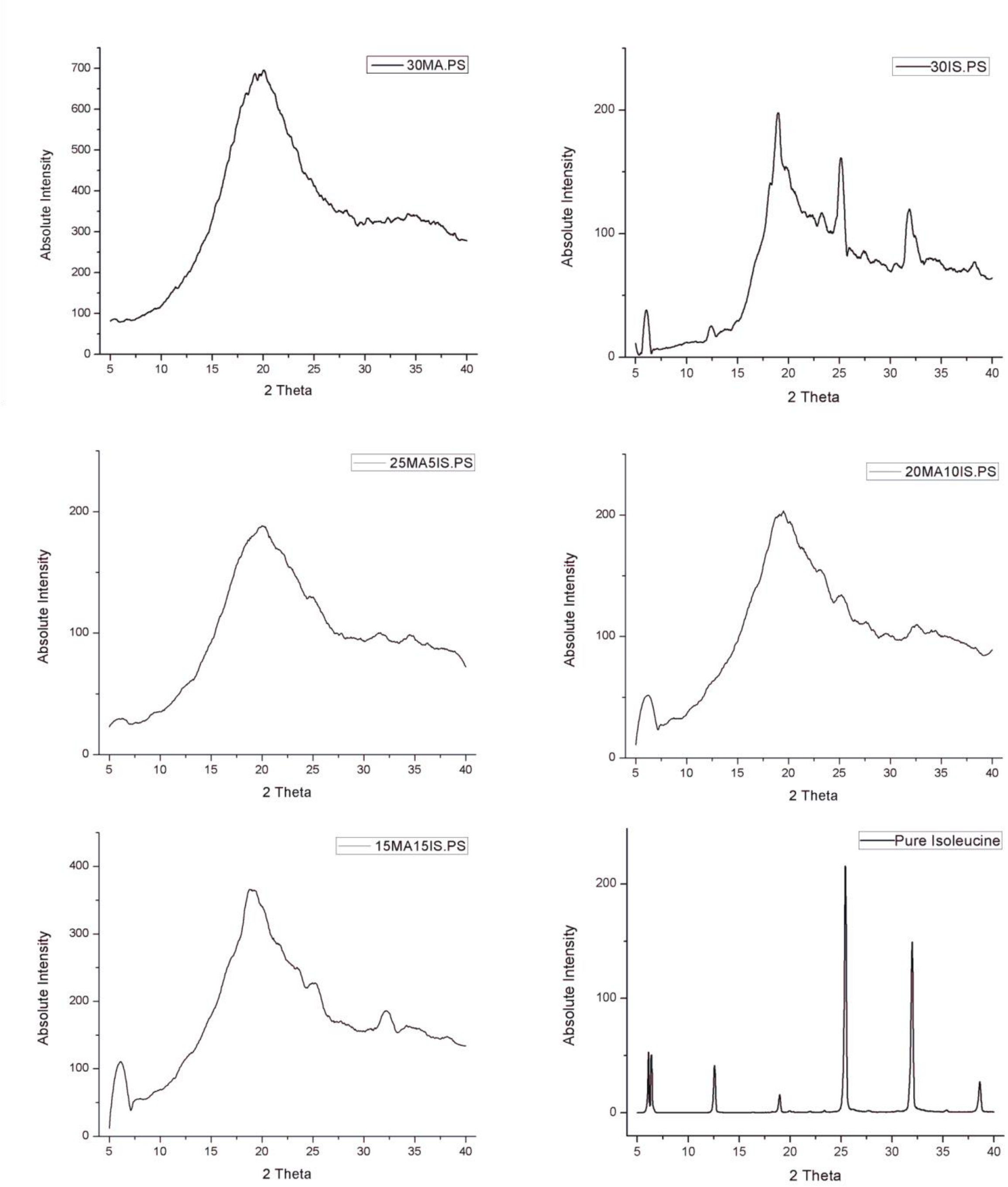


Figure 5.6 X-ray Diffractograms of Pure Isoleucine and freshly produced isoleucine plasticized and co-plasticized TPS powder after spray drying

The XRD peaks of pure isoleucine were observed at 2Ɵ = 6.3°, 12.6°, 25.4°, 31.9°, and 38.6°. In isoleucine plasticized and co-plasticized sample diffractograms these peaks were also visible. So, this was attributed to presence of isoleucine. The solubility of isoleucine is 4.1 g/100g in aqueous solution at 25° C. So the degree of super saturation in case of

30IS.PS was higher which leads to increase in crystal formation. The SEM analyses also supported the XRD results in case of isoleucine plasticized and co-plasticized formulations. However the B- and V- type crystallinity in raw starch were completely absent after spray drying in case of malic acid plasticized and butyric acid plasticized and co-plasticized formulations. The plasticizer interacts and disturbed the inter and intra molecular hydrogen bonding in between starch chains. The relocation of starch chains were inhibited by fast drying and rapid cooling of powder samples offered by spray drying operation [59].

Table (5.2) showed the comparison of prepared powder samples with the literature. Almost all the samples were amorphous after spray drying except for isoleucine plasticized and co-plasticized and asparagine plasticized TPS powder samples that was because of their crystalline nature.

Table5.2 Comparing nature of sample with literature

Plasticized TPS Samples	Nature of prepared sample powder	References
Malic Acid	Amorphous	This Work
Isoleucine	Semi Crystalline	
Butyric acid	Amorphous	
Malic & Butyric acid	Amorphous	
Malic acid & Isoleucine	Semi Crystalline	
Glycerol	Amorphous	[45, 46, 55]
Urea	Amorphous	
Asparagine	Semi Crystalline	
Citric acid	Amorphous	
Malic acid & Glycerol	Amorphous	
Malic acid & Urea	Amorphous	
Citric acid & Glycerol	Amorphous	

5.3 Crystallinity of Thermoplastic Starch T-bones

TPS T-bones were produced by compression molding and the crystallinity was studied for the 1st and 7th day at RH50%. It was observed that compression molding did not cause any effect on the crystallinity of the produced T-bones. Almost all the produced T-bones were hazy and non-transparent except for 30MA.PS.

As mentioned earlier that malic acid plasticized and butyric acid plasticized and co-plasticized formulated powder samples were amorphous (Section 5.2). Similarly the T-bones also remained amorphous till the 7th day. Moreover no significant retrogradation was observed in the starch matrix during the 7th day due to absence of starch peak in the formulations figure (5.7-5.8). Isoleucine plasticized T-bones remained brittle and crystalline upon storage for 7 days at RH50% figure (5.7), however the co-plasticized isoleucine decreased the brittleness and the degree of crystallinity of the T-bones due to the co-plasticization effect of malic acid as shown in figure (5.9). The crystallinity of co-plasticized T-bones started to appear on 7th day at 50% RH due to the crystalline nature of isoleucine. This recrystallization was because of the influence of water that rearrange the amorphous starch chains. The degree of crystallinity of isoleucine plasticized and co-plasticized T-bones increased with increase quantity of isoleucine figure (5.9). 30MA.PS formulated T-bones stored at 50% relative humidity were transparent and became flexible upon storage due to the moisture absorption. It remained amorphous during the 7th day as shown in figure (5.7). One of the importance of using malic acid as co-plasticizer was that the T-bones remained flexible and maintained structural integrity during storage. Furthermore malic acid inhibit the retrogradation of starch for 56 days even at RH 100% [55].

The results indicated that amphiphilic plasticizer i.e. isoleucine crystallizes in the process of spray drying unlike the other commonly used plasticizers [46]. It was mainly because of low solubility in water, which resulted in poor control of crystallinity. However with co-plasticized mixed formulations of isoleucine resulted in better control of crystallinity and retrogradtion. The non-polar part of isoleucine provide a barrier to prevent the absorption of water. Also the semi crystalline peaks of starch i.e. at $2\Theta = 15.04^{o}$, 17.23^{o}, and 23° were missing in the isoleucine co-plasticized samples of 1st and 7th day as shown in figure (5.10). However the peaks of isoleucine tend to appear over time.

On the other hand butyric acid co-plasticized T-bones have better retrogradation control and have no crystallinity in the formulation. The visual properties of formulated samples were also observed. Isoleucine and butyric acid plasticized and co-plasticized T-bones were hazy, non-transparent and mat. However co-plasticized T-bones exhibited transparency on increasing the amount of co-plasticizer.

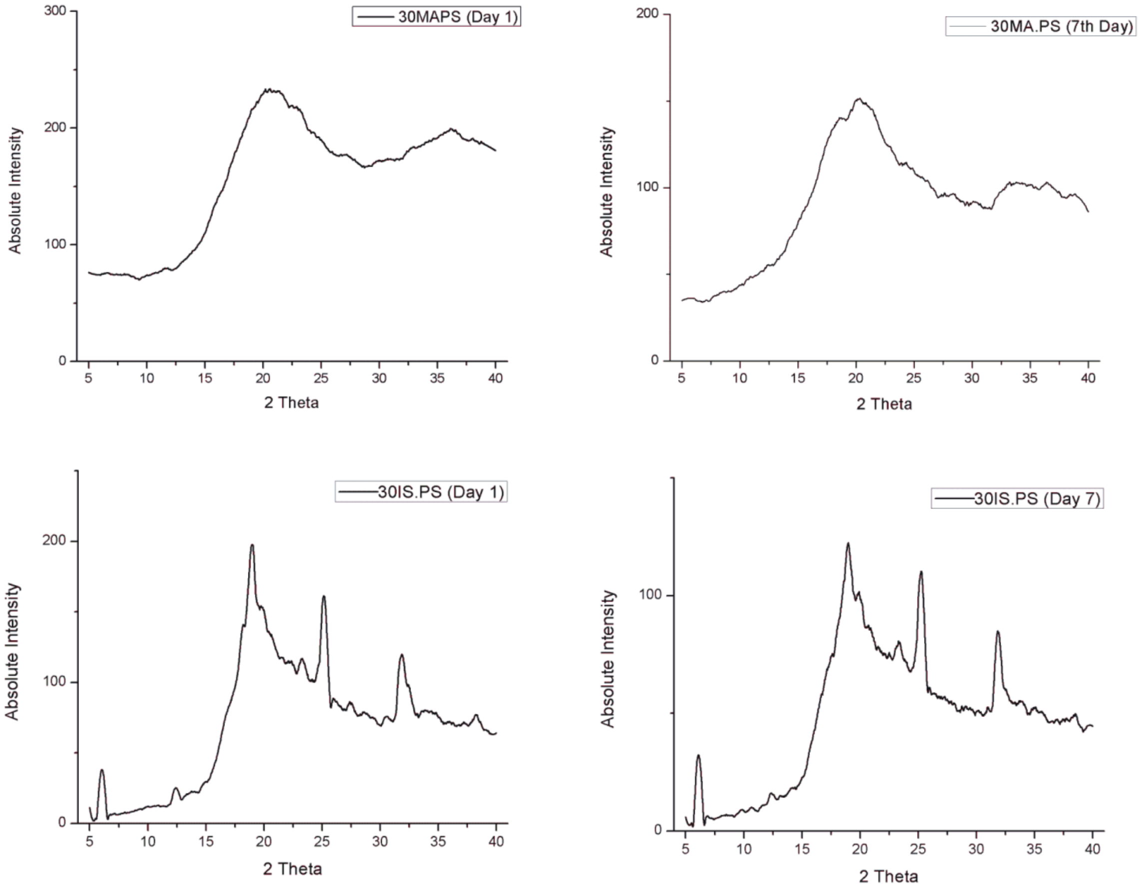


Figure 5.7 Malic acid and isoleucine plasticized T-bones for 1st day and 7th day

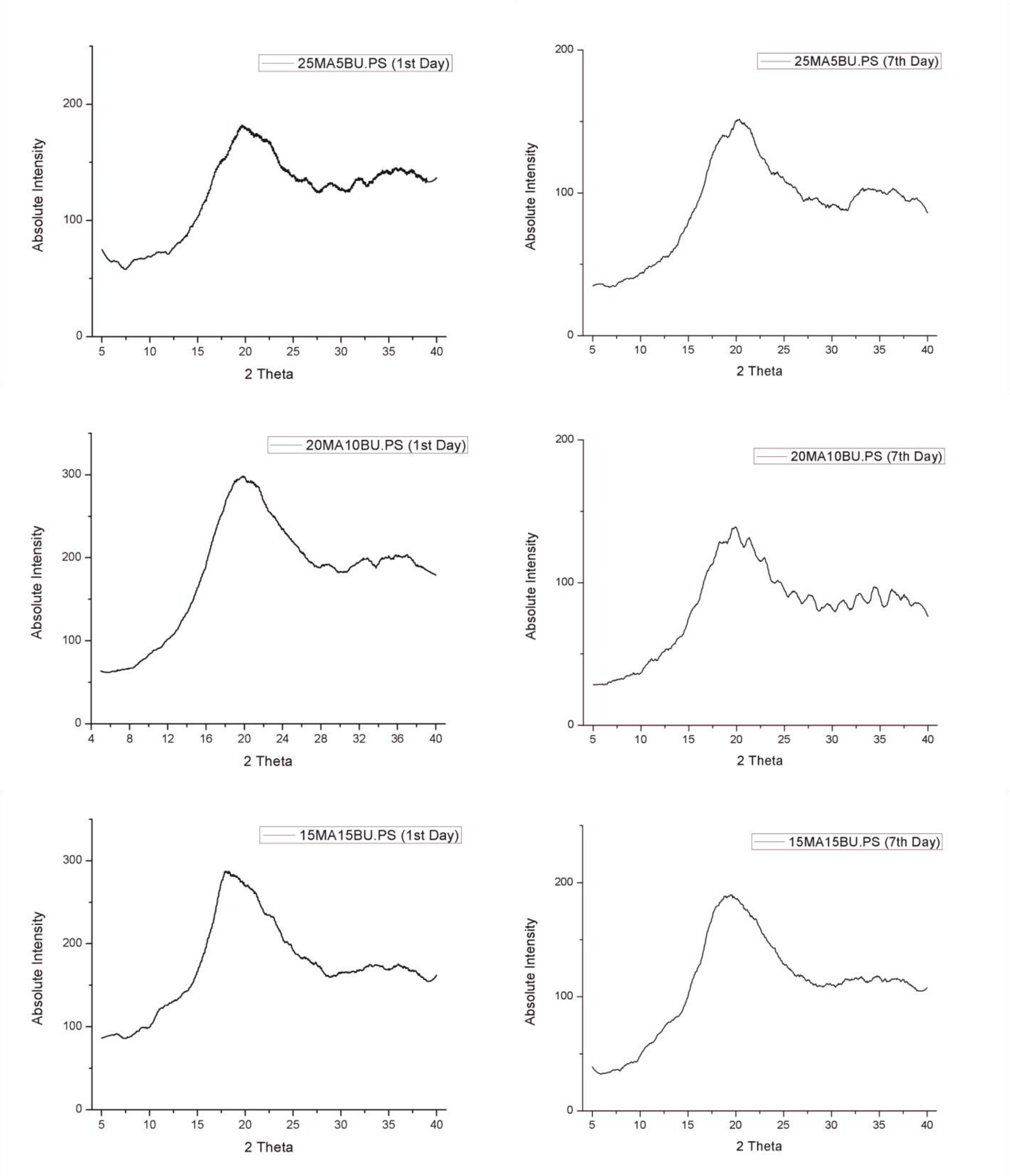


Figure 5.8 Butyric acid co-plasticized T-bones for 1st and 7th day

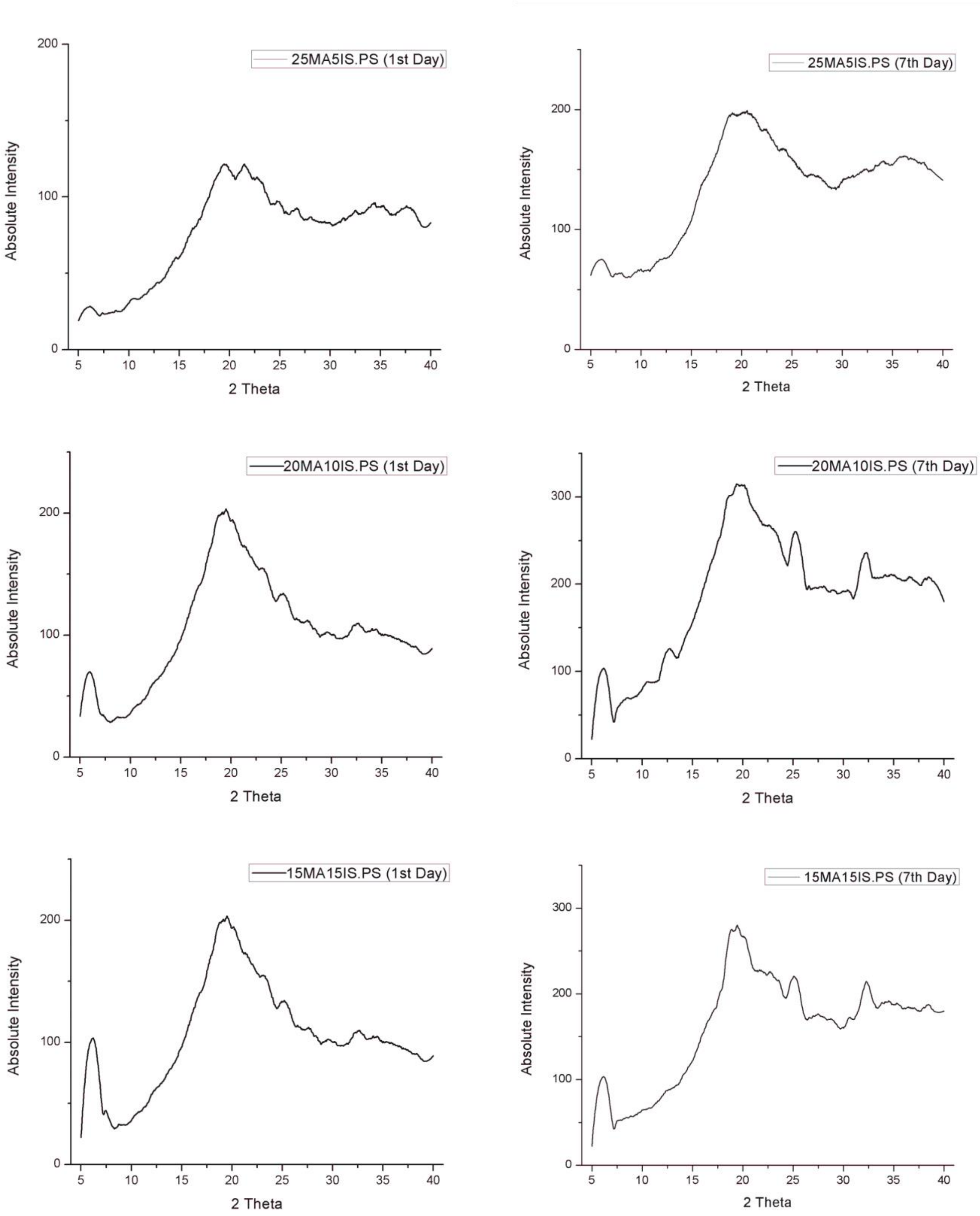


Figure 5.9 Isoleucine co-plasticized T-bones for 1st and 7th day.

Niazi at al compared the degree of crystallinity between films produced via solution spray drying and solution casting technique and suggested lower ultimate crystallinity levels and rate of retrogradation in the films obtained from solution spray drying than the ones obtained from solution casting [46]. In another work Malic acid, citric acid, glycerol, urea and their mixed plasticized samples were used and found out to be transparent. They also controlled the crystallinity much better. Likewise malic acid prevented retrogradation and control the crystallinity. It acted as a strong anti retrogradation agent for 56 days even at full level of humidity [55].

Table 5.3 Comparison of XRD results with the literature.

Plasticized TPS Samples	**Retrogradation Control**	**Transparency**	**References**
Malic Acid	Controlled	Transparent	This work
Isoleucine	Controlled	Hazy, Non-Transparent	
Butyric acid	Controlled	Hazy, Gritty, Non-Transparent	
Malic & Butyric acid	Controlled	Hazy, Non-Transparent	
Malic acid & Isoleucine	Controlled	Hazy, Non-Transparent	
Glycerol	Controlled	Transparent	[45, 46, 55]
Urea	Controlled	Transparent	
Asparagine	Controlled	Hazy, Non-Transparent	
Citric acid	Controlled	Transparent	
Malic acid & Glycerol	Controlled	Transparent	
Malic acid & Urea	Controlled	Transparent	
Citric acid & Glycerol	Controlled	Transparent	

5.4 TGA and DTGA Analysis

TGA was performed to investigate the thermal properties of TPS powders. The threshold decomposition temperature called the onset of degradation shows the highest temperature at which the material can be processed. The DTGA was also calculated to allocate different sections based on DTGA minima. Depending upon the composition of formulations, the curve was divided into 3 or 4 identifiable regions. The thermal analysis indicated the weight loss profile for all the samples. Water and other volatiles lost up to 110^{o}C from the samples (section a). Afterwards the presence of plasticizers in the sample were observed (section b_1, b_2), whereas the starch degradation zone is located in section b_3. The propagating zone (section c) leads to carbonaceous residue [55].

The addition of plasticizers caused an increased or decreased in the decomposition temperature depending on the nature of plasticizer used. A co-plasticized formulation indicated an extra peak in the DTGA. In plasticized TPS formulations i.e. isoleucine and butyric acid plasticized samples the isoleucine plasticized samples showed the lowest T_{dec} and butyric acid plasticized samples the highest i.e. 175^{o}C and 232^{o}C respectively. While in co-plasticized TPS formulation i.e. MAIS.PS and MABU.PS as the quantity of malic acid decreased, $T_{dec,\ b1}$ increased. So malic acid showed better interaction with starch. On the other hand with increase in isoleucine quantity the temperature also increased which indicated low interaction of isoleucine with starch (Table 5.4). Similar trend was observed in butyric acid plasticized and mix plasticized formulations. The presence of malic acid in the formulation suggests more interaction of starch and malic acid and homogeneous blending. Therefore malic acid was used as co-plasticized with amphiphilic plasticized starch. Also because of its formation of distinct phase during the mixing and drying operations indicating better stability of the samples. Improved thermal stability can also be explained by strong hydrogen bonding which can be observed in malic acid plasticized samples. On the other hand the presence of isoleucine indicated low interaction with starch, supported by FTIR and SEM.

The TGA and DTGA of butyric acid plasticized and co-plasticized formulation did not provide clear indication of the decomposition temperature of butyric acid, as also observed in the DTGA that no extra peak was present and two step degradation was observed (figure 5.12). The second minima in the DTGA was composed of two overlapped peaks i.e. butyric acid and starch. The degradation temperature for butyric acid and starch was probably similar. J.M. Cervantes-Uc et al reported the TGA on thermal degradation of polymethacrylates containing carboxylic groups which indicated the degradation temperature of butanoic acid at 327°C which was close to that of degradation temperature of spray dried starch i.e. 332°C [60]. The overlapping occurred which may be the reason that extra peak was missing in the butyric acid plasticized formulations.

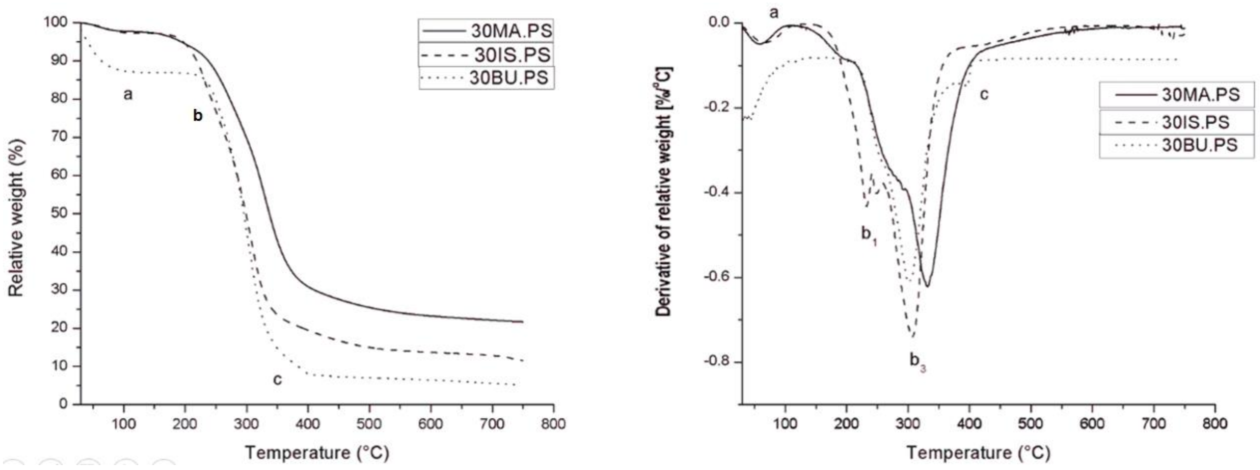


Figure 5.10 TGA and DTGA curves of solution spray dried TPS plasticized powder samples

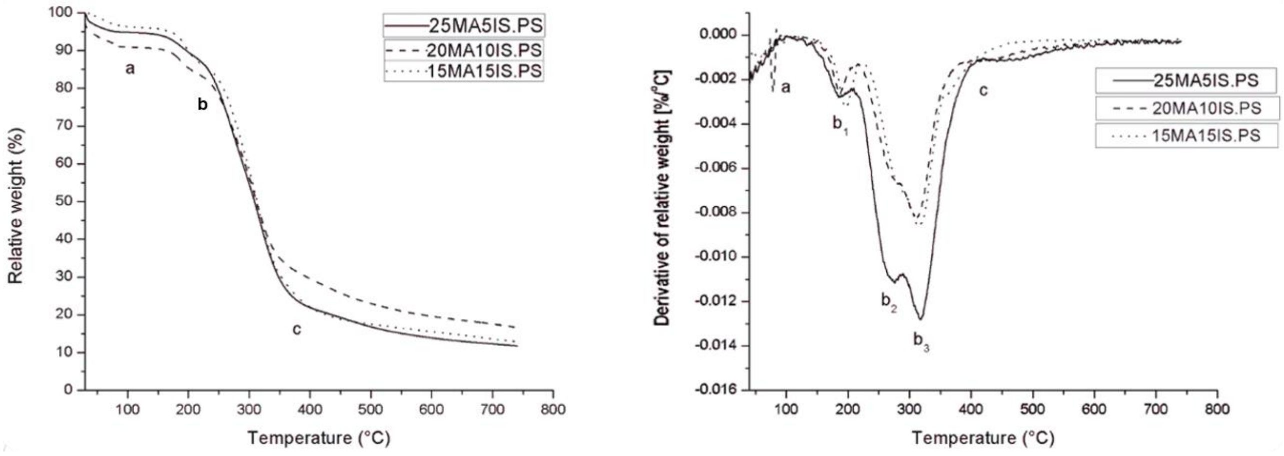


Figure 5.11 TGA and DTGA curves of isoleucine co-plasticized powder samples

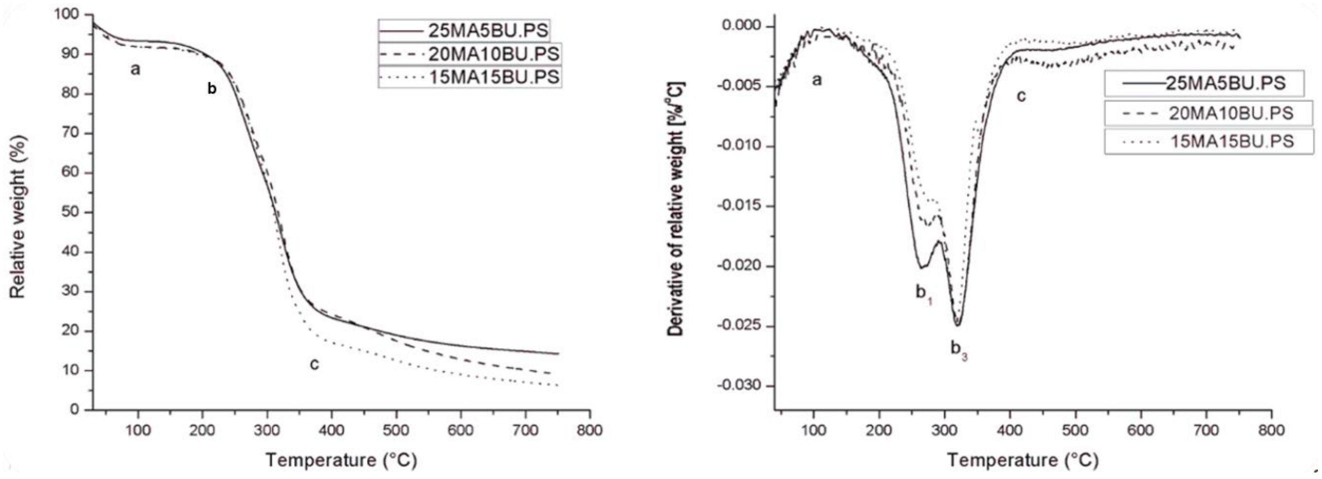


Figure 5.12 TGA and DTGA curves of butyric acid co-plasticized powder samples

Table 5.4 Thermal Properties of the Studied Samples

Samples	**Onset, T_{dec} (ºC)**	**Peak, $T_{dec,b1}$ (ºC)**	**$T_{dec,b2}$ (ºC)**	**$T_{dec,b3}$ (ºC)**
30MA.PS	209	291	-	331
30BU.PS	232	-	-	303
30IS.PS	175	232	-	309
25MA5IS.PS	160	186	276	317
20MA10IS.PS	163	188	285	313
15MA15IS.PS	170	195	296	314
25MA5BU.PS	211	263	-	320
20MA10BU.PS	212	273	-	322
15MA15BU.PS	214	276	-	320

Table (5.5) showed the comparison of this work with the literature .Amphiphilic plasticized and co-plasticized samples were as thermally stable as other commonly used plasticizers formulations and mixed formulations like glycerol, urea, asparagine, citric acid and their mix plasticized formulation [45, 46, 55].

Table 5.5 Comparison of Thermal behavior with literature

Plasticized TPS Samples	**Thermal Stability (^oC)**	**References**
Malic Acid	209	This work
Isoleucine	175	
Butyric acid	232	
Malic & Butyric acid	214	
Malic acid & Isoleucine	170	
Glycerol	160	[45, 46, 55]
Urea	165	
Asparagine	193	
Citric acid	227	
Malic acid & Glycerol	182	
Malic acid & Urea	156	
Citric acid & Glycerol	190	

5.5 FT-IR Analysis

The interactions of starch and plasticizers were analyzed by FTIR to gain better insight of the functional groups. A shift in the absorption bands indicated the interaction between starch and plasticizers. The properties of TPS mainly relied on hydrogen bond forming abilities between starch and plasticizer [59]. The untreated starch spectrum was used as a reference sample to interpret the absorption bands for the prepared samples. As reported in the literature [45, 51], stretching vibrations of O-H, C-O, and C=O of starch will occur upon hydrogen bond interactions, and known as red shift. Hydrogen bonding also induce bond elongation, resulting in lower stretching vibrations. The absorption band characteristic of formulated TPS T-bones are represented in table (5.6). The peaks at 3565-3259 cm^{-1} were allocated to O-H stretching [42]. The peaks at 2933-2917 cm^{-1} was described by C-H stretching [42]. Bands at 1729-1705 cm^{-1} indicated the presence of carbonyl group. Bands at 1638-1613 cm^{-1} were attributed to C-O stretching and N-H bending and bands at 1422-1339 cm^{-1} were ascribed by C-H bending [61]. Finally bands at 1027-1019 were allocated to C-O bond stretching [62].

Table 5.6 FT-IR Absorption Bands of the Studied Samples

Samples	**3565-3259 (O-H stretching)**	**2933-2917 (C-H stretching)**	**1729-1705 (presence of carbonyl group)**	**1638-1613 (C-O stretching)(N-H bending) (amide)**	**1422-1339 (C-H bending)**	**1027-1019 (C-O bond stretching)**
U.S	3427	2921	-	1632	1384	1022
30MA.PS	3397	2926	1729	-	1395	1027
30IS.PS	3259	2922	-	1615	1330	1021
30BU.PS	3565	2917	1705	-	1422	1027
25MA5IS.PS	3260	2922	1729	1638	1400	1019
20MA10IS.PS	3362	2923	1729	1619	1403	1023
15MA15IS.PS	3289	2922	1716	1613	1403	1019
25MA5BU.PS	3396	2924	1728	-	1396	1027
20MA10BU.PS	3327	2925	1729	-	1403	1026
15MA15BU.PS	3357	2933	1729	-	1396	1020

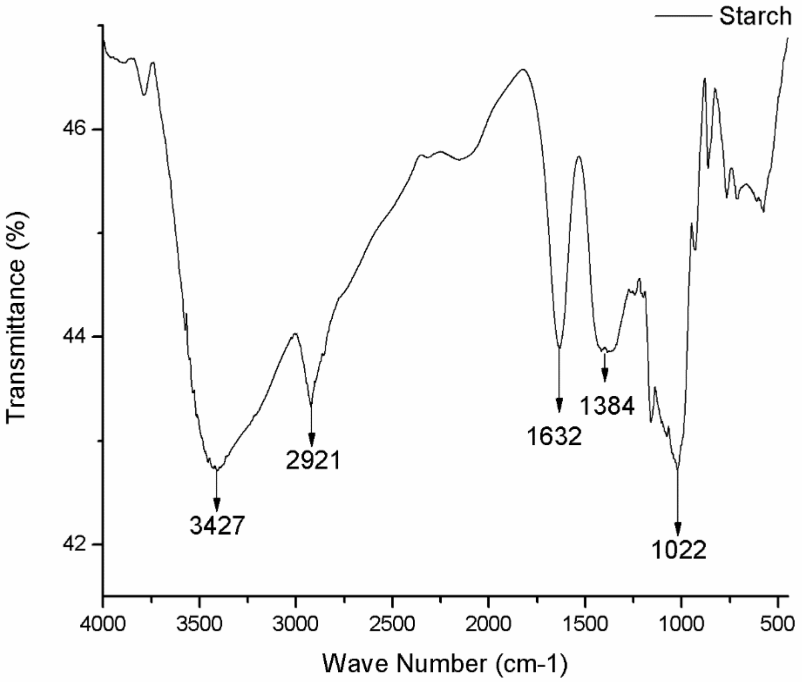


Figure 5.13 FT-IR Analysis of Untreated Starch

To signify the interaction between starch and plasticizers, all the spectra indicated shifts in the fingerprint region of starch. Malic acid plasticized and co-plasticized TPS powder indicated carbonyl absorption bands at 1729-1705 cm^{-1}. Esterification of starch has been reported in these ranges of peak [63]. Observing the spectra of butyric acid with co-plasticized malic acid formulated powder samples, a red shift was visible upon decreasing the malic acid quantity and increasing butyric acid as the peaks shifted towards high wavenumber. Hence increasing the amount of butyric acid gave rise to increased hydrogen bond interactions because of its low molecular weight.

Conversely giving rise to isoleucine concentration in isoleucine co-plasticized formulations resulted in decreased amount of hydrogen bonding between starch and plasticizer, as the peaks shifted towards low wavenumber and indicated a blue shift. The blue shift was due to hydrophobic part of isoleucine which results in low interactions with starch. All co-plasticized malic acid formulations showed absorption bands at 1729-1705 cm^{-1}. These ranges also include the carboxylic absorption bands which overlapped in case of malic and butyric acid mixed formulations. In untreated starch and 30IS.PS this peak was missing. The peak at 1638-1613 cm^{-1} was assigned to C-O stretching from functionalities of amide from isoleucine.

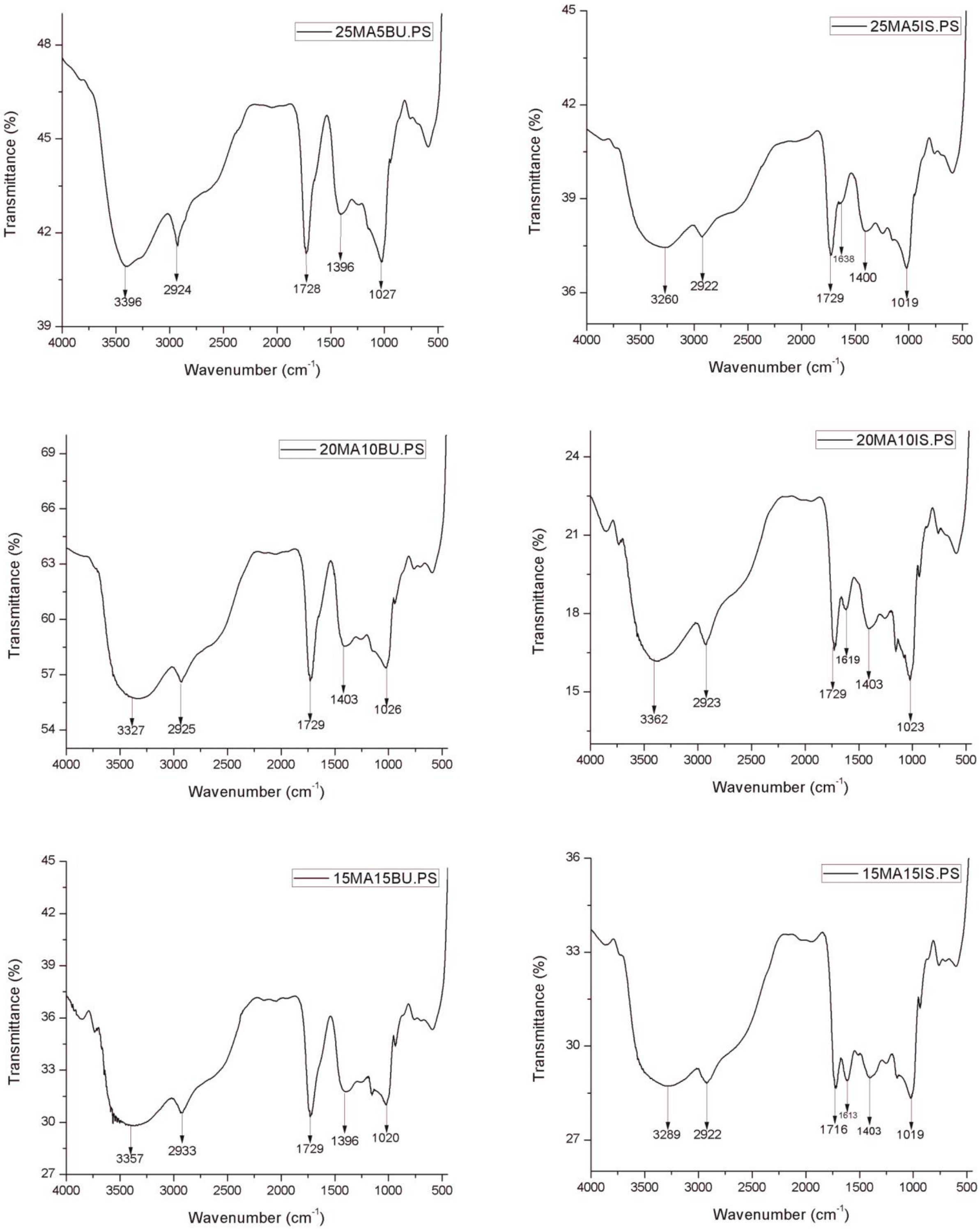


Figure 5.14 FT-IR Analysis of solution spray dried amorphous TPS powder plasticized samples

In literature Carboxylic acids i.e. malic acid and citric acid showed an increase in hydrogen bond interactions when their quantity was increased in other commonly used co-plasticizers [55]. Malic acid plasticized and mixed plasticized formulations exhibits absorption bands at 1729-1705 cm^{-1} which indicated the esterification of starch [46]. A red shift was observed for glycerol and urea and their mixed plasticized formulations which suggested strong hydrogen bonding between starch and plasticizers [45].

Table 5.7 Comparison of FTIR data with literature

Plasticized TPS Samples	**Starch – Plasticizer Interactions**	**References**
Malic Acid	Stronger	This work
Isoleucine	Weak	
Butyric acid	Strong	
Malic & Butyric acid	Stronger	
Malic acid & Isoleucine	Weak	
Glycerol	Strong	[45, 46, 55]
Urea	Stronger	
Asparagine	Stronger	
Citric acid	Stronger	
Malic acid & Glycerol	Stronger	
Malic acid & Urea	Stronger	
Citric acid & Glycerol	Stronger	

5.6 Powder Morphology

The TPS powder morphology was examined by scanning electron microscopy (SEM). The untreated starch (U.S) which was the feedstock material showed oval and spherical structured particles of different sizes, with a homogenous surface of particles as shown in figure (5.15). The surface of particle appeared to be homogenous.

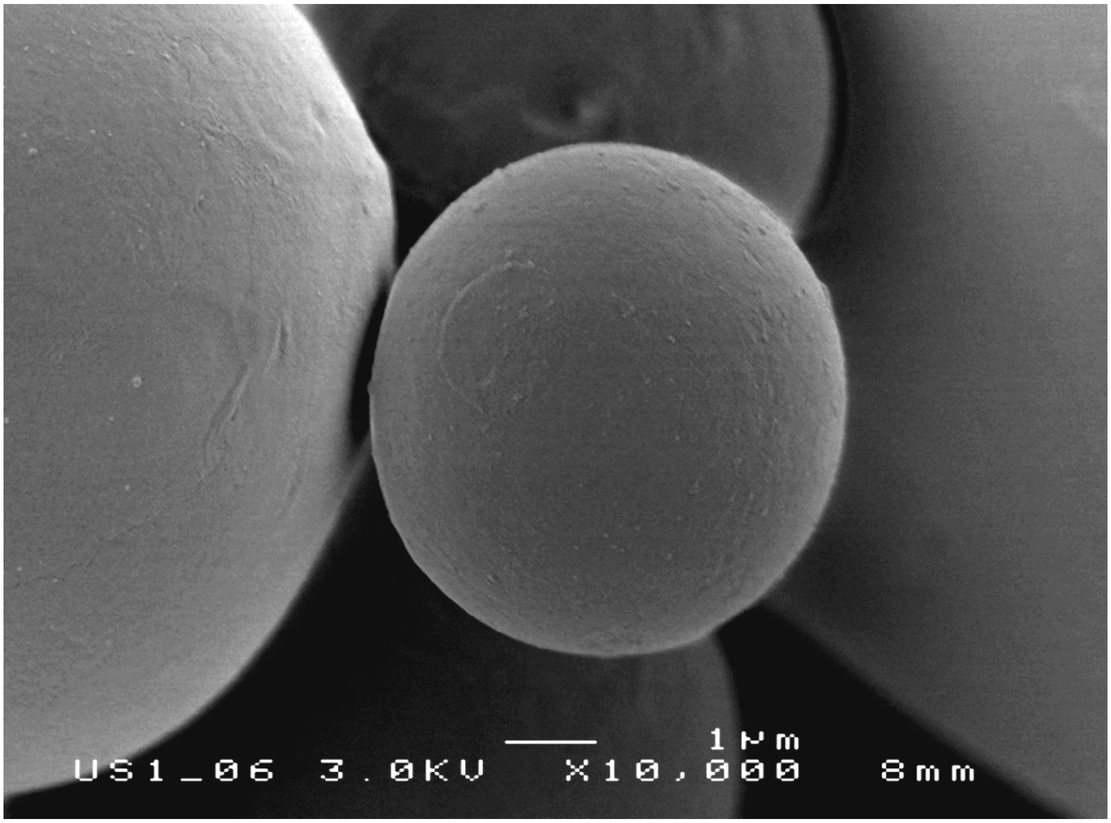


Figure 5.15 SEM Micrograph of Untreated Starch

Spray drying produced a white powder for all the samples. Morphology of powder entirely varied from the feed stock material after spray drying. The particles showed spherical nature however they contained dents, which are usual for the powder after spray drying [51]. Furthermore the higher the drying rate the higher will be the degree of shrinkage [64]. The formation of dents were attributed to the formation of a shell from the surface of droplet during the spray drying resulting in the entrapment of remaining liquid inside the shell. On further drying the diffusion of the entrapped liquid through the dried surface results in contraction of particle size.

Furthermore, all the isoleucine plasticized and co-plasticized samples exhibited a broken hallow particles. The observed hallow particles may be justified by the hydrophobic characteristic of amphiphile i.e. the non-polar part of isoleucine. Due to this typical property of isoleucine, they appeared to be unsuitable for the moisture rich starch droplet during the spray drying process. Therefore the amphiphilic plasticizer was exuded to the outer vicinity of the particle where it readily forms a crystalline barrier for the evaporating moisture. However broken hallow particles were not observed in the case of butyric acid plasticized and co-plasticized samples (figure 5.16).

The intensity of hallow broken particles depends on the quantity of isoleucine. As the isoleucine plasticizer quantity increased, dents also enhanced and became more visible. On the other hand in butyric acid formulated TPS samples the sharp edges on the particle surface was not found. However, dents were observed and were directly proportional to plasticizer amount. Furthermore SEM micrograph clearly indicated that particles were well dispersed and surface appeared to be homogenous.

Niazi et al reported the particle morphology of various plasticized and co-plasticized formulations like glycerol, urea, asparagine, citric acid, malic acid and their combinations by spray drying technique and concluded well dispersed and homogenous surface of particles (table 5.8). The particles were also found to be dented and deformed [45, 46, 55].

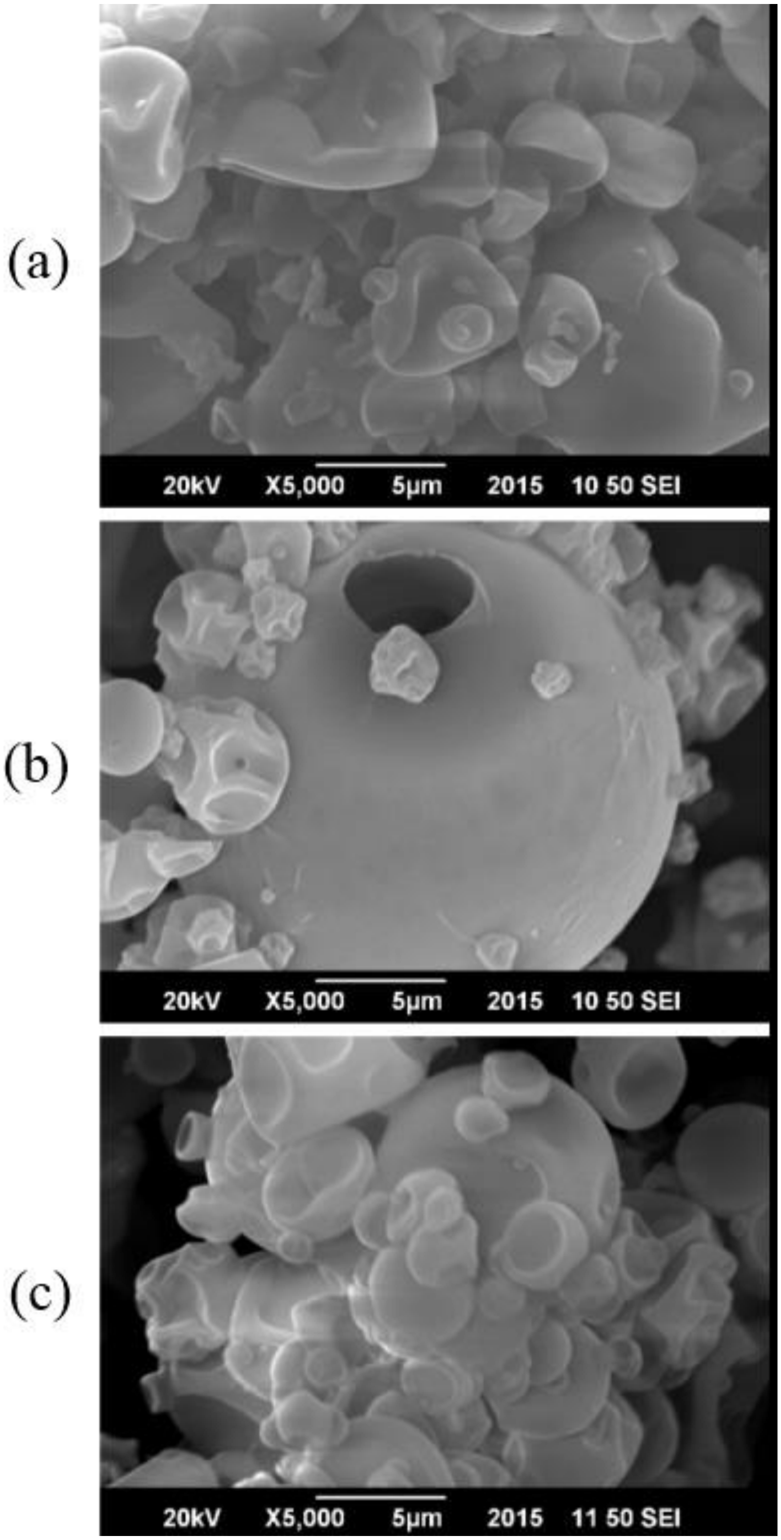


Figure 5.16 SEM Micrographs of spray dried TPS plasticized powders (a) 30MA.PS, (b) 30IS.PS, (c) 30BU.PS

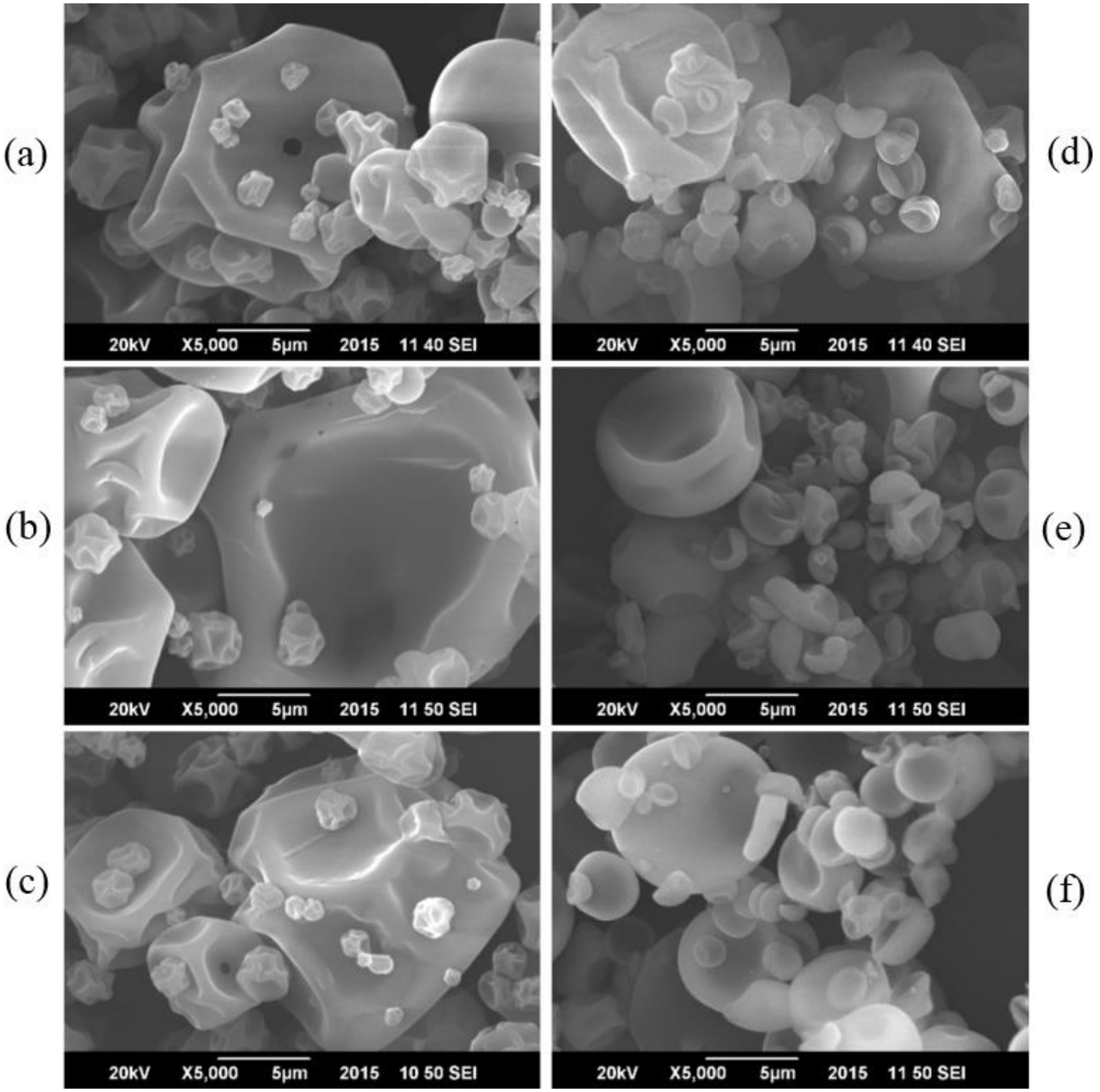


Figure 5.17 SEM Micrographs of spray dried TPS co-plasticized powders (a) 25MA5IS.PS, (b) 20MA10IS.PS, (c) 15MA15IS.PS, (d) 25MA5BU.PS, (e) 20MA10BU.PS, (f) 15MA15BU.PS

Table 5.8 Comparison of SEM results with literature

Plasticized TPS Samples	**Homogeneity**	**Surface**	**References**
Malic Acid	Homogeneous	Dented and deformed	This work
Isoleucine	Homogeneous	Hollowed, Dented, Deformed	
Butyric acid	Homogeneous	Dented and deformed	
Malic & Butyric acid	Homogeneous	Dented and deformed	
Malic acid & Isoleucine	Homogeneous	Hollowed, Dented, Deformed	
Glycerol	Homogeneous	Dented and deformed	[45, 46, 55]
Urea	Homogeneous	Dented and deformed	
Asparagine	Homogeneous	Dented and deformed	
Citric acid	Homogeneous	Dented and deformed	
Malic acid & Glycerol	Homogeneous	Dented and deformed	
Malic acid & Urea	Homogeneous	Dented and deformed	
Citric acid & Glycerol	Homogeneous	Dented and deformed	

5.7 Powder Recovery

Powder yield is one of the important factor in spray drying technology. In every process, a high yield is required to increase the efficiency of the process. Spray drying is an important unit operation and factors that affect the yield are the type and amount of plasticizer used in the formulation, the operating parameters and the solution properties [45]. The operating parameters were constant throughout the process for all the samples while the nature and quantity of plasticizers altered. The major loss of powder which was prominent throughout the process of spray drying was the disposition of the powder to the wall of the heating chamber in spray dryer. The yield of spray dried starch without any plasticizer was taken as reference in this regard which indicated the maximum powder yield i.e. 79 ± 1. Table (5.9) and figure (5.18) showed the powder yield of all the plasticized and co-plasticized TPS samples.

Table 5.9 Powder recovery of formulated samples

Sample	**Powder Recovery (%)**
SD.S	79 ± 1
30MA.PS	63 ± 1
30IS.PS	77 ± 1
25MA5IS.PS	64 ± 2
20MA10IS.PS	69 ± 2
15MA15IS.PS	73 ± 1
30BU.PS	69 ± 2
25MA5BU.PS	59 ± 1
20MA10BU.PS	63 ± 2
15MA15BU.PS	66 ± 1

Results clearly indicated the decrease in the yield with addition of plasticizer, but the difference in yield was less. It was due to the characteristics and nature of plasticizer. Malic acid as discussed earlier absorbed more water among all plasticizers, made the material more flexible, rubbery and sticky. Therefore the formulations contained malic acid as plasticizer or co-plasticizer decreases the powder yield. Isoleucine on the other hand had more crystalline and brittle nature and absorbed less water, therefore the powder recovery was high. The samples comprised of isoleucine with co plasticized i.e. malic acid showed a decreasing trend in powder yield as the amount of malic acid increased.

Butyric acid was a high density low molecular weight molecule compared to isoleucine and malic acid, allowed it to have better interaction with the starch molecule. Moreover, the rate of moisture uptake was high as compared to isoleucine. Therefore the powder yield was lower than isoleucine but higher than malic acid.

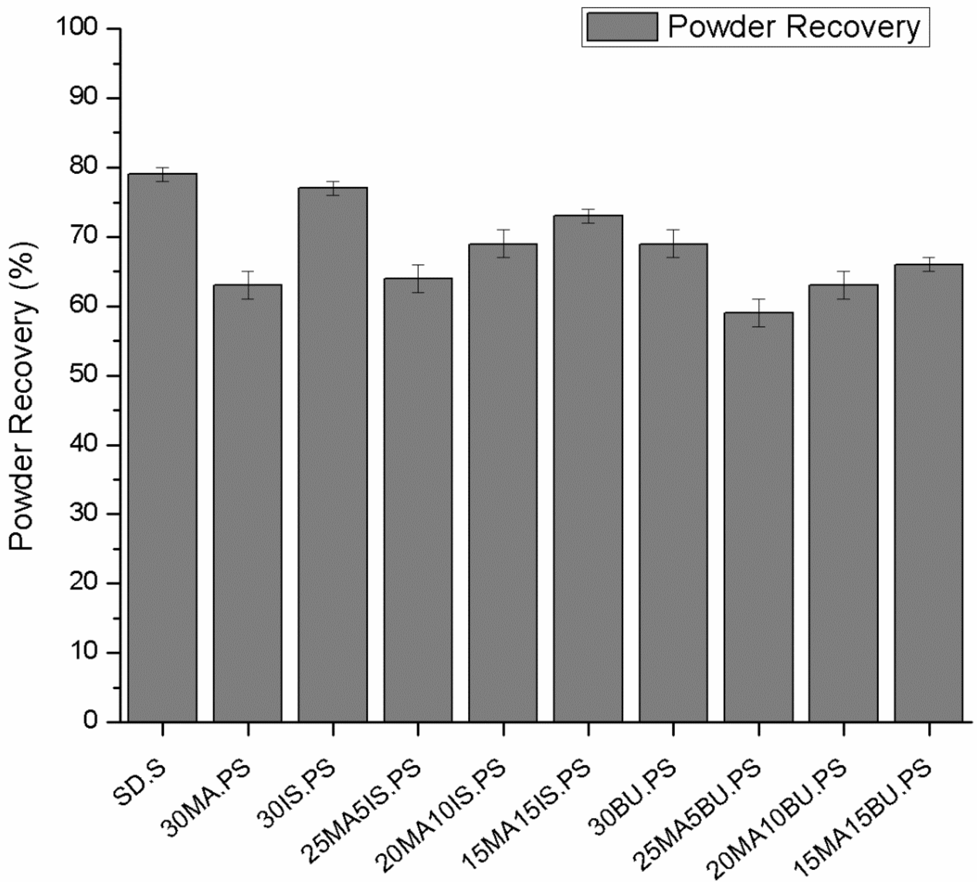


Figure 5.18 Powder Recovery after Spray Drying of plasticized and co-plasticized TPS samples

5.8 Mechanical properties

The important criterion to assess the polymer T-bones is the mechanical strength particularly for application of packaging material. The mechanical behavior of amphiphilic plasticized and mixed plasticized TPS T-bones were analyzed after conditioning for 1 day in 50%RH. The spray dried starch was not tested due to its brittle nature.

Figure (5.19) showed the tensile strength and strain at break of all formulated samples. The flexibility of prepared plasticized TPS T-bones increased in order malic acid > isoleucine > butyric acid. The higher strain at break of malic acid could be explained by the hydrogen bond capabilities. The more the hydrogen bonding functionalities, the higher will be the capability of plasticizer to disturb the inter and intra-molecular hydrogen bonds of starch. Moisture uptake of malic acid plasticized samples was also high, resulted in chain mobility of starch and the elongation at break increased. On the other hand isoleucine plasticized T-bones exhibited low flexibility and high brittleness due to increased crystallinity of T-bones. However, butyric acid failed to act as plasticizer alone as the T-bones prepared were too hazy and gritty. Furthermore the tensile strength of isoleucine plasticized TPS T-bones indicated high strength than malic and butyric acid plasticized TPS T-bones due to the lipophilic property of isoleucine which lowered the hydrogen bonding with the starch matrix and resulted in less moisture absorption, thus lowering the chain mobility of starch and increasing the strength of the samples.

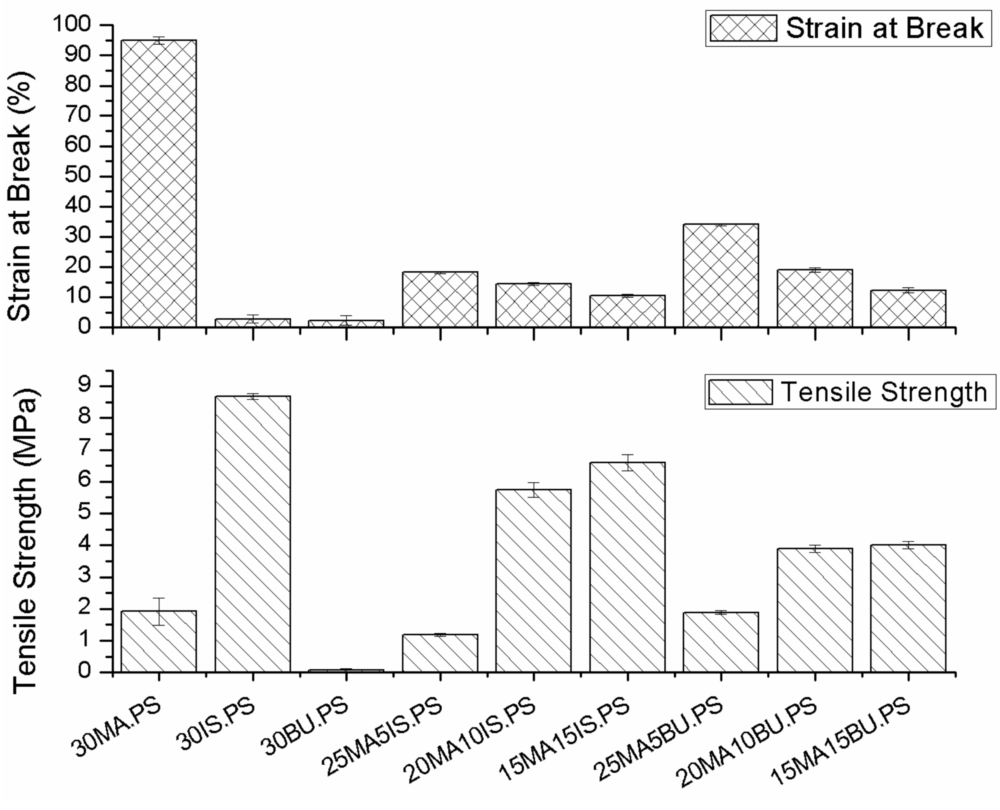


Figure 5.19 Tensile strength and elongation at break of plasticized and co-plasticized TPS T-bones at RH 50% for 1day

Isoleucine and butyric acid was co-plasticized with malic acid. The addition of malic acid was to ensure a balance between strain and strength of the formulated samples. It was observed that addition of malic acid as co-plasticizer exhibited more flexibility in the amphiphilic plasticized T-bones. The more the amount of malic acid the higher will be the flexibility of amphiphilic plasticized T-bones. The hydrogen bond capabilities of malic acid with starch increased the flexibility, while the hydrophobic part of amphiphile prevent hydrogen bonding, thus result in less water absorption and decreased flexibility. However the strength of the samples decreased with increase in malic acid quantity. Isoleucine plasticized T-bones were comparatively stronger than that of butyric acid because of its brittle and crystalline nature. The lipophilic part of isoleucine also prevented hydrogen bonding with starch matrix resulting minimum absorption of moisture thus increasing the strength.

Olivato et al reported the influence of citric acid, malic acid and tartaric acid in starch and mechanical properties of the films were examined at different relative humidities. Higher concentration of tartaric and citric acid produced films with improved tensile strength (6.8 and 6.7 MPa, respectively). Moreover greater concentration of malic acid and high relative humidity increase the elongation of the films [65]. In another research glycerol, urea, asparagine, citric acid and their mixed plasticized formulations were used (table 5.) and mechanical properties of the films were examined. Citric acid and asparagine gave better tensile properties whereas urea plasticized and co-plasticized with malic acid indicated better elongation at break [45, 46, 55].

Table 5.10 Comparison of Mechanical Properties with literature

Plasticized TPS Samples	**Strength (MPa)**	**Strain (%)**	**References**
Malic Acid	1.9	95	This work
Isoleucine	8.68	2.8	
Butyric acid	*	*	
Malic & Butyric acid	4.0	34	
Malic acid & Isoleucine	6.6	18.24	
Glycerol	0.7	42	[45, 46, 55]
Urea	0.2	99	
Asparagine	6.0	10.5	
Citric acid	5.4	12	
Malic acid & Glycerol	2.5	24	
Malic acid & Urea	0.09	155	
Citric acid & Glycerol	4.8	25	

* Butyric acid TPS T-bones were not tested due to grittiness

Chapter 6 – Conclusions and Recommendations

6.1 Conclusion

TPS T-bones were prepared by compression molding of solution spray dried powder. Isoleucine and butyric acid was used as amphiphilic plasticizer whereas malic acid as co-plasticizer in the formulations.

The moisture absorption of the produced T-bones were analyzed at RH50% for first 7 days, afterwards the calculations were done on weekly basis. The amphiphilic plasticized and mixed plasticized T-bones showed resistance to the moisture because of its lipophilic property, which prevented the retrogradation of starch chains. X-Ray diffraction showed that butyric plasticized and co-plasticized samples were amorphous, whereas crystallinity was observed in isoleucine plasticized and co-plasticized samples upon storage at RH50%, which was attributed to crystalline isoleucine. Thermal properties were analyzed by TGA. The moisture loss was at 100°C and all the plasticized formulations were thermally stable up to 160°C. The starch degradation phase was between 300-350°C followed by char production above 350°C temperature. Different regions or peaks were indicated in DTGA that related to plasticizers decomposition. FTIR spectra for he prepared samples were investigated and were found in line with literature. All the spectra showed shifts towards the fingerprint region of starch, showing the interaction of starch and plasticizers. A red shift was observed in case of butyric acid mixed plasticized samples showing better hydrogen forming abilities whereas isoleucine formulations indicated low hydrogen bonding as blue shift was observed. SEM analyses showed hallow particles in isoleucine plasticized and co-plasticized samples apart from dents, whereas butyric acid mixed plasticized samples were found to be dented and deformed. However the homogeneity were found in all formulated samples. Isoleucine plasticized showed high strength but low strain at break, however the strain at break was improved by mixing a co-plasticizer. Butyric acid plasticized T-bones were too hazy and gritty however upon mixing with co-plasticizer, it showed better strength and strain at break.

6.2 Recommendations

This research is a gate way to new directions to replace the conventional polymer products. Plasticizers were used to make starch as thermoplastic starch to produce biodegradable food packaging material by spray drying.

- The spray drying method used in this context to produce TPS is under developed but it is considered a potential thermal route to produce amorphous materials. Apart from labs, pilot plants should be establish to produce TPS materials.
- Powder yield in spray drying should be improved by altering the design parameters of spray drier so to get maximum yield.
- Plasticizers are the important additives and property enhancer of polymers. On commercial scale the TPS polymers is greatly affected by source, cost, quality, safety and functionality of plasticizer. Measure should be taken to reduce the cost and enhance the quality and functionality.
- Other co-plasticizers like citric acid which is also a carboxylic acid should be used with amphiphilic plasticizer, as it also gave good mechanical and thermal properties.

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