

Physical and Chemical Investigations of
Starch Based Bio-Plastics

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

in

Material Science

by

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May 2015



University of
Leicester

Parts of this work have already been published in the following occasions:

(a) Published papers:

A. P. Abbott, T. Z. Abolibda, S. J. Davis, F. Emmerling, D. Lourdin, E. Leroy and W. R. Wise, *RSC Advances*, 2014, **4**, 40421-40427.

(b) Two papers in preparation.

(c) Conferences:

(i) Talks:

- **Tariq Z. Abolibda**, Andrew P. Abbott, Stefan Davis & William Wise, Development of plastic & Bio-Plastic, Optimising processing parameters and investigating the chemical and physical properties of thermoplastic starch (TPS), RSC Molten Salt Discussion Group (MSDG 2014) Postgraduate students' meeting, 10th January 2014 at University of Warwick in United Kingdom.
- **Tariq Z. Abolibda**, Andrew P. Abbott, Stefan Davis & William Wise, Development of plastic & Bio-Plastic, Optimising processing parameters and investigating the chemical and physical properties of thermoplastic starch (TPS), Molten Salts and Ionic Liquids XXV (EUCHEM 2014) Postgraduate students' meeting, 6-11 July 2014 at University of Tallin in Estonia.
- **Tariq Z. Abolibda** & Andrew P. Abbott, Development of plastic & Bio-Plastic, Optimising processing parameters and investigating the chemical and physical properties of thermoplastic starch (TPS), Saudi Student Conference VIII, Postgraduate students' meeting, 31 January to 1st February 2015 at London Imperial College in London.

(ii) Posters:

- **Tariq Z. Abolibda** & Andrew P. Abbott, Development of plastic & Bio-Plastic, Optimising processing parameters and investigating the chemical and physical properties of thermoplastic starch (TPS), RSC Molten Salt Discussion Group (MSDG 2013) Postgraduate students' meeting, 10th January 2014 at University of Leicester in United Kingdom.
- **Tariq Z. Abolibda** & Andrew P. Abbott, Development of plastic & Bio-Plastic, Optimising processing parameters and investigating the chemical and physical properties of thermoplastic starch (TPS), Annual Chemistry PhD student event, Postgraduate students' meeting, 10th January 2014 at University of Leicester in United Kingdom.

(iii) Awards:

- Best presentation in British Conference (Molten Salt Discussion Group), judged by Warwick University and Royal Society of Chemistry.
- Best paper in the 8th Saudi Student Conference, judged by Imperial College and KAUST.
- Best presentation in the 8th Saudi Student Conference, judged by Imperial College and KAUST
- Invitation to participate in an international conference (EUCHEM 2014) to present my results, this conference had the biggest international names in molten salt liquids.
- Four distinction certificates from the Saudi Cultural Bureau in London.

Statement of originality

The experimental work in this thesis has been carried out by the author in the material centre at the University of Leicester between October 2011 and October 2014. The work has not been submitted, and is not presently submitted, for any other degrees at this or any other university.

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Physical and Chemical Investigations of Starch Based Bio-Plastics

Tariq Z. Abolibda

Abstract

Starch is one of the most common and easily obtained natural polymers, making it attractive as a potential bio-based alternative to synthetic polymers. The plasticisation of starch is complex due to the extensive hydrogen bonding between chains. This study shows that a simple quaternary ammonium salt combined with hydrogen bond donor (HBD) forms effective modifiers that produce flexible plastics with good mechanical properties that are comparable to some polyolefin plastics. Starch-based plastics can be formed by the same processes as current commercial plastics, giving similar mechanical strength to some polyolefin plastics. The processing conditions are shown to significantly affect the structure of the polymer which has a concomitant effect upon the mechanical and physical properties of the resulting plastic. Using a glycerol based modifier results in a totally sustainable and biodegradable material which can be formed by extrusion, pressing, vacuum forming and injection moulding. Most significantly, it is shown that these plastics are environmentally compatible, recyclable, bio-degradable and compostable.

This study has demonstrated the optimisation of the parameters for a range of techniques that are currently used in processing this type of plastic. These include: temperature profiling for both compression moulding and extrusion, residence time in the extruder, drying time and pressing time. Glycerol/choline chloride is the plasticiser that was found to give optimal properties and has been used for most of this study. The optimum ratio is shown to be 1:3 by weight plasticiser: starch.

In addition, five different systems of fillers have been added to the starch based plastics to study their effect on tensile strength and strain, glass transition temperature, viscoelasticity, crystallinity, morphology and rheology. The chemical changes have also been investigated after the addition of the five fillers which are eggshell, wood-flour, silk, zein and lignin.

Furthermore, the fillers have an effect on stabilising water content in thermoplastic starch. Water uptake and water loss have been examined using thermogravimetric analysis, water absorption isotherms, water absorption capacity and contact angle. Finally, some applications have been presented for protecting these plastics from surrounding moisture.

Acknowledgments

First and foremost, I praise and thank God for the blessings, good health and wellbeing that were necessary to complete this project and thesis successfully.

I would like to express my deep appreciation and sincere gratitude to the following people:

- My supervisor, Professor Andrew Abbott for providing me the opportunity to work on this project and for his patience, encouragement, guidance and support over the last four years.

- My colleagues and the members of the ionic liquid group for their assistance and friendship during my degree, helping to make the lab an enjoyable place to work in. I would like to thank them all and in particular Dr William Wise, Dr Andrew Ballantyne, Dr Alex Goddard, Dr Rachel Sapstead and Stefan Davis.

- My brothers, Wail, Bassim, Hatim and Abdulla and my sister Hala (God bless her soul) for motivating and supporting me to continue my studies as well as my cousin Ali Baseer and my uncle Nassir Shobak.

- My wife, Mona Sirajaldeen, who was not just my wonderful wife but also the greatest and most supportive person anyone could have. I would like to give her very special thanks for being with me every step of my PhD and also for her love, patience and understanding during my PhD.

- My parents, Khyriya Shobak and Ziyad Abulibda, for raising me up in a good and healthy environment, which gave me a great starting point. I know I cannot thank them enough and there are no words that can truly express the level of gratitude and appreciation I have for them. I am very grateful from the bottom of my heart for everything they have done and sacrificed for me. "My Lord, have mercy upon them as they brought me up [when I was] small."

- Everyone in the Saudi Arabian Government and the Saudi Cultural Bureau in London for funding, supporting and easing everything during my studies.

Finally, in loving memory of my sister, Hala Abulibda, who I really miss. I will never forget her and her last words about me; I will carry her words and memory with me in every moment of my life as long as I live. I am really grateful she was proud of me which was, and still is, a motivation of my life.

Dedicated to

my better half, my wife Mona Sirajaldeen, who is the real partner of all what have been achieved in this stage.

Tariq Abolibda
Leicester, 2015

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Abbreviations and symbols

BP	British Petroleum
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
ChCl	Choline chloride (2-hydroxyethyl-trimethylammonium chloride).
DES	Deep Eutectic Solvent.
DMA	Dynamic Mechanical Analysis
DMSO	Dimethyl sulfoxide.
DNA	Deoxyribonucleic Acid. It is the genetic code for all living life forms.
DSC	Differential Scanning Calorimetry.
E100	Starch based bio-plastic, plasticised by glycerol/ChCl, extruded at 100 °C.
E130	Starch based bio-plastic, plasticised by glycerol/ChCl, extruded at 130 °C.
E160	Starch based bio-plastic, plasticised by glycerol/ChCl, extruded at 160 °C.
EPDM	Ethylene Propylene Diene Monomer.
EPR	Ethylene-Propylene Rubber.
f_0	Frequency.
FTIR	Fourier transform infrared spectroscopy
G130	Starch based bio-plastic, plasticised by glycerol, extruded at 130 °C.
HBD	Hydrogen Bond donor
HDPE	High Density Polyethylene.
HHFW	Half Height Full Width.
HPLC	High performance liquid chromatography.
IL	Ionic Liquid.
LCMS	Liquid Chromatography Mass Spectrometry.
LDPE	Low Density Polyethylene.
LLDPE	Linear Low Density Polyethylene.
MDF	Medium Density Fibreboard
MFI	Melt Flow Index
MFR	Melt Mass Flow Rate
M _w	Molecular Weight.
NMR	Nuclear Magnetic Resonance.
PB	Polybut-1-ene.
PCL	Polycaprolactone.

PE	Polyethylene.
PEA	Polyesteramide.
PET	Polyethylene terephthalate.
PHBV	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate).
PI	Polyimides.
PLA	Poly (lactic acid).
PMP	Polymethylpent-1-ene.
PP	Polypropylene.
PVC	Polyvinyl Chloride.
Q-factor	Quantified resonance.
QCM	Quartz Crystal Microbalance.
RH	Relative Humidity
SEM	Scanning Electron Microscopy.
SBS	Styrene-butadiene-styrene.
TGA	Thermogravimetric Analysis
TMA	Thermomechanical Analysis
TPS	Thermoplastic Starch.
T _g	Glass Transition Temperature.
UTS	Ultimate Tensile Stress
U _o	Peak Intensity Value.
XRD	X-ray Diffraction.
WAC	Water Absorption Capacity

Chapter 1: Introduction

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1. Starch Based Bio-Plastics

1.1. Introduction

Plastics are one of the most important petrochemical based products and they are used in all aspects of life. Most polymers are oil based and are made by either addition or condensation polymer techniques. Most are considered to have a detrimental effect on the environment as they do not readily biodegrade. The consumption of oil-based plastic in 2007 was 260 million tonnes.¹ This is a significant issue as oil resources will dwindle rapidly over the next thirty years.^{2,3}

Although polymer collection for recycling is widely carried only a small proportion is actually remade into materials. The majority is incinerated to reclaim energy.^{4,5} There are many other reasons that motivate industries and researchers to find alternatives to non-renewable resources; however it is noted that all replacements for current plastics should meet some important conditions, they need to be low cost, renewable, sustainable and biodegradable.

However, environmental issues have led researchers to study the degradation of plastics. The development of short-lived bio-degradable plastic is seen as a major goal and so the use of starch as a natural, raw material for degradable thermoplastics is seen as an important goal.^{6,7} Starch alone cannot, however form plastics with satisfactory mechanical or chemical properties, thus using a modifier is important to improve these properties. The topic of thermoplastic starch (TPS) is therefore important and the work to date is elucidated in greater detail in **Section 1.4.2** below.

1.2. Polymers

The word polymer is derived from the Greek *poly* meaning many and *meros* meaning parts.⁸ Macromolecule is another term that can be used where a polymer is made up of repeating structural units linked by covalent bonds.^{8,9}

Polymer science saw its most significant developments in the 1930 when the first natural polymers were produced.¹⁰ Today polymer science is a very important research subject and

plastic production is one of the biggest industries. A large theme of polymer research is modifying the chemical and physical properties and trying to produce environmentally friendly polymers.¹¹

Polymers can be categorised in many different ways including their:

- **Source:** natural, semi- synthetic and synthetic polymers.
- **Polymer chain type:** linear polymers, branched chain polymers and cross linked (network polymers).
- **Mode of polymerisation:** addition polymers and condensation polymers.
- **Properties:** elastomers, fibres, thermoplastic polymers and thermosetting polymers.
- **Polymerisation method:** relying on the polymerisation mechanism e.g. bulk, solution, suspension and emulsion.
- **Monomer composition:** homopolymers and copolymer (heteropolymers): block and graft.
- **Functional group type:** polyester, polyamide, polyether, polyolefin, etc.
- **The degradability:** degradable in nature, degradable in industry and non-degradable polymers.

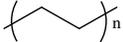
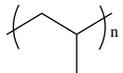
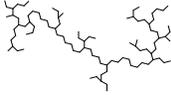
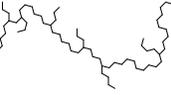
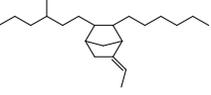
Natural polymers or biopolymers are those formed in the natural environment by living organisms, they are usually extracted from plants or animals.^{12, 13} Proteins, natural rubber, and polysaccharides are all examples of natural polymers that are widely used in modern life.¹⁴ There is currently a significant interest in biopolymers as an alternative to oil-based plastics in some applications.^{15, 16} The most important advantages of using natural polymers especially those based on proteins and polysaccharides is that they can degrade biologically in the environment much more easily than oil-based polymers, and that they also offer the potential to be renewable.^{13, 17, 18} Mankind has used natural biopolymers for millennia and these include wood, leather, wool, cotton and silk.

The most common polymers that are used are polyolefin, polyester and polyamide due to their ease of manufacture and their advantageous chemical and physical properties.¹⁹ Polyolefins are the most common (approximately 60% by mass) synthetic oil-based-

polymers. They are produced by addition polymerisation of olefin such as ethylene or propylene, and they can be classified as homopolymers, copolymers and terpolymers.^{8, 19-21}

Table 1-1 shows some examples of the most common polymer types.

Table 1-1: Most common polyolefins polymers and their structures and applications.

Name	Abbr.	Recycling codes	Structures	Applications
Polyethylene	PE	n/a		HDPE, MDPE, LDPE or LLDPE
Polypropylene	PP			Drinking bottles ²² , packaging food ²³ , textile ²⁴ , carpets, rugs, , filters and soft containers ²⁵
Polybutene-1	PB	n/a		Hot and cold water plumbing and heating piping systems ²⁶
High density polyethylene	HDPE			Orthopedic implants ²⁷ , Biomedical applications ²⁸ , milk and water bottles ²² , fuel tanks ²⁹ , telecom ducts, containers, plastic bags, storage sheds ³⁰ and piping ³¹ .
Low density Polyethylene	LDPE			packaging in retail trade, packaging food ³² , biomedical application ³³
Linear low density polyethylene	LLDPE	n/a		Stretch wrapping market ³⁴ , piping, commodity, packaging, agricultural filming, cable covering ³⁵ , greenhouse films. ³⁶
Ethylene-propylene rubber	EPR	n/a		Electrical insulating material of power cables, ³⁷
Ethylene propylene diene monomer	EPDM	n/a		Automotive tires, wires, cables, footwear, barriers, non-automotive mechanical goods, ^{38, 39} and aerospace ⁴⁰

Condensation polymers, as their name implies, are generally formed from the reaction between two bi-functional molecules eliminating a molecule of water in the process. Each

bond is formed in a discrete step which is independent of all other bond formation. All monomers and complementary chain ends can react, not just the initiated chains. The most important condensation polymers are polyesters and polyamides. Polyamides are generally produced from a reaction between diamides and diacids (or more commonly diacid chlorides) resulting in long chains with amide linkages. This is also the method by which proteins form using amino acids where each monomer has the acid and amine functionality. They are found extensively in nature particularly in proteinaceous materials such as silk and wool. Nylon 6-6 is one of the most commonly synthesised polyamides as shown in **Figure 1-1**. Intermolecular hydrogen bonds in adjacent chains of nylon 6-6 give strength to the fibre.⁴¹ Polyamides are usually used in producing textiles, sportswear and carpeting, due to their strength and durability.

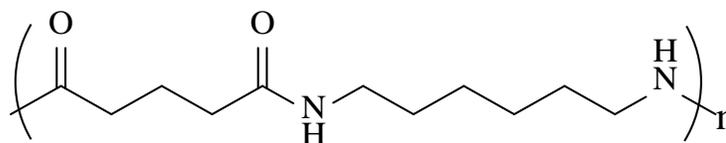


Figure 1-1: The repeating unit of nylon 6-6 polymer.

Polyesters are similar to polyamides but contain ester linkages in the main chain. However, some polymers contain a number of ester groups in side chains and they are not, in general, considered as polyesters e.g. poly(vinyl acetate).⁴² **Figure 1-2** shows polyethylene terephthalate (PET) which is the most common polyester; worldwide annual production is about 4.5 million tonnes, it is commonly used for drinking bottles and fibres for clothes.⁸ PET is a resulting product from the reaction of a diacid and a diol. Natural and some synthetic polyesters degrade in environment but most of the synthetic polyesters do not naturally biodegrade.

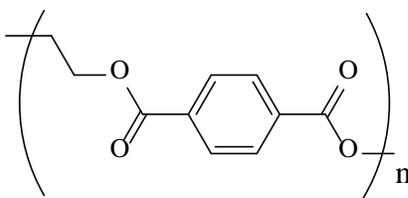


Figure 1-2: The repeating unit of polyethylene terephthalate (PET).

Bi-functional monomers ensure the production of straight chain polymers. Chain branching or cross linking can be achieved by the addition of tri or multifunctional alcohols and these can result in low density or thermoset polymers.

1.3. Thermal Properties

Polymeric materials differ from most inorganic or metallic materials because of their unusual thermal properties. At low temperatures, polymers are mostly crystalline because the motion of one polymer chain that relative to another is difficult. Polymers are usually brittle but strong and they have a short elastic region. As the temperature increases rotation around the C-C bond is possible so the crystalline regions dissolve, and slip of neighbouring chains is possible. The temperature at which a polymer changes from a rigid to a flexible material is known as the glass transition temperature (T_g), that can be determined by measuring the specific volume of a sample as a function of temperature. Many other properties change markedly around T_g such as refractive index, stiffness, thermal conductivity and hardness.

Very few materials are made up of just polymeric components. Usually a variety of additives are included to achieve the required properties of the material. These can include; fillers such as carbon black to reduce cost; plasticisers such as alkyl phthalates to change mechanical properties; lubricants to aid processing; pigments to change the optical properties; stabilisers to stop the degradation of the polymer by heat; anti-wear agents; antistatic agents to spread the charge on materials introduced by friction; curing agents to increase rigidity; flame retardants and blowing agents to produce foams. Some additives fulfil many roles e.g. carbon black is a filler, stabiliser and pigment. In many cases the

additives can be the major component of the material. The combination of polymer and additive is known as a *plastic*.

Polymers can be classified into 2 types depending on their thermal response. Thermoplastics make up 90% of all processed polymers; they become soft and fluid on heating and set on cooling. This cycle can be repeated i.e. the polymers can be re-cycled. Thermosets are highly cross-linked polymers generally formed by condensation polymerisation, where heating leads to decomposition and so they cannot be recycled.

1.3.1. Thermoset

Network polymers that decompose before they can be liquefied or reformed are called *thermoset* plastics; they are typically obtained by cross-linking a linear polymer.¹⁹ Therefore, thermosets have a three dimensional cross-linked structure and heating does not allow polymer flow. The structure of the plastic can be formed by different methods including:⁴³

1. Condensation type polymerisation: such as silicone resins, aminoplastics and phenolics.
2. Crosslinking species to form crosslinks between polymer molecules: such as epoxy resins and unsaturated polyesters.
3. Addition polymerisation of monomers containing two double bonds: Such as polymerised diallyl phthalate.

In the first mechanism, the material passes through two stages, one to form low molecular weight polymers, then in the second stage the materials are solidified. These materials are relatively stable at 25 °C and can be shaped as required.⁴³ Heating or a catalyst is used to crosslink the polymer chains together through covalent bonds. **Figure 1-3** shows an example of a high molecular weight elastomer formed when polybutadiene is heated with sulphur, forming cross-links. This increases the strength but decreases the resilience and makes the material difficult to be recycled. Many thermosets are now formed using ultraviolet light to initiate cross linking at room temperature.⁴³

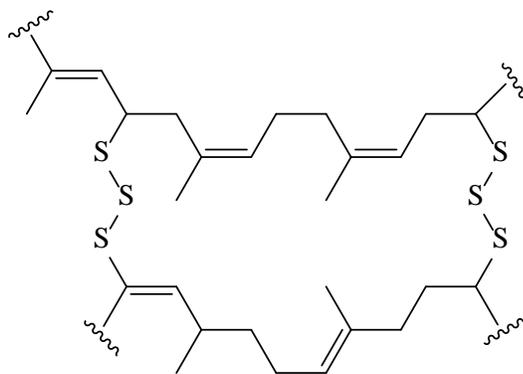


Figure 1-3: Repeating unit of a synthetic rubber as an example of thermoset plastic.

1.3.2. Thermoplastic

Linear polymers that can be softened and/or reshaped by application of heat and pressure are called *thermoplastics*.¹⁹ Thermoplastics consist of high molecular weight polymers and their chains connect via intermolecular forces such as; Van der Waals forces, dipole-dipole interactions and hydrogen bonding as shown in **Figure 1-4**.⁴⁴ There are some thermoplastic elastomers that contain chemical or physical cross-links, but most of the elastomers are thermoset. The first thermoplastic elastomers called plastisols were derived from plasticised polyvinylchloride (PVC) and most common thermoplastic elastomers are styrene-butadiene-styrene (SBS) block copolymer.

Thermoplastic materials are most commonly supplied as pellets, marbles or chips in different sizes and they may contain the desired amount of additives. Thermoplastics soften and flow as viscous liquids when heated above the glass transition temperature and then can be cooled to shape as desire in a mould, using a variety of techniques and for virtually all applications in reflection of their stability at 25 °C, to high temperatures depending on the plastic type.^{8, 45}

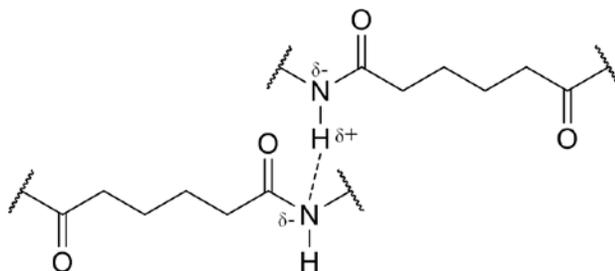


Figure 1-4: Hydrogen-bonding interactions between polyamide chains.

1.4. Thermoplastic Starch (TPS)

Most plastics currently used are non-biodegradable, and cause environmental damage particularly when washed into water-courses.⁴⁶ Reuse and recycling of oil-based plastics is not the simple answer as re-grinding and then re-extrusion causes loss in some of the mechanical properties.⁴⁷ Some semi-synthetic bio-based plastics are currently in common use such as cellulose acetate, viscose and polylactic acid (PLA). PLA can be derived from corn starch through fermentation to produce lactic acid, **Figure 1-5**. It is the last of these which is currently attracting significant attention as a biodegradable biopolymers and it is commercially used in some packaging applications due to its high strength.⁴⁸

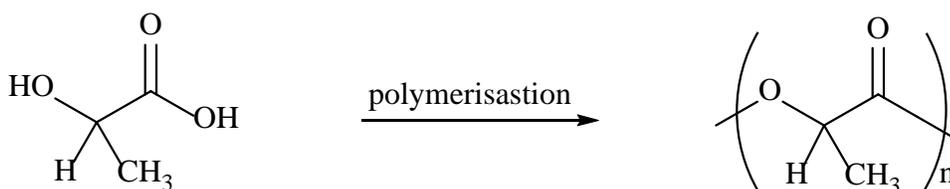


Figure 1-5: Polymerisation of lactic acid to PLA.

It can be combined with starch to increase its biodegradability and reduce cost however PLA is still more expensive than most common polyolefins.¹² The increased use of biopolymers can be seen in **Table 1-2**.

Table 1-2: The global market for biodegradable polymer (million kg).¹²

Applications	2006	2007	2012
Compost Bags	78	110	266
Loose-Fill Packaging	69	73	97
Other Packaging	23	37	105
Miscellaneous	15	25	78
Total	186	245	545

Due primarily to the cost of PLA and its relatively slow biodegradability several studies are investigating the use of starch as a raw material for plastics with short-lived applications e.g. packaging.

1.4.1. Starch as a raw material

Starch and cellulose are two of the most abundant polysaccharides, and both are homoglycan polymers.^{49, 50} D-glucose is the monomer unit in both starch and cellulose; however, they have very different mechanical and chemical properties from each other due to a small difference in their structure.⁵¹

The D-glucose of the monomer of cellulose that linked at the β (1-4) position as shown in **Figure 1-6**, while the other glucose monomer rotated 180° around the axis of the polymer chain due to the β sign which means the linking oxygen is in the equatorial position.⁵² Subsequently, the alkyl alcohol branch causes interaction between cellulose chains by strong hydrogen bonding, which gives a strong mechanical structure.

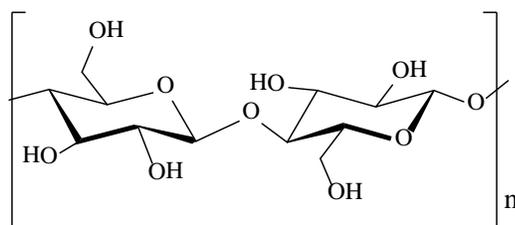


Figure 1-6: The structure of section of cellulose showing the β (1-4) glycosidic linkage.

Starch is made up mostly of amylose and amylopectin. The linking oxygen atom is in the axial position which helps all monomer glucose units to be oriented as each other, indicating that polysaccharide starch is connected by α (1-4) glycosidic linkage, consequently the starch chains interact in a helix. Amylopectin is a branched version of amylose, where α (1-6) glycosidic linkage form a branch.^{53, 54} The glycoside linkages begin to breakdown at 150 °C while its granules start to decompose above 250 °C. A slight degree of reorganisation of hydrogen bonds arises at low temperatures which straightens the polymer chains.¹²

The ratios and distributions of amylose and amylopectin vary in each starch depending on its source.^{55, 56} The amylose and amylopectin ratio of different plants affect the properties of the starch.⁵⁷ Conversely, cellulose cannot be branched like amylose, due to the strong structure that gained from the strong hydrogen bonding as shown in **Figure 1-7**.

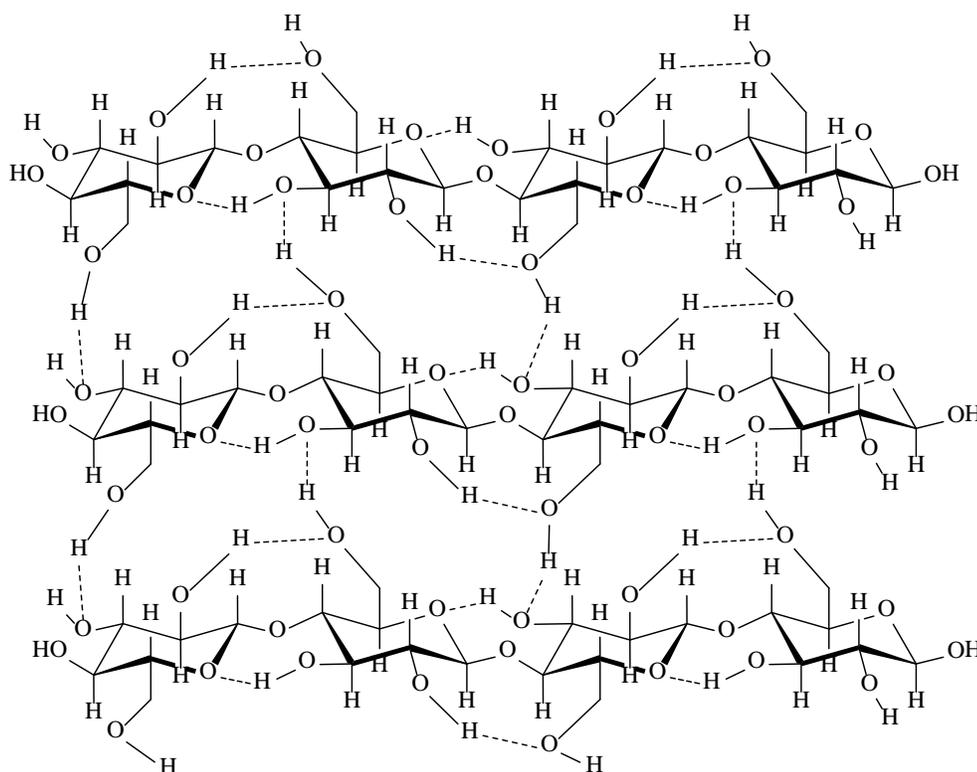


Figure 1-7: Structure of cellulose polymer chains layered due to hydrogen bonding.

Both amylose and amylopectin structures, shown in **Figure 1-8 (a)** and **(b)** respectively can be broken down by a specific enzyme which degrades the polymer. Some organisms digest starch using amylase and maltase enzymes to convert it into glucose, for energy. On the other hand, the internal order is lost by heating in the presence of water, eventually destroying the structure, dispersing the polymer chains into the water.

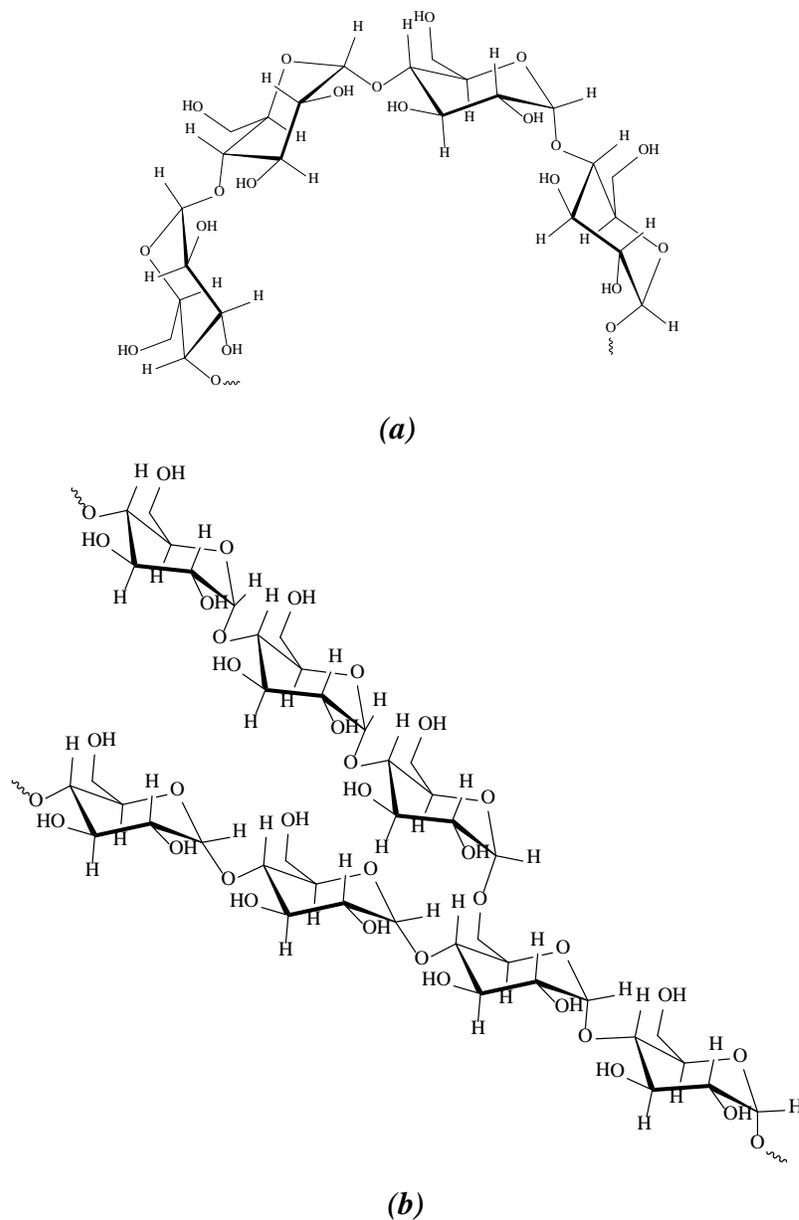


Figure 1-8: representative partial structure of amylose (a) and amylopectin (b)

1.4.2. Modifiers

Many modifiers have been used to plasticise starch including; glycerol,⁵⁸ sorbitol,⁵⁹ water,⁶⁰ urea,⁶¹ ethanolamine⁶² and formamide.⁶³ All of these plasticisers have hydroxyl groups allowing compatibility with starch granules and they plasticise starch by breaking the internal hydrogen bonding between the glucose rings in starch.

The macromolecular chains of amylose and amylopectin in native starch are linked by strong intermolecular and intramolecular hydrogen bonding. The plasticiser at high temperatures (90 °C – 180 °C) converts starch granules to thermoplastic starch, enabling it to be extruded, pressed or injection moulded, dissolving starch granules and lowering its melting temperatures. Breaking up the starch granules results an increase of macromolecular chain mobility and consequently the material softens and becomes less brittle. The semi-crystalline granules are converted into a homogeneous and amorphous material, which is known as the plasticisation of starch.^{64, 65}

Various mechanisms for the plasticisation of starch have been proposed. These include *lubricity theory* which suggests the plasticiser expedites the mobility and movement of starch macromolecules over each other, while the *gel theory* supposes the plasticisation is a result of the disruptions that occur in-between polymer interactions due to either hydrogen bonds and van der Waals or ionic forces. The *free volume theory* considers that the free volume between polymer chains increases by the addition of a plasticiser causing a decrease in the glass transition temperature. In all of these theories the main role of a plasticiser is to intervene between starch chains and reduce the internal interaction between starch chains and these are replaced by starch-plasticiser interaction.⁶⁵⁻⁶⁷

An effective plasticiser needs to be polar, hydrophilic and small enough to fit between the starch chains. Additionally, the boiling point of the plasticiser should be higher than manufacturing conditions so that it does not evaporate during processing.⁶⁵ Water and glycerol are the most common and effective plasticiser as they can be inserted easily in to starch.^{65, 67} Some plasticisers such as urea, formamide and ethylene bisformamide contains amide functionalities have proved to act as good plasticisers.^{65, 68-72}

The strength of hydrogen bonding also varies from one TPS to another relying on the plasticiser type. The hydrogen bond energy between urea-starch and glycerol-starch has been calculated by Ma and Yu⁶¹ who found the hydrogen bond of urea-starch was stronger than the glycerol-starch hydrogen bond. However, in food packaging and edible films, amide groups are not recommended for food safety.^{65, 73}

The amount of plasticisers, including water, is very important for optimising starch gelation. A plasticiser and water content are strongly dependent on the relative humidity (RH), where plasticiser molecules replace the position of water molecules at low RH causing a decrease in water content and increase in plasticiser. However, for RH higher than 43% water content increases due to an interaction between the existence plasticiser and water. With high plasticiser content phase separation can occur between starch chains and plasticiser.^{64, 74, 75}

In contrast, a low content of plasticiser causes antiplastification as a result of the strong interaction of starch-plasticiser, making a network to be established and reinforcing the final plastic, while the addition of more plasticiser causes plastification due to the interaction of plasticise-plasticiser.^{74, 76}

The presence of heat during processing thermoplastic starch plays a very important role in improving and accelerating the gelation. Smith *et al.*⁷⁷ who studied the interaction between starch and glycerol and ethylene glycol based plasticisers, reported that an interaction between starch and the plasticiser occurred during storage at room temperature similar to the interaction that occurred upon heating during processing.

Deep eutectic solvents can be used as a plasticiser and an alternative to the use of ionic liquids (IL).⁷⁸ Sankri *et al.* have studied the effects of the Ionic liquid (IL) anion and cation in plasticising starch by 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), they have shown that hydrogen bonds, between the anions of the imidazolium salt and the protons of the hydroxyl groups of the polysaccharides, were formed as a result of starch solvation. However, the cation functions depends on its size and hydrophobicity and the specific role of the cation is not understood.⁷⁹

1.4.3. Deep eutectic solvent (DES)

Deep eutectic solvents can be used as a plasticiser and an alternative to the use of ionic liquids (IL). ILs are salts that have a melting point below 100 °C where they are liquid in room temperature and below the boiling point of water.⁷⁸ DESs are a sub-category of ionic liquid (IL). They are fundamentally molten salts that interact either by hydrogen bonding or by metal halide bonding.⁸⁰ They are produced by mixing two components together in a certain ratio. The low freezing temperature that arises at the *eutectic point*, **Figure 1-9** results from non-ideal mixtures which have a low lattice energy.⁸¹ The expression DES has been applied to discriminate them from ionic liquids which have a discrete anion.

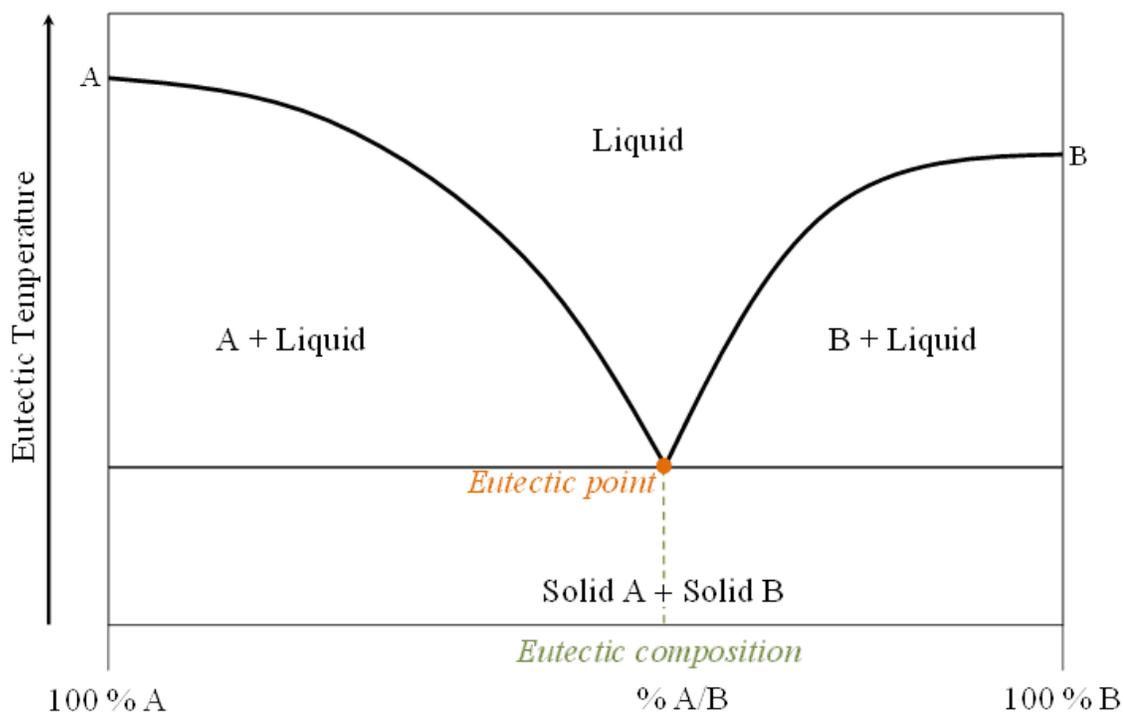


Figure 1-9: phase diagram for a eutectic mixture.

1.4.3.1. Types of DES

DESs are classified into four types as shown in **Table 1-3**:

Table 1-3: The four types of deep eutectic solvent.

Type I	Metal salt + organic salt
Type II	Metal salt hydrate + organic salt
Type III	Organic salt + hydrogen-bond donor
Type IV	Metal salt hydrate + hydrogen-bond donor

DESs have been used for a variety of applications including metal deposition, electropolishing, metal oxide processing and some of these applications have been scaled up to > 1 tonne. For most applications Type III eutectics have been the most applicable due to their low cost and their low eco-toxicity. The topic of DESs has recently been reviewed in depth by Smith *et al.*⁸² Type III eutectics are mixture of complex quaternary ammonium salts with hydrogen bond donors, **Figure 1-10**.⁸¹ These systems contain a cation, an anion and a hydrogen bond donating species as well. Carboxylic acid, amides and alcohols are examples of appropriate hydrogen bond donors. The first of these systems to be described was the choline chloride (ChCl)/ urea system mixed in a 1:2 mole ratio.⁸³ The DES has a freezing point of 12 °C while the freezing point of choline chloride is 303 °C and that of urea is 135 °C. This mixture was used as a reagent and solvent for the quaternisation of cellulose.^{84, 85}

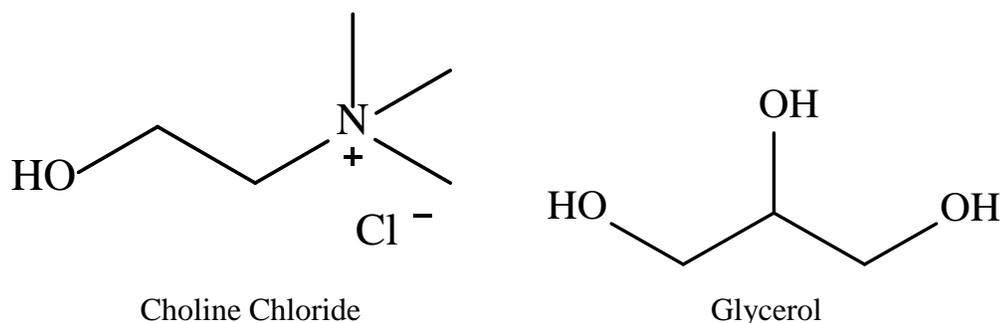


Figure 1-10: Glyceline, a type III of DES made from choline chloride and glycerol.

Choline chloride (2-hydroxyethyl-trimethylammonium chloride) is the most common quaternary ammonium salt used for making DESs due to the asymmetry and polar functional group.^{83, 86} Choline chloride is relatively inexpensive and non-toxic (it is a pro-vitamin B4 and commonly used as a food supplement).

In this study Type III eutectics are the only ones being studied. In an analogous study Type IV systems are currently being applied to TPS but they were not used in this study.

1.4.4. Starch gelation

Thermoplastic starch is biodegradable plastic based on starch. The semi-crystalline starch granules must be broken by thermal and mechanical processing to obtain TPS.^{60, 87} The important role of a plasticiser, accompanied with heat and pressure, is to break up the crystalline structure of starch granules and form a continuous amorphous polymer phase.⁸⁸ After TPS is produced, slight recrystallization can occur which improves the tensile strength but allows more ductility.^{12, 89}

Gelation of starch occurs by disrupting the crystalline structure freeing the starch helices, producing amorphous thermoplastic starch. Heating the mixture of starch and the plasticiser is important to make the starch granules swell and amylose disperses out of the starch granules, while amylopectin is held in. Thus the gelation breaks down starch-starch –OH bonds and forms new interactions between starch and the plasticiser.¹⁶ Starch granules need at least 33% moisture to be plasticised when water used as the plasticiser. The amount of water in the mixture affects the glass transition temperature and melt flow index. However, addition of glycerol results in stronger thermoplastics due to the strong interaction forces between the starch monomer units and glycerol.¹²

Since starch is extremely abundant from several sources, thermoplastic starch is inexpensive, biodegradable and renewable. The materials produced can also be modified by adding another additional material such as fillers.^{90, 91} Owing to the ease and the ability to produce TPS using the same industrial processing techniques of the current commercial plastics including extrusion, injection moulding and vacuum formation,¹² TPS can be an

alternative to some non-degradable plastics especially those used in short-lifetime applications.

1.4.5. Hygroscopic nature of TPS

The high hygroscopic nature and swelling of starch in the presence of water is due to the penetration of water between the carbohydrate chains.^{3, 92} The hygroscopic nature of starch is very dependent on temperature and relative humidity.⁹³ Use of a hygroscopic plasticiser also increases the hygroscopic nature of the final product.^{12, 94} Regardless of how 'green' a bio-plastic may be, it must be cost effective to compete against current synthetic plastics.

1.4.6. Applications of TPS

Thermoplastic starch has been used widely in several applications such as packaging, adhesives, paper, bio-composites, tissue engineering and in food and pharmaceutical industries.⁹⁵

Moreover, many studies on blending starch with synthetic polymers have been investigated.⁹⁶ The idea was to decrease oil consumption and allow faster biodegradation.¹² TPS can be blended with synthetic biodegradable polyester such as polycaprolactone (PCL), polyesteramide (PEA),⁹⁷ polylacticacid (PLA), polypropylene⁹⁸ and poly-3-hydroxy butyrate-co-valerate (PHBV).⁹⁹ These blends improve the mechanical properties and improve hydrophobicity, comparing to pure TPS.¹⁰⁰

1.4.7. Additives as composites or fillers

Mechanical, chemical and physical properties of plastics can be modified with a range of additives as described above. The most common additives are *fillers* to reduce cost for example, or to enforce physical properties such as tensile strength which so-called *composites* material. However, stabilisers are the additives that control material deterioration, while colorants are usually small particle size that used to change plastics colour without making any chemical reaction or phase separation. The particle size of composites has a significant effect on the properties. Most commonly these fillers are small

(10s of μm) and roughly similar dimensions in all direction to have the most efficient reinforcement.^{101, 102}

Composites can be categorised into many ways, the most common used composites are illustrated in **Figure 1-11**.^{103, 104}

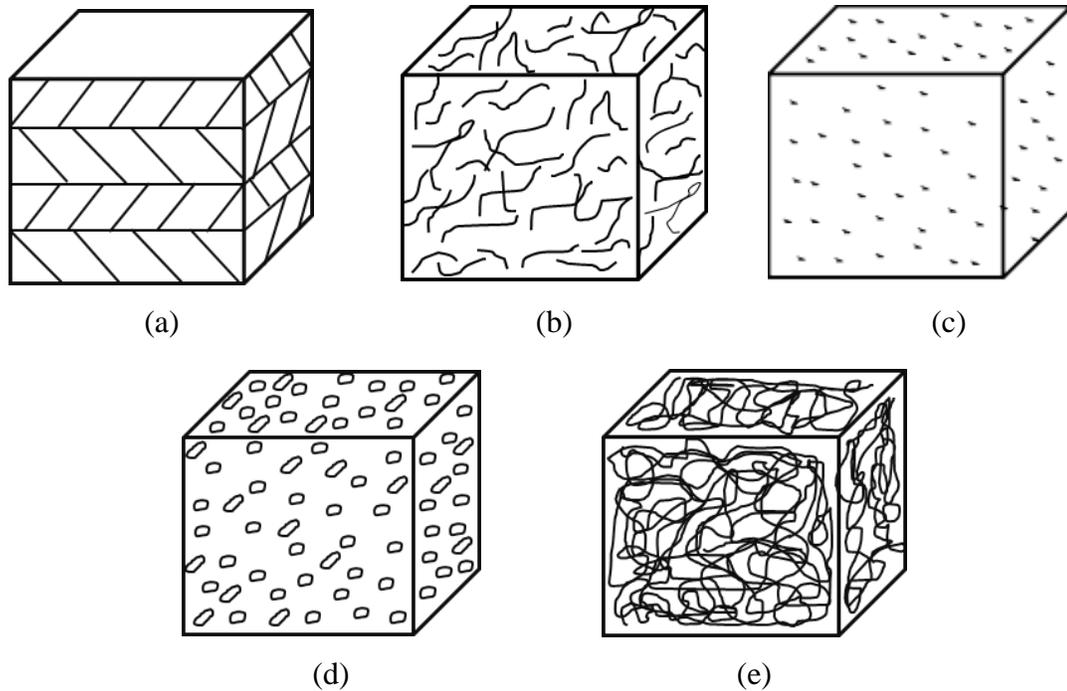


Figure 1-11: Most common types of composites. Laminar composite (a), fibre composite (b), particulate composite (c), flake composite (d), filled composite (e).¹⁰³

Fibres (particularly of wood, glass and carbon) are the most common composites due to their low cost. Such materials are produced on the millions of tons per year scale internationally. Natural fibres are an example of the suitable composites that can be used in thermoplastic starch where they are recyclable, biodegradable, renewable, sustainable and environmentally friendly.¹⁰⁵

1.5. Properties of plastics

The mechanical properties of a polymer are controlled by the way that the chains interact and indirectly then to its molecular weight.¹⁰⁶ Higher molecular weight polymers have

larger probabilities of chain interaction increasing the strength, glass transition temperature and crystallinity.

Table 1-4: Inter-chain interaction energies.¹⁰¹

Bonding Type	Dissociation Energy (kJ mol ⁻¹)
Covalent bond	300-1000
Hydrogen bonding	10-30
Dipole-dipole interaction	2-5
Van der waals forces	≤ 4

Table 1-4 shows that most polyolefins are significantly weaker than polyester/amide polymer, due to the inter-chain bonding type *viz.* van der Waals forces *vs.* hydrogen bonding. In thermoset, a network solid is formed due to the covalent bonds between polymer chains, instead of intermolecular forces, showing greater strength than hydrogen bonding.

Polyolefins are, however, much more ductile than polyesters and polyamides and **Table 1-5** illustrates the comparison of mechanical properties for some common polymers. The large difference in Young's modulus between polyolefins and polyester/polyamides shows the stiffer nature of polyester/polyamides. The rigidity shows the strength of the interaction between the chains and in covalently cross-linked polymer chains the rigidity of the thermoset polymer is remarkable.

Table 1-5: Mechanical properties of some common synthetic polymers.

Polymer	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
HDPE	20-32	180-1000	600-1400
LDPE	8-12	600-650	200-400
PP	25-30	500-800	800-1300
PET	70	130	3100
Nylon 6-6	80-85	12-300	1700-2000
PI	85-90	5-7	3100

Synthetic polymers show slow biological decomposition, making them persistent in the environment. This could be very useful for some applications, e.g. cold water piping, but poor for short use products such as packaging. Biodegradable synthetic polymers including: poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polycaprolactone (PCL) and poly(lactic acid) (PLA), **Figure 1-12**, have been commercially available since the 1990's.¹² These are however more expensive and more complicated to produce than oil-based polymers.

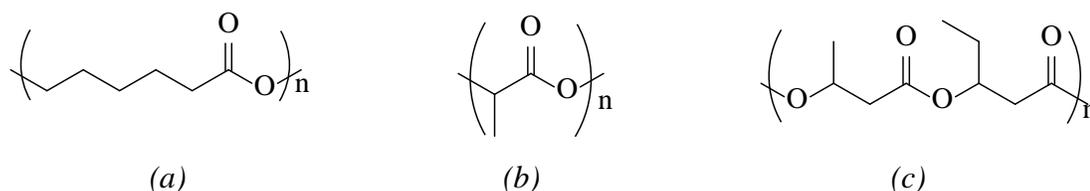


Figure 1-12: Examples of biodegradable polymers PCL, PLA and PHBV respectively.

By comparison TPS is easier to produce as it requires no chemical modification and no polymerisation step. Its properties depend on the content of plasticiser and adding more plasticiser increases the polymer chain mobility, reduces the glass transition temperature, increases the flexibility but decreases the tensile strength. Plasticising TPS using glycerol instead of water decreases the recrystallisation rate, and glycerol hinders chain mobility because of the intermolecular interactions between glycerol and starch chains.⁵⁹ However, glycerol increases moisture content due to its hygroscopic nature, and then consequently lowers the glass transition temperature and aids recrystallization.¹⁰⁷ The glycerol quantity and the moisture content increase TPS density.¹² **Table 1-6** compares the densities of typical polymers with TPS and it can be seen that TPS covers a wider range of densities depending upon its processing conditions.

The weak interaction between starch chains allow them to incorporate a plasticiser that modify starch and manipulate required properties.¹¹¹ Adding more plasticiser increases the macromolecular mobility allowing for greater elongation but less tensile strength.¹¹² In contrast, addition of urea to the plasticiser has the opposite effect.¹¹³

Table 1-6: Comparison of polymer densities.

Plastic	Density (kg m ⁻³)
TPS	790 – 1280
Polyethylene	917 – 950 ¹⁰⁸
Polystyrene	1030 – 1050 ¹⁰⁹
Polysaccharide	1300– 1410 ^{52, 110}

1.5.1. Viscoelasticity of polymers

Viscoelasticity is a category of deformation showing the mechanical properties from viscous fluid to elastic solid material.¹⁰¹ Two terms are commonly used to describe polymers; viscoelastic and rheologic referring to solid and liquid polymers respectively.¹¹⁴

Polymers are viscoelastic substances owing to their characteristics behaviour when they are exposed to external forces. Viscoelastic bodies have the properties of elastic solid in some conditions, but in other conditions they have the property of viscous liquids.¹¹⁵ Amorphous polymers act as glasses, rubbery or viscous liquids depending on the surrounding conditions especially temperature.^{101, 116}

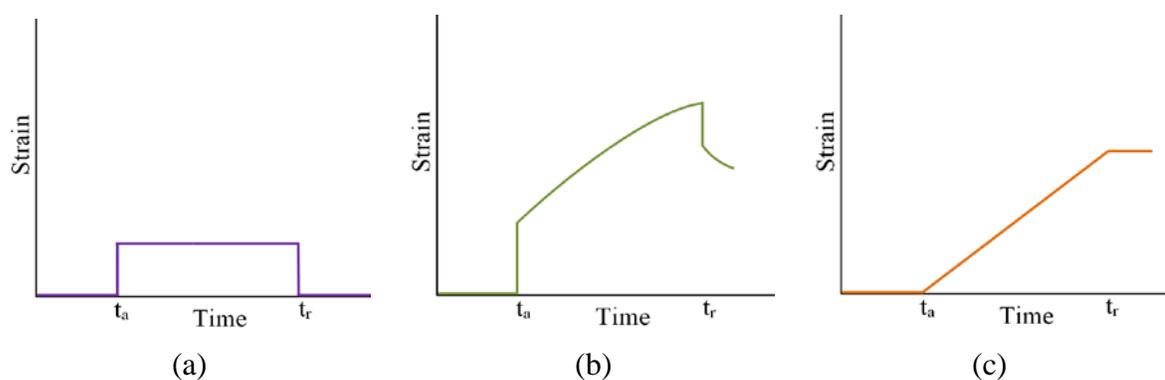


Figure 1-13:¹⁰¹ Behaviour of different deformation of polymers when subjected to external force, totally elastic (a), viscoelastic (b) and viscous (c). t_a and t_r are times when a load, is applied and released respectively.

Figure 1-13 shows the deformation occurring to a polymer when it is subjected to an external load. The deformation is totally recovered and the specimen returns back to its original dimensions, **Figure 1-13 (a)**. However, the deformation of very viscous polymer is not recoverable and it occurs as a function of time, **Figure 1-13 (c)**, while the viscoelastic material behave like an elastic once the load applied but, when load is continually applied it acts like a viscous material until it fractures **Figure 1-13 (b)**.¹⁰¹

One of the benefits of using thermoplastic starch is that its physical and mechanical properties can be controlled by the processing parameters, starch type and primarily the plasticiser type and amount. The viscoelasticity of thermoplastic starch depends on the plasticiser amount in the mixture including the water content.¹¹⁷

Several techniques are used to determine the viscoelasticity behaviour of plastics such as Thermomechanical Analysis (TMA), Differential Scanning Calorimetry (DCS) and Dynamic Mechanical Analysis (DMA).¹¹⁶

1.5.2. Plastic deformation

Deformation of an object occurs when a force or stress is applied to that object. Tensile stress and strain determine the degree of that deformation, and they have a relationship as shown in Hooke's law, **Equation 1-1**.¹³

$$\sigma = E\epsilon$$

Equation 1-1

Where σ is stress, ϵ is strain and E is modulus

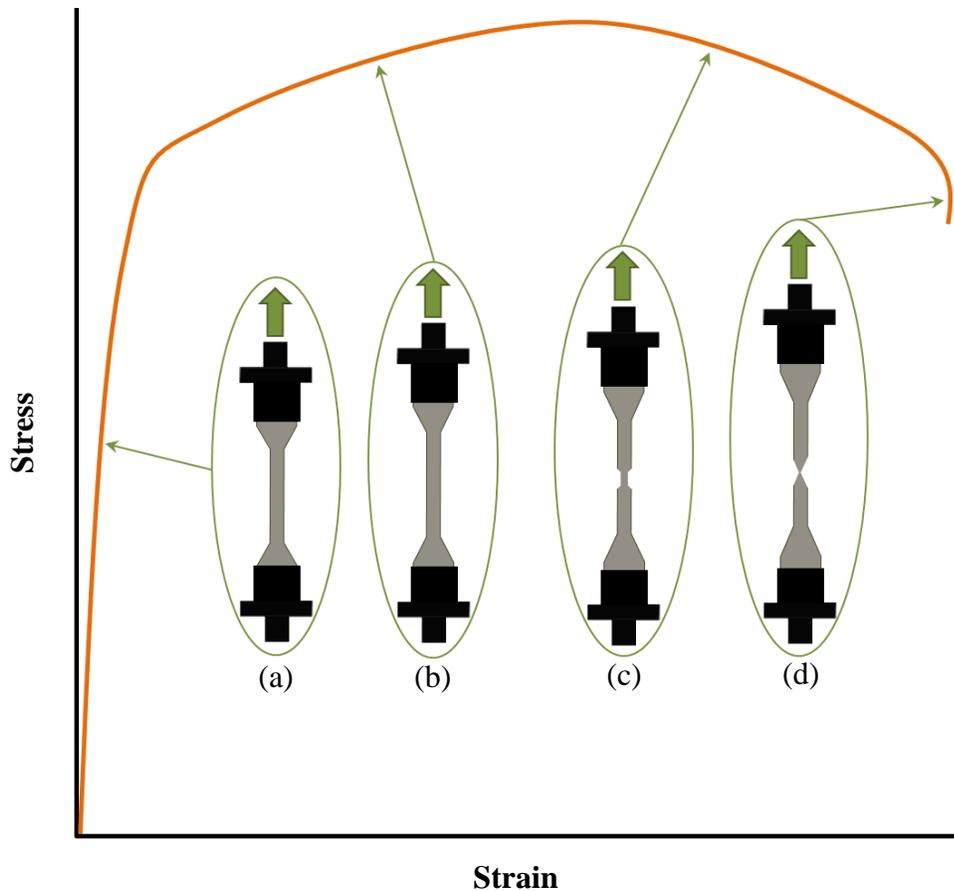


Figure 1-14: stress-strain curve during plastic deformation when a load is applied to a dog-bone (a), when dog-bone started to extend and before the maximum tensile stress (b), the crack propagation starts (c) and the fracture just occurs.

When the stress and strain are proportional the deformation is elastic, and the slope refers to the elasticity modulus (E). The modulus increases with the increasing stiffness of the tested material. The elastic material returns to the initial shape when the applied stress is released. However, when the deformation is non-recoverable and it is permanent that identified as plastic deformation. In plastic deformation the tensile stress increases with the continuous load till it reaches the maximum and then decreases till the material breaks as shown in **Figure 1-14**.¹³

1.5.3. Crystal structure

The crystallinity of a material indicates the order of the atomic arrangement which, for a polymer depends on the way the molecular chains are packed. The degree of crystallinity has a significant impact on the mechanical and thermal properties of most materials, due to the changes in the intermolecular secondary bonding that occur when the crystallinity changes. Commonly, polymers that have higher crystalline are stronger and more brittle.¹⁰¹

Some regions in starch granules are crystalline and are formed from short amylopectin chains creating clusters, while other regions are amorphous.¹² The crystallographic structure classifies the starch into A, B and C types,¹¹⁸ where they show three types of polymorphic structure known as A-, B- and C-type starches. In A-type polymorphic structures orthogonal packing of double helices occurs while more open hexagonal packing of double helices appears in B-type polymorphic structure.¹¹⁹ The starch type depends on the plant source.

Three new types of crystal structure, based on single helices of amylose are formed a period of time after processing TPS. These types are: V_A (non-hydrated), V_H (hydrated) and E_H .¹¹⁸ The E_H type is not stable and is converted to V_H by the influence of moisture.¹²⁰ Plasticising starch using glycerol gives a chance for amylose and amylopectin to recrystallize into A and B type polymorphs.⁵⁸ Moreover, the source of starch, the moisture conditions and the plasticiser content play an important role in the rate of recrystallization.¹²¹

1.6. Extrusion

Extruders are mechanical mixers consisting of long metallic screws used for processing solids and viscoelastic materials. Many different types of extruder can be used to produce plastics, the main two commercial types are single-screw extruders and twin-screws extruders and they differ in the transport mechanism.¹²² In most single-screw extruders the processed material rotates with the screw and is kneaded by contact with the barrel wall. The material characteristics and the channel wall affect the transport mechanism of this type of extruders. In contrast, the material cannot rotate with the screws in the twin-screws extruders as a result of the intermeshing occurred between the two screws. Therefore, twin-

screws extruders are more suitable for TPS because of the water content and twin-screws extruder is less dependent on the material properties than a single-screw extruder.¹²

Figure 1-15 shows the most common single-screw and twin-screws extruders' types:¹²

- The single-screw extruder (a) is the most common extruder; it is a short length extruder with high rotation rates.
- A co-kneader extruder (b) is a single-screw extruder with kneading pins to prevent the material rotating with the screw and it can control the temperature. It oscillates during processing allowing better mixing.
- Twin-screws extruders (c and d) they are counter rotating and they are good for the very elastic materials.
- Closely intermeshing extruders (e and f) are very stable extruders and they are the best in conveying the processed material.
- Conical extruders (g) are a closely intermeshing twin-screw extruder most suitable for materials of low bulk density.
- A self-wiping extruder (h) is a twin-extruder where the screw configurations can be changed by changing the screws elements to increase or decrease the shear rate and consequently affect the extrudate properties.^{123, 124} Kneading elements can be added with different angles between the individual kneading elements, controlling these angles can increase mixing and kneading processes.¹²⁵ This extruder is very good in conveying material, mixing and kneading.¹²⁶

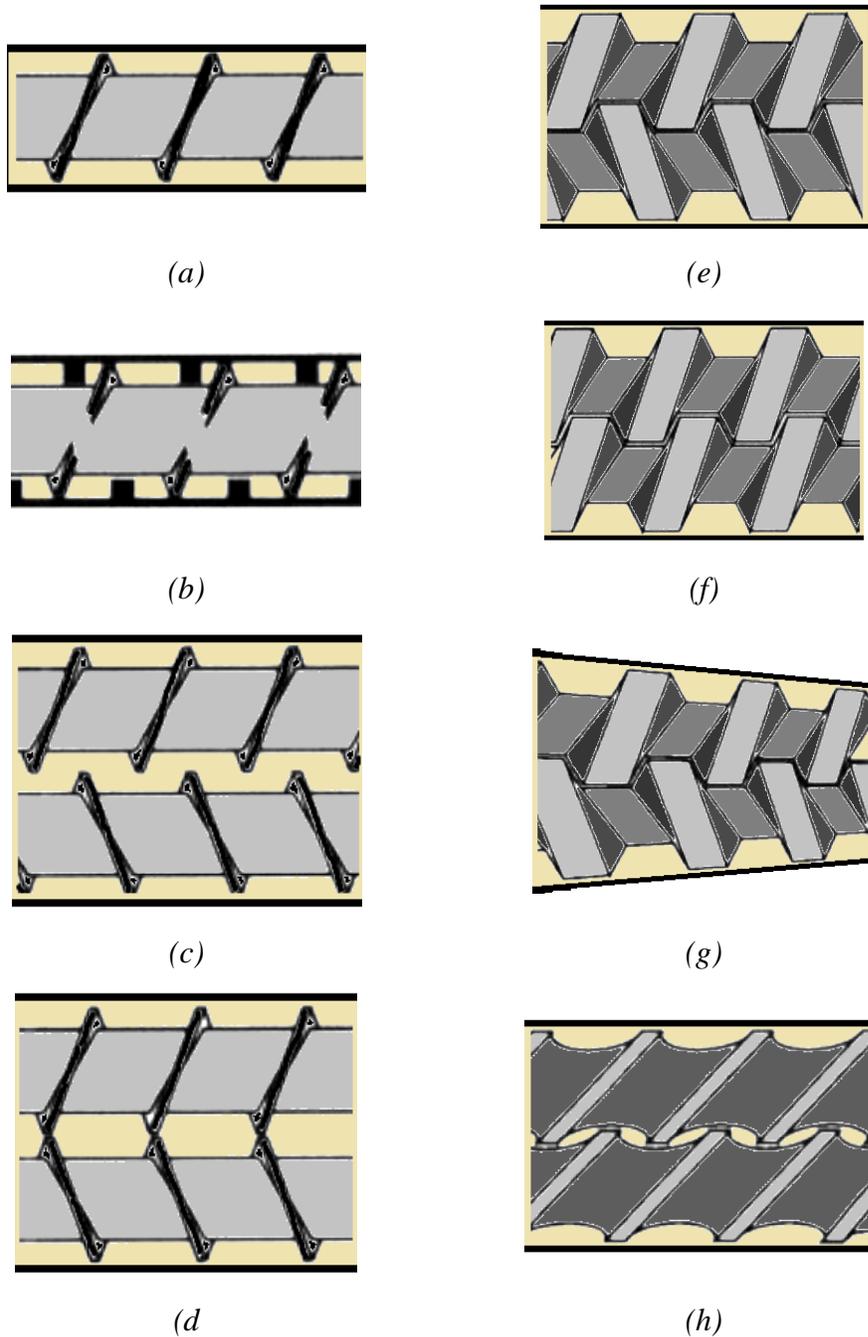


Figure 1-15:¹² Extruders types: single-screw (a); co-kneader (b); non-intermeshing, mixing mode (c); non-intermeshing, transport mode (d); counter-rotating, closely intermeshing (e); co-rotating, closely intermeshing (f); conical counter-rotating (g); self-wiping, co-rotating (h).

Figure 1-16 shows a twin-screw extruder which has several temperature zones that can be controlled. The temperature in an extruder plays a very important role in the physical and mechanical properties of the extruded material.¹²⁷ The closest zone to feed hopper is usually cooler than the rest to start cooling the mixture after plasticisation. The gelation of starch occurs in the middle zones, where its molecular weight decreases and crystallinity changes depending on shear rate intensity, till it reaches the last zone which is completely filled, and then it comes out as TPS through a die.^{128, 129} Thermoplastic starch rope needs to be cooled down before being cut into small chips.¹²

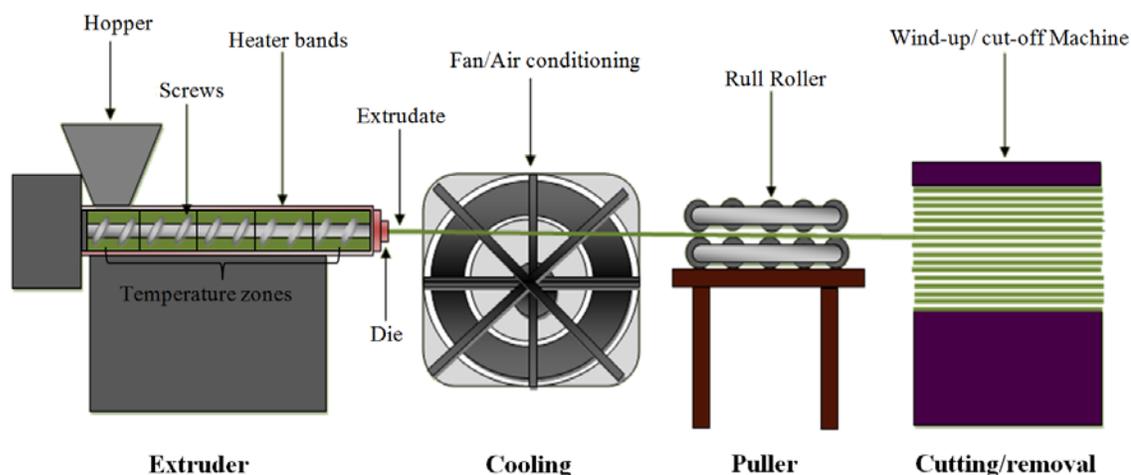


Figure 1-16: Stages of the extrusion process

In this research a five zones extruder was used to produce thermoplastic starch, the first zone, close to the feed, is to dry the mixture of starch and the appropriate plasticiser, before it starts to gel in the next zone. After starch gelation the extruder screws mix and knead the gel to be more homogeneous. The last zone is close to the die and is completely occupied with gelled starch leading to an increase in the pressure. Any gasses can escape through a venting hole. The thermoplastic starch comes out as a rope through two small dies. **Figure 1-17** shows a diagram of extrusion temperature zones.

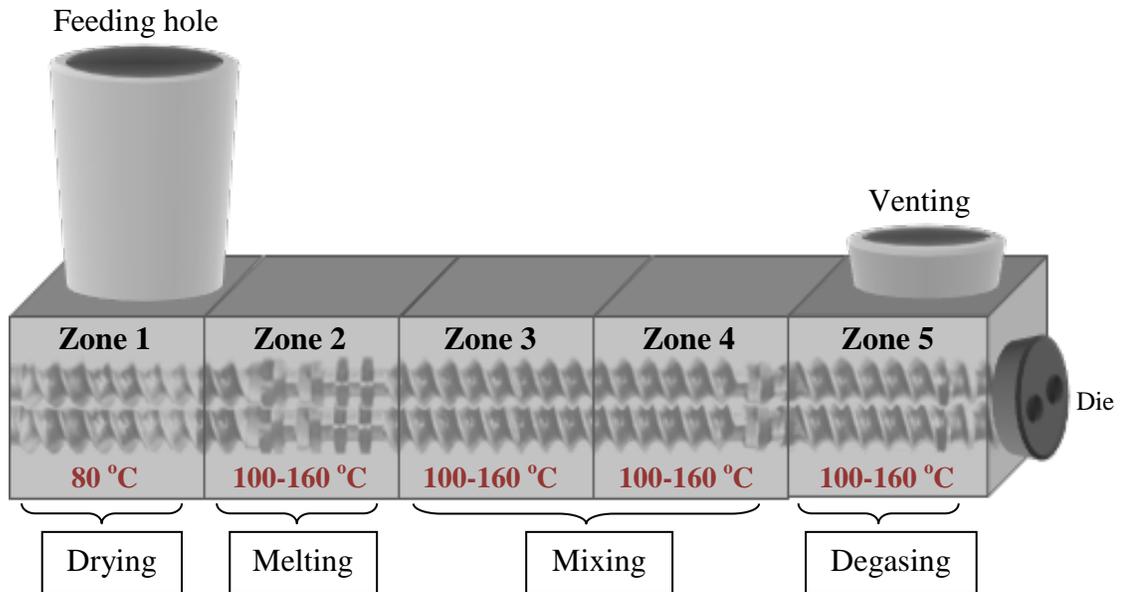


Figure 1-17: extruders' temperature zones diagram shows the process during Thermoplastic starch extrusion.

1.7. Research Aims

The aim of this research is to develop starch-based plastics with suitable mechanical properties. Deep eutectic solvents will be used to improve the plasticisation of the starch as the chloride anion of the quaternary ammonium salt will be better able to break up the intermolecular hydrogen bonds between the starch chains. The stronger hydrogen bonds will prevent the starch recrystallizing with itself and should lead to more stable materials which are easier to plasticise.

The study will be split into three sections: The first will optimise the properties of TPS by optimising the DES type and composition and optimise the processing conditions. This section will also investigate the mechanism by which gelation occurs. In the second section a variety of composites will be produced and the properties will be characterised and in the final part the effect of moisture will be quantified together with methods to reduce the hydrophilicity of the materials.

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Chapter 2: Experimental procedure

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2. Experimental procedure

2.1. Formation and preparation of liquids and TPS

2.1.1. Chemicals

Corn flour (Weikfield Foods Ltd.) was dried in an oven for 24 h at 70 °C before use. Glycerol, urea, ethylene glycol, propylene glycol and choline chloride (all Sigma Aldrich >99%) were used as received. In this thesis corn flour will be called corn starch from now on.

2.1.2. DES synthesis

Four DESs were used in this study. Each involved choline chloride mixed with a hydrogen bond donor in a 1:2 molar ratio. The four DESs were ChCl:2 urea (Reline 200) ChCl:2 ethylene glycol (Ethaline 200) ChCl:2 glycerol (Glyceline 200) and ChCl:2 propylene glycol (Propaline 200). The method of synthesis was the same for all of the liquids.

In a beaker, choline chloride was mixed with the hydrogen bond donor in a 1: 2 molar ratio and stirred manually for 30 min. The mixture was placed in oven at 70 °C for six hours until it liquefied whereupon it was moved to magnetic stirrer at 50 °C and left over night, until it became homogenous. The newly formed liquid was transformed to sealed flask and stored at 40 °C.

2.1.3. Mixing and baking starch and DES

Corn starch and the DES were mixed in the appropriate amounts using a Kenwood BL330 Series food processor. The mixture was then placed in oven at 50 °C for three hours. After 3 hours the mixture was poured in a bag to be extruded immediately.

2.1.4. Adding bio-fillers to thermoplastic starch

The three components of starch, filler and Glyceline 200 were mixed and prepared by following the same procedure of mixing and baking starch and DES solvent. The only

difference was the replacement of appropriate amount of corn starch with the desired filler depending on the experiments.

2.1.5. Fillers

The fillers that were used in this project were:

Orange and banana peels that were collected and then dried in an oven at 50 °C for approximately 2 weeks before they were dried again in a vacuum oven at 70 °C. The dry peel was ground using Restch ZM 200 grinder. The powder was sieved through a Fisherbrand analytical sieve with a 200 µm aperture.

Eggshell were collected and then dried in an open lab before being bleached in water with sodium hypochlorite solution (Sigma Aldrich) for about 24 hours. After bleaching the eggshells were dried in oven at 50 °C for a day. The dried eggshells was ground in a Restch ZM 200 grinder and sieved through analytical sieves (Fisherbrand) to have particle sizes of less than 53, 100, 200, 500 µm.

Wood-fibre from Brooke Saw Mill was used after sieving it through analytical sieves (Fisherbrand) with apertures of 100, 200 and 500 µm.

Wood-flour were obtained by drying a mixture of hardwood and softwood sawdust (Brooke Saw Mill) in vacuum oven at 70 °C, and then ground using a Restch ZM 200 grinder and the powder sieved through a Fisherbrand analytical sieve with a 200 µm aperture.

Silk powder, superfine (From Nature with Love (FNWL) 100%) and lignin and zein powders (both Sigma Aldrich) were all used as received.

2.1.6. Adhesives

Lignin adhesive was prepared by mixing lignin (Sigma Aldrich) with Glyceline 200 with the appropriate ratio (1:1, 1.5:1 and 2:1) in a beaker. The mixture was stirred manually before it was placed in the oven at 50 °C for about 24 hours with intermittent manual stirring. After the lignin was completely dissolved in the Glyceline solution was used in the experiments with and without the addition of the other components.

2.2. Experimental Techniques

2.2.1. Compression Moulder

Samples for mechanical analysis were prepared by making sheets of TPS using a compression moulder. The powdered mixture or extruded pellets were placed between two copper plates lined with anti-stick silicone sheets with a 1 mm copper separator, as shown in **Figure 2-1**, on the middle between the two copper plates (9.1 cm square aperture). The sandwich was then placed in a hydraulic press (Fontune Grotnes Laboratory Press TH400) and a force of 120 kN was placed on the sample for 10 minutes at different temperatures. After ten minutes, the temperature was cooled down by passing water through the press plates after switching the heat off, while the pressing force was still maintained.

The mould was made from copper and it consisted of three plates of the same size, but the middle one has a square hole. The plates have dimensions of 131 mm x 131 mm, and the hole dimensions are 91 mm x 91 mm as shown below in **Figure 2-2**, and its thickness is 1 mm.

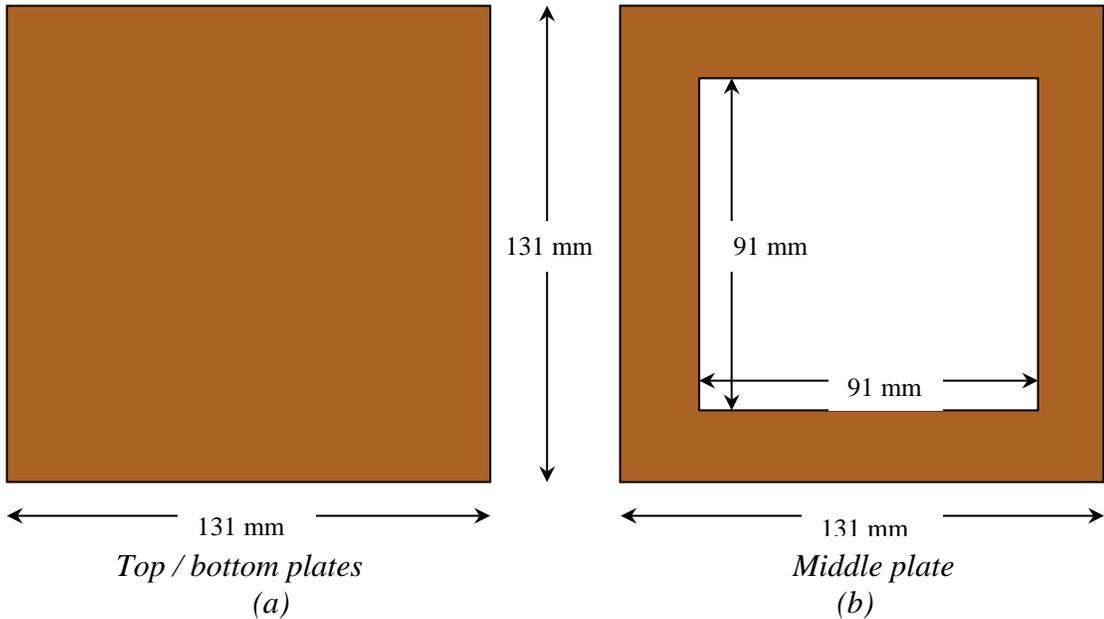


Figure 2-1: A diagram of the three plates that are used to shape the plastic in the

compression moulding: the top and bottom plates (a) and the middle plate with a square hole (b).

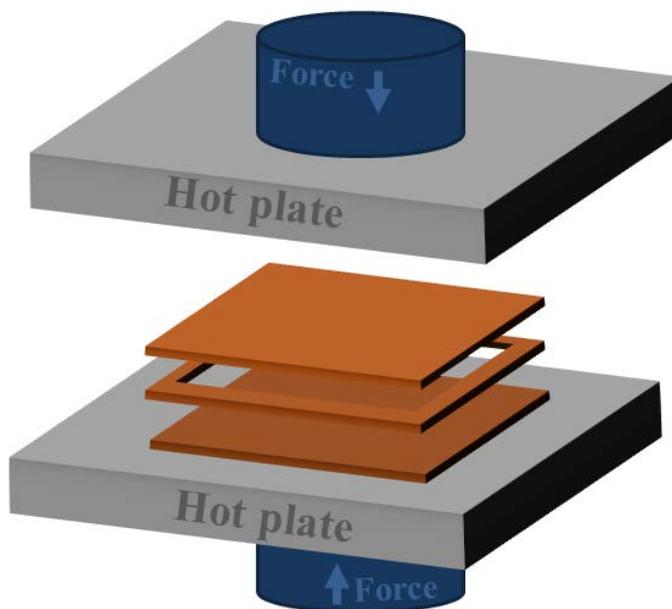


Figure 2-2: A diagram of the three plates placed in the press where temperature and force are controllable.

2.2.2. Tensiometer

When the thermoplastic starch sample was ready to test the sample was cut into five specimens shown in **Figure 2-3**. Each specimen thickness was measured by a micrometer, and then was subjected to strain at a rate of 2 mm/min using an Instron 3343 tensile apparatus (Instron Ltd, USA) with a load cell of 500 N. The Instron Bluehill 2 software programme recorded the maximum tensile strength, extension at maximum tensile strength and Young's modulus. An average was taken of 10 repeat experiments and the error reported as the standard deviation.

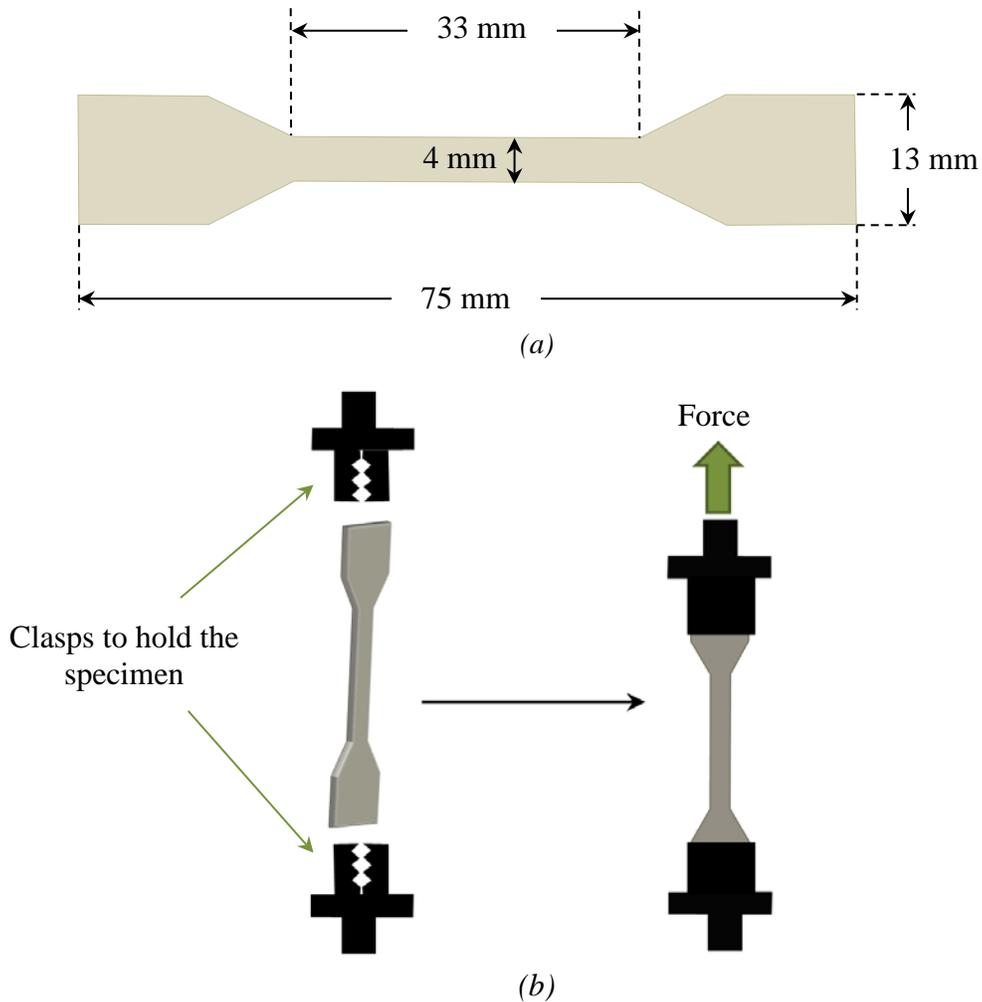


Figure 2-3: A diagram of a sample prepared for tensiometric measurements (a) and process of measuring the tensile strength of the dog-bone (b).

2.2.3. Extruder

The mixture of starch and DES was extruded by a Prism TSE-24-TC co-rotating twin screw (20 length to diameter ratio (L/D)) extruder with a Prism volumetric feeder and an air swept face-cut pelletising system. The extruder has 5 temperature controlled zones; the first was held at 80 °C and the other 4 were changed between 100 °C to 160 °C depending on the experiment. The feed zone was maintained at 15 °C and water cooled. The screw speed was

set to approximately 100 rpm, at which the die pressure was approximately 20 bar. The air swept face-cut pelletising system's blades were set at 95 rpm with only one blade set-up to cut as shown in **Figure 2-4 (a)**.

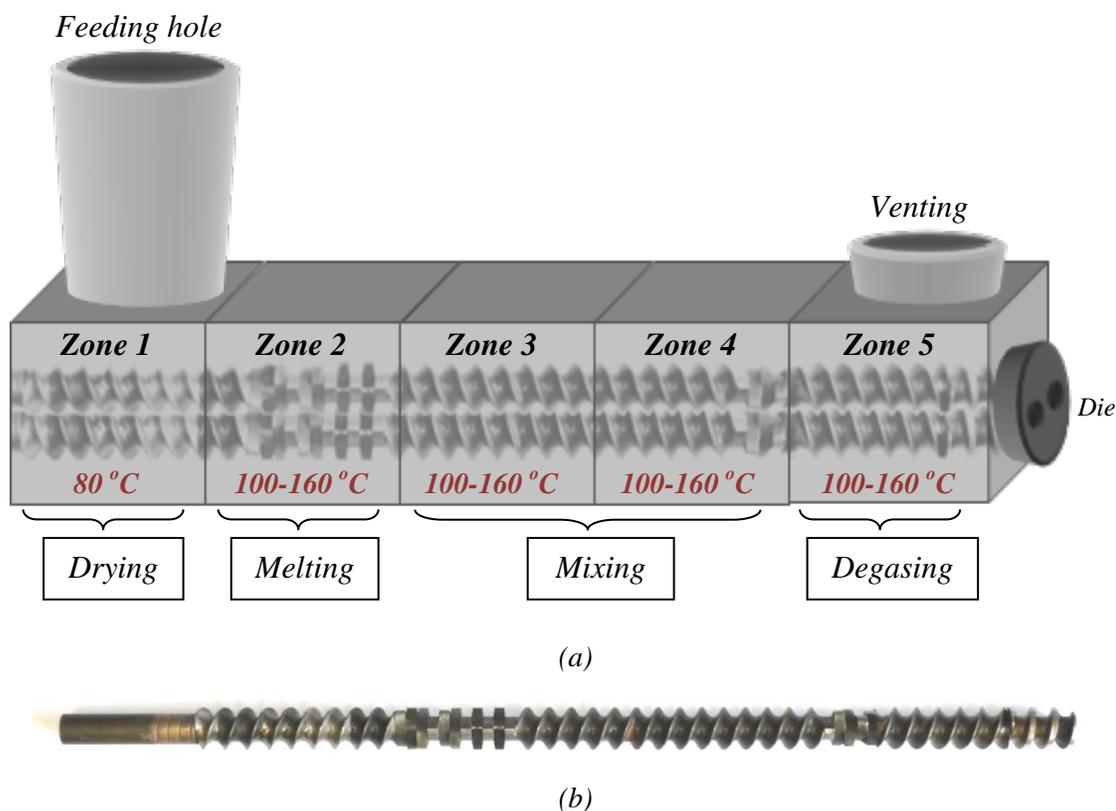


Figure 2-4 Diagram shows the temperature controlled zones, feeding and venting holes of the extruder (a) and an image one of two screws used in the extruder, showing the different profiles, showing its configurations (b)

The screw profile was as follows: 4.5 L/D conveying screw, 0.75 L/D 30 kneading, 0.75 L/D 60 kneading, 1.25 L/D 90 kneading, 7 L/D conveying screw, 0.5 L/D 60 kneading, 0.75 L/D 90 kneading, 3 L/D conveying screw, 1.5 L/D single lead discharge screws. **Figure 2-4 (b)** shows an image of the screw configuration.

2.2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was carried out using a Metler Toledo DSC1 STARe system.

Freshly extruded pellets samples were ground and then sieved through a 100 μm grating. 10 mg of the powder was placed in a 40 μm aluminium pan with a pierced lid and subjected to a temperature profile which started at 25 $^{\circ}\text{C}$ to -100 $^{\circ}\text{C}$ with rate of 2 $^{\circ}\text{C}/\text{min}$, and then it was held at -100 $^{\circ}\text{C}$ for ten minutes before increasing the temperature to 250 $^{\circ}\text{C}$, at a rate 2 $^{\circ}\text{C}/\text{min}$. The glass transition and decomposition temperatures were analysed using STARE software.

2.2.5. Scanning electron microscopy (SEM)

Surface analysis was carried out using scanning electron microscopy with a PhillipsXL30 ESEM instrument. The accelerator voltage was between 15 and 20 keV, giving an average beam current of ca. 120 μA . Freshly extruded pellets of TPS samples were used in this experiment.

2.2.6. Quartz crystal microbalance (QCM)

The general procedure used for the QCM experiments was the same as that outlined by Abbott *et al* in a previous study.¹ Quartz crystal microbalance experiments were performed on an AT-cut 10 MHz quartz resonators with unpolished Au electrodes (0.23 cm^{-2}). All experiments were carried out at a frequency range close to the resonance frequency of the quartz crystal using a Hewlett-Packard HP8751A network analyser operating in reflectance mode utilising a HP87512A transmission/reflectance test unit.

The gelation experiment was done following the procedure of Abbott *et al*¹, the difference being the type of the plasticiser used was Glyceline 200. To a cell containing the resonant quartz crystal, the mixture of corn-starch and Glyceline 200 was added then held at 120 $^{\circ}\text{C}$, such that the surface of the crystal was completely covered. The acoustic impedance spectrum, $U(f)$, was then continually recorded (*c.a.* one spectrum every 4–5 s) over a frequency band width encompassing the crystal resonance for a total period of 1675 s during which the slurry had solidified. A sample of the full data set is presented as a function of time.

2.2.7. X-ray diffraction (XRD)

X-ray diffraction was carried out using a powder diffractometer, Bruker D8 Advance that was equipped with a LynxEye linear position sensitive detector and a 90-position autosampler.

The extruded pellets of TPS were ground using a Restch ZM 200 grinder and sieved through analytical sieves (Fisherbrand) to have particle sizes of 100 μm . The XRD test was performed on the powdered samples.

The diffraction patterns were collected using the following conditions: 2θ range: 4° - 60° , step size: 0.02° , step time: 15 s taken over 11.5 hours. All samples were measured on a conventional sample holder with no adhesive substances being used. The diffraction pattern of the sample “corn starch” can be assigned to the data base entry for corn starch (PDF 39-1911).

2.2.8. Chronoamperometry

Chronoamperometry was carried out using an Autolab PGSTAT20 potentiostat (Echochemie, Holland) with PES2 software. The mixture of starch/ glycerol/ ChCl was arranged between the two copper plates of the press. The copper plates were connected to the potentiostat and a chronoamperometry experiment was performed using an applied voltage of 0.5 V at 140°C with 100 kN force applied.

The chronoamperometry was done in the compression mould. Wood plates were used as electrical insulators between the hot plates of the press and the copper plates. The separator between the two copper electrodes was the same as that shown in **Figure 2-1(b)** but it was made out of wood so as to act as an electrical insulator. The electrodes wires were attached to the copper plates and the current flow was measured for a set voltage as shown in **Figure 2-5**. The data was collected over a five minute period, where the software recorded the current change as a function of time. The current data was converted to conductivity manually using Ohm's law.

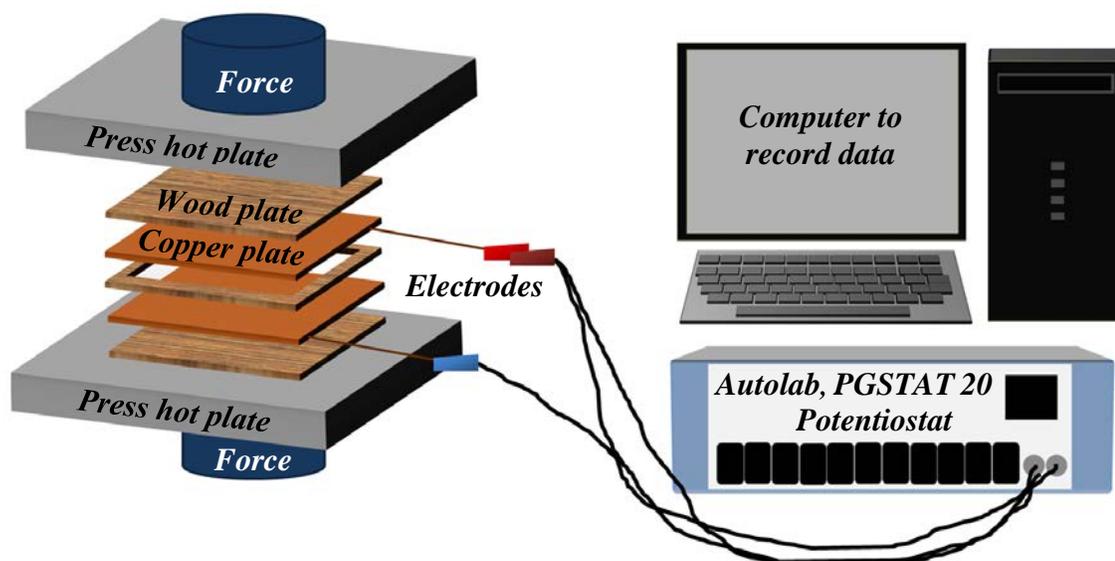


Figure 2-5: Chronoamperometry experimental setup to measure the conductivity of modified starch during its gelation in the press.

2.2.9. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis measurements were carried out using a Mettler Toledo DMA1 STARe system, operating in the single cantilever bending mode using titanium clamps, **Figure 2-6**. Tests were performed at 1 Hz and the temperature was ramped from -70 °C to 160 °C at a rate of 3 °C/min, and the displacement was set to 10 μm .

The dimension of each single sample was 3-4 mm in length and a cross section of 4 x 4 mm. These dimensions were measured accurately by a micrometre before every single experiment.

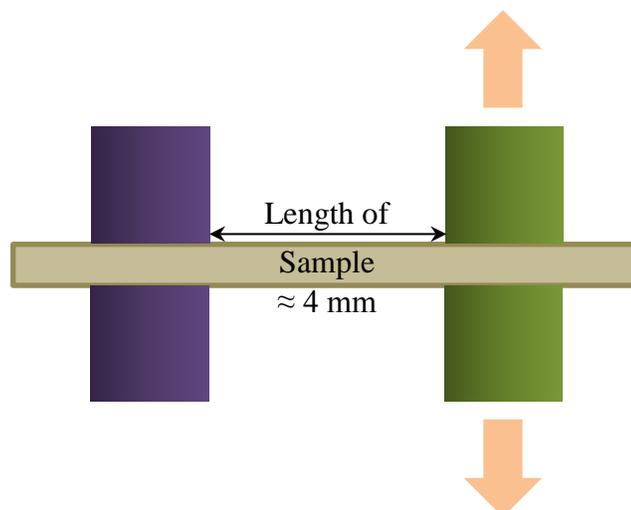


Figure 2-6: A diagram showing the single cantilever mode in DMA.

2.2.10. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Mettler Toledo TGA/DSC1 STARe system using open aluminium pans. The mass of each sample in all TGA experiments ranged between 15 – 20 mg and all samples had a 200 μm particle size.

Water removal experiments were started at room temperature for 2 minutes, then increased to 100 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ then held constant for 90 minutes. The percentage of mass change was measured by the provided STARe system software, and then the raw data was transferred and re-drawn by Origin software.

Water removal experiments, as a function of temperature were started at 25 $^{\circ}\text{C}$ then increased to 180 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}/\text{min}$. Water uptake experiments were performed at 50 $^{\circ}\text{C}$ and 50% relative humidity, the relative humidity was controlled by connecting a pro umide modular humidity generator, type MHG-23 with a pro umide MHG control system, version 3.03 and the software was used MHG method editor, version 3.02, software. The percentage of mass change was measured by the provided STARe system software.

2.2.11. Melt Flow Index (MFI)

Melt Flow Index was carried out using plunger-type rheometry (Instron CEAST MF30 and CeastVIEW 6.20 2C software). The instrument was preheated to 150 °C, before the putting the extruded pellets of each sample into the saviour section of the capillary die (2.095 ± 0.005 mm). The plunger was placed at the top of reservoir section to push down the melted thermoplastic by a 21.6 kg weight. The extruded plastic rods that emerged from the MFI instrument were cut five times every 10 mm length. The weight of each 10 mm plastic rod was measured by using micro balance and then melt flow rate (MFR) was calculated using **Equation 2-1**, provided by the instrument manufacturer.

$$MFR (150\text{ }^{\circ}\text{C}, 21.6\text{ kg}) = \frac{600\text{ }m}{t} \quad \text{Equation 2-1}$$

Where:

m is the average mass of the cut offs in grams,

t is the time interval between samples cutting.

2.2.12. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy was carried out using a Perkin Elmer spotlight 400 frontier spectrometer with Spectrum Image R1.7 software. The test was run on TPS sheets 1 mm thick.

2.2.13. Morphology

3-D imaging was carried out using Zeta-200 optical profiler system with 3D imaging software. The test was run on TPS sheets of 1 mm thick.

2.2.14. Contact Angle

Contact angle experiments were carried out using a Cam 100 optical (Angle Meter KSV Instruments Ltd., Finland) with the provided software.

TPS sheets 1 mm thick were formed by pressing the extruded pellets at 130 °C, 20 bar and 100 screw speed. A drop of pure water was put on the surface of the thermoplastic. Eleven images were recorded: once immediately after the drop and the subsequent 10 images over a 1 minute time period. The procedure was repeated 5 times for each TPS type. The contact angle was recorded and measured the average contact angle of each image at each time was calculated.

2.2.15. Water absorption isotherm

The powder of each sample (200 µm particle size) was accurately weighed, then all samples were placed in a desiccator in an oven set at 25 °C. The relative humidity was controlled by using the appropriate oversaturated salt solution of LiCl, MgCl₂, NaBr, NaCl and BaCl₂, where the water activities of the oversaturated solution differ depending on the salt as shown in **Table 2-1**. After four weeks TPS samples were weighed (0.00001 g precision). The weight gain was calculated and then the percentage of uptake was measured.

Table 2-1: relative humidity of oversaturated salt solutions at 25 °C.

Salt	% RH
LiCl	12
MgCl ₂	35
NaBr	58
NaCl	76
BaCl ₂	98

2.2.16. Density measurements

The TPS sheet mass (m) were measured before their volume (v) were determined by immersing them in a cylinder contains hexane (Fisher Scientific >99%), then the density (ρ) was calculated using **Equation 2-2**.

$$\rho = m/v$$

$$\text{Equation 2-2}$$

2.2.17. Waxing TPS sheet and water absorption capacity (WAC)

A sheet of TPS was prepared by pressing extruded pellets of blank TPS for 10 minutes in a mould at 100-110 N. After ten minutes, the temperature was cooled down by passing water through the machine plates after switching the heat off, while the pressing force still maintained between 100-110 N.

The surface of the TPS sheet was covered with wax by either waterproof spray (Woly, 3 x 3 projector) or melted paraffin wax (Sigma Aldrich). After the surface was protected the mass of each sample was measured before and after it was immersed in distilled water for 24 hours. The water absorption capacity (WAC) was calculated using **Equation 2-3** then the percentage of water uptake was calculated.

$$WAC = \frac{m_2 - m_1}{m_1} \times 100 (\%) \quad \text{Equation 2-3}$$

Where **WAC** is water absorption capacity, m_1 is the initial mass and m_2 is the mass of TPS after 24 hours in distilled water.

2.3. References

1 A. P. Abbott, A. D. Ballantyne, J. P. Conde, K. S. Ryder and W. R. Wise, *Green Chem.*, 2012, **14**, 1302-1307.

Chapter 3: Optimisation and characterisation of thermoplastic starch (TPS) and definition of the standard system

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3. Optimisation and characterisation of thermoplastic starch (TPS) and definition of the standard system

3.1. Introduction

Starch is a ubiquitous carbohydrate found in most plants. It is hygroscopic and crystalline due to an extensive network of intra- and inter-molecular hydrogen bonds. Numerous studies have shown that native starch granules can be melt processed in the presence of water and other polar hydrogen bonding molecules such as alcohols and amides.¹ Such molecules lower the melting temperature of starch's crystalline structure. Industrial thermo-mechanical processes, such as extrusion, can thus be applied in order to obtain a thermoplastic material.¹ The same hydrogen bonding molecules thus act as plasticisers of the resulting amorphous polymer network, modifying its physical properties, in particular the glass transition temperature.² Other recent reviews give a more detailed summary of advances in this field.^{3,4}

It is noteworthy that contrary to petroleum based plastics, native starch granules cannot be completely molten just by increasing the temperature.⁵ Unless a minimum specific mechanical energy (typically 100 kJ/kg) is applied by intense shearing, a "phantom" structure of the granules may remain in the final material. Nevertheless, too much mechanical energy may also result in a strong degradation of the starch macromolecules.⁶ Thus, twin screw extrusion is generally preferred in order to fine tune the thermomechanical history of the material and efficient modelling software have been developed to optimize the process.⁷ Nevertheless, remaining issues associated with the thermoplastic starch materials obtained with conventional plasticisers are that they are not particularly strong and they exhibit a tendency to recrystallize with time and become brittle.

Recently, it was shown that liquid salts, such as ionic liquids or deep eutectic solvents with polar modifiers like urea, can be used as efficient new plasticisers of starch.^{8,9} Significant reductions of the necessary specific mechanical energy needed for melt processing were observed.⁹ In addition, materials with improved tensile strength which do not recrystallize rapidly could be produced.^{8,9} It was shown that the water sensitivity of starch materials could be decreased in the presence of the ionic plasticisers.^{10,11} These materials behave like

true thermoplastics and can be recycled without significant loss of mechanical integrity. The thermoplastic starch has also been used as a binder for wood particles to make a thermoplastic material which can be recycled.¹⁰

The current study aims to optimise the components of the deep eutectic solvents by replacing the urea component with ethylene glycol, propylene glycol or glycerol. Mixtures of glycerol and quaternary ammonium salts have been shown to have enhanced solvent properties due to decreased viscosity and increased hydrogen bonding ability.¹¹ They are also of note as their synthesis has a Sheldon E-factor of zero. Here it is demonstrated that the plasticiser and processing conditions significantly change the properties of the material and this is explained in terms of the crystallinity.

3.2. Effect of pre-treatment

Baking the starch after it is mixed with the plasticiser is required to dry the mixture from the absorbed moisture.⁸ If the mixture contains too much moisture the resultant plastic is mechanically compromised but if it is totally dry then the plastic will not form. Thermogravimetry showed that the original unbaked mixture of TPS contained 9.1 wt% moisture. **Table 3-1** shows the maximum tensile strength and the tensile strain of TPS for different drying times in an oven at 50 °C. The strongest un-extruded TPS is the mixture that is dried for three hours in an oven at 50 °C; giving an ultimate tensile strength, UTS, of 6.01 MPa. It is possible that if the starch is too dry then it is too crystalline to allow the glycerol and salt to penetrate the granular structure and plasticise it. It appears from **Table 3-1** that the optimum water content of the pre-extruded mixture is 8.2 wt%.

Table 3-1: The effect of pre-baking time on the mixture of corn-flour, glycerol and choline chloride before pressing. These samples were not extruded but directly pressed at 140 °C with 110 kN.

Time of baking (hours)	Tensile Stress (MPa)	True Strain (mm/mm)	Water (wt %)
1	1.607	0.304	8.9
2	4.864	0.107	8.6
3	6.010	0.045	8.2
4	n/a	n/a	7.8

3.3. Optimisation of physical properties

The ratio of starch to plasticiser has a significant effect upon the tensile strength and strain of the resulting material. When there is an excess of plasticiser this weakens the plastic but it increases the ductility of the material. This section investigates the effect of the starch: plasticiser ratio on the tensile strength by using different ratios to achieve the strongest thermoplastic starch (**Figure 3-1**).

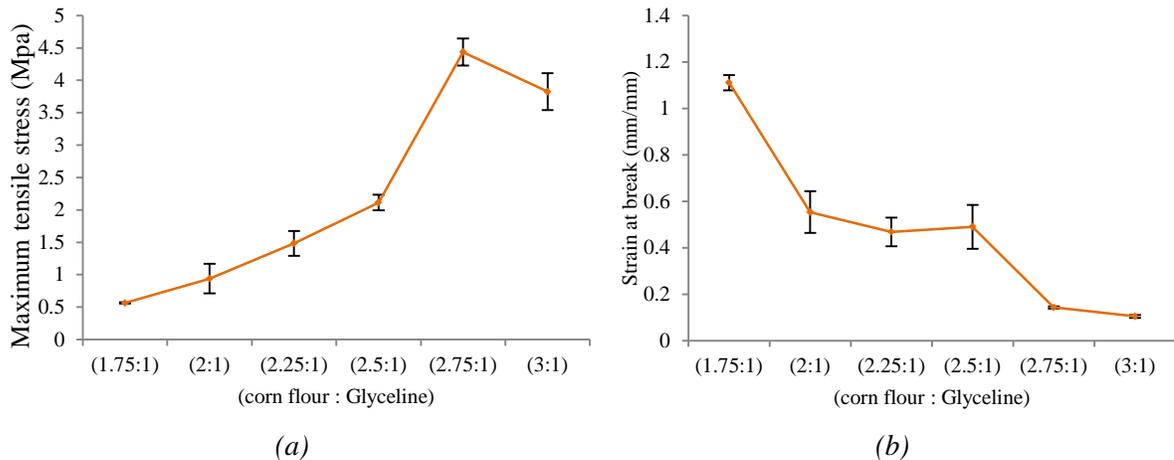


Figure 3-1: The effect of plasticiser content on the mixture of corn-flour, glycerol and choline chloride. These samples were not extruded but were dried at 50 °C for two hours and then directly pressed at 140 °C with 110 kN.

It was found that mixing starch and Glyceline 200 (2 mole glycerol and 1 mole choline chloride) with the ratio of 2.75: 1 by weight produced the strongest TPS. The glass transition temperature and tensile strength decrease with increasing glycerol content, but the tensile strain increases.¹²⁻¹⁴

3.4. Gelation of starch

The gelation of starch causes changes in the starch structure, physical-, rheological- and mechanical properties. These changes occur when the hydrogen bonds of starch are broken by the modifier and then new intermolecular hydrogen bonds are formed, meaning starch gel usually contains both liquid-like phases and solid-like phases.¹⁵ The starch gelation temperature is higher than its glass transition temperature and lower than its melting temperature. The gelation occurs in two steps; (i) a phase separation that produces polymer-rich and polymer-deficient regions, and (ii) a crystallization within this polymer rich region.¹⁶

The gelation of starch was studied by using a quartz crystal microbalance (QCM) and by measuring the electrical resistance of starch/ glycerol/ ChCl mixtures during conversion from a slurry to TPS. This enables the gelation temperature and time to be determined *in situ*.

3.4.1. Quartz Crystal microbalance (QCM)

QCM technique delivers data on the viscoelastic properties of a substance by applying an alternative electric field across the quartz crystal through two metal electrodes; one above and one below the quartz crystal resonator as shown in **Figure 3-2**. A mechanical oscillation of characteristic frequency, f , is produced in the crystal.¹⁷

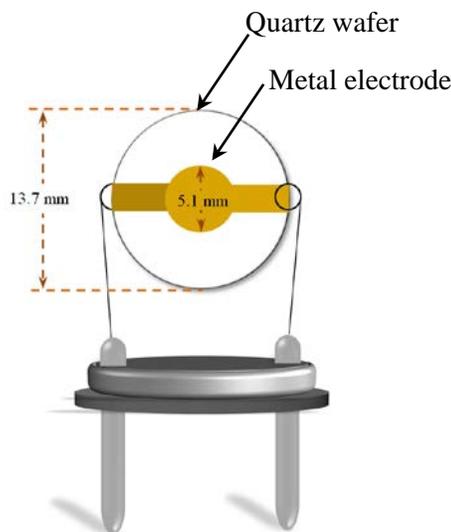


Figure 3-2: Diagram of QCM cell show dimensions of the cell and electrodes.

The crystal's oscillation frequency changes with the mass of substance that is attached to the QCM cell. The frequency is higher and intensity- frequency plot is sharper with less mass attached.¹⁷ **Figure 3-3 (a)** illustrates a very sharp oscillation frequency peak of an empty QCM cell. The frequency shifts to lower values when the mixture of starch/glycerol/choline chloride is added to the QCM cell, as consequence the peak moves to lower frequency and become broader when the sample starts to gel as shown in **Figure 3-3 (b)**. Heating the mixture at high temperature changes the viscosity due to the water evaporation and mixture converts to TPS, and consequently the frequency peak becomes much broader **Figure 3-3 (c)**.

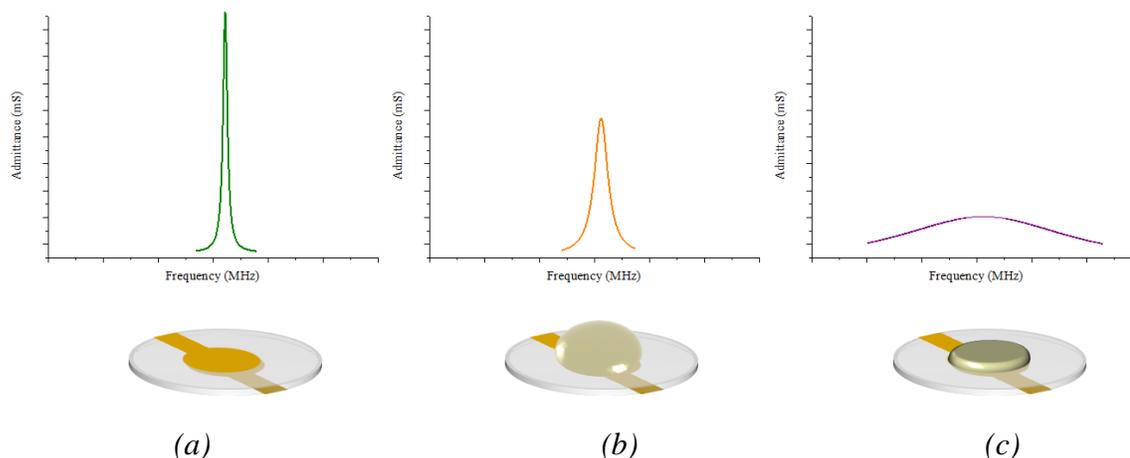
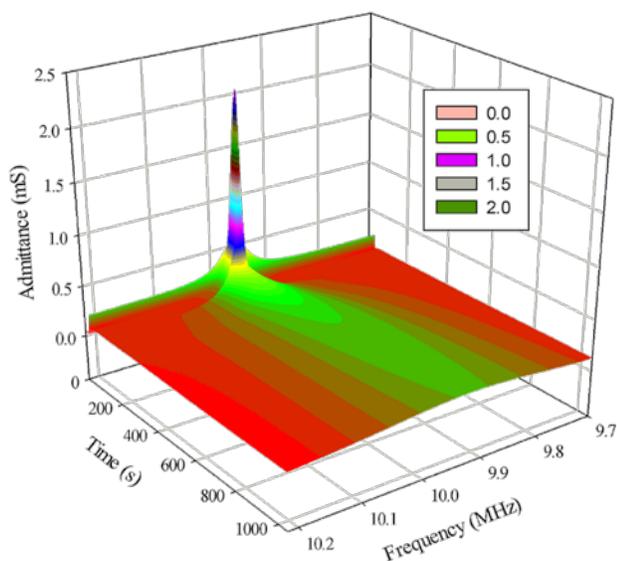


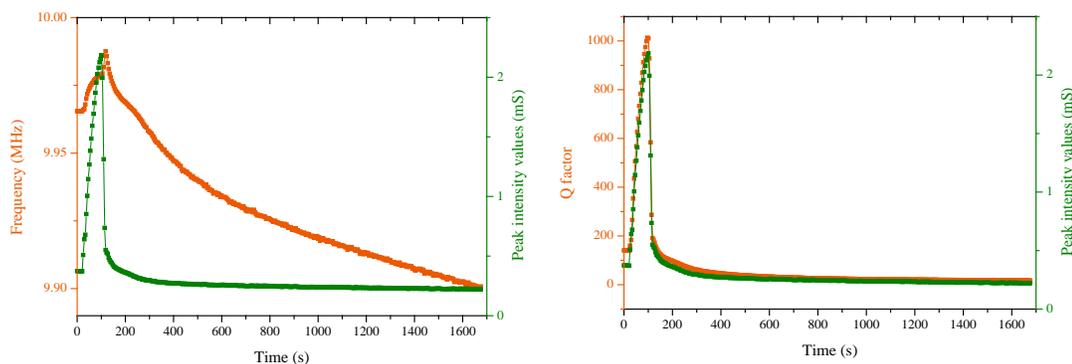
Figure 3-3: Admittance spectrum without a load (a), with a mixture of starch/glycerol/ChCl before gelation (b) and after gelation to form TPS (c).

Using the QCM techniques to study the gelation of starch was demonstrated by Abbott *et al.*⁸ The QCM technique has been used widely to examine the viscoelastic effect in thin-film polymers.^{18, 19} The gelation experiment was done following the procedure of Abbott *et al.*⁸ the difference being the type of the plasticiser used Glyceline 200 was used in this work compared to Reline 200. This experiment for Abbott *et al* was designed to investigate the physical transformations and consequential mechanical viscoelastic losses of the starch Glyceline mixture as it gelled.

To a cell containing the resonant quartz crystal, the mixture of corn-starch and glyceline 200 was added then held at 120 °C, such that the surface of the crystal was completely covered. The acoustic impedance spectrum, $U(f)$, was then continually recorded (*ca.* one spectrum every 4–5 s) over a frequency band width encompassing the crystal resonance for a total period of *ca.* 1675 s during which time the slurry solidified. A sample of the full data set is presented as a function of time in **Figure 3-4(a)**.



(a)



(b)

(c)

Figure 3-4: QCM gelation experiment results of starch and Glyceline 200 mixture in a 3:2 weight ratio held at 120 °C. (a) Admittance spectra $U(f)$. (b) Peak resonant time frequency values, f_o and peak intensity values U_o . (c) Q -factor data overlaid with U_o data.

The resonance line shape was very sharp at the beginning of the experiment, and then it shifts to lower frequencies and becomes broader. **Figure 3-4 (b)** shows that the value of f_o rises immediately after the slurry was added to the crystal because of the low temperature of the heated cell, and then the resonant frequency increased as a result of the reduction of the local viscosity due to the heating of the slurry in contact with the cell. With time the slurry becomes more rigid, increasing in coupled mass to the crystal. The maximum peak intensity, U_o , changes in a corresponding trend to the maximum in frequency, f_o , which is

shown in **Figure 3-4 (b)**. The value of U_o does not change much with time because the composition of the gelation material is relatively constant. However, the coupled mass of the gelled layer is increased where its size becomes thicker resulting in a slight correlated frequency response. **Figure 3-4 (c)** shows that the initial sharpening of the resonance is related to the quantified resonance (Q -factor) for the fitted acoustic impedance spectra with U_o , where: $Q = (f_o/w)$ and w/Hz is -height full-width of the resonant line.

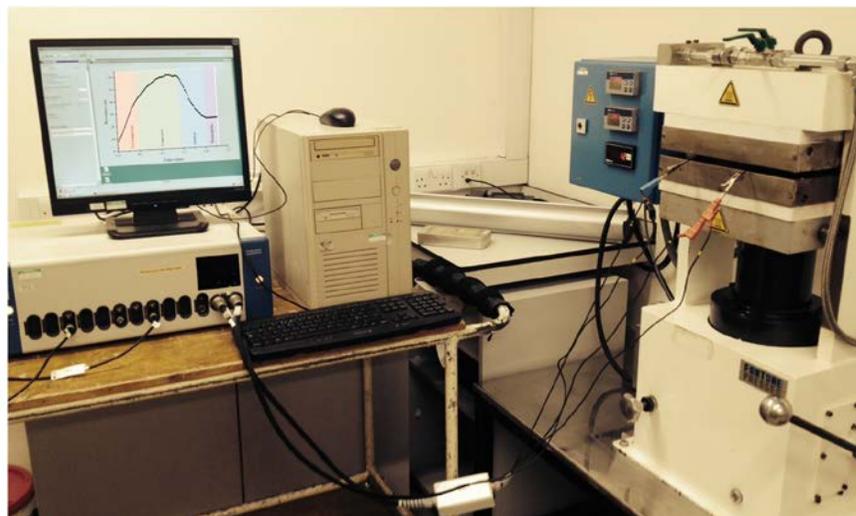
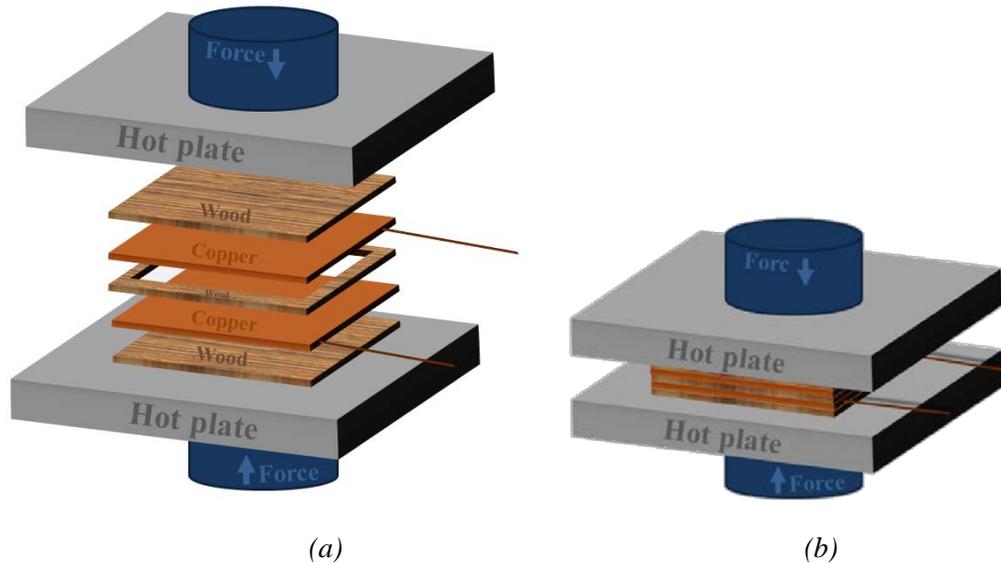
The gelation results in an increased viscosity as the TPS gels where the peak becomes very broad, while the U_o peak remains roughly constant shortly after the slurry is added showing that gelation is fast. It is interesting to note that the results with Glyceline 200 are almost identical to those obtained with Reline 200 reported in the literature⁸ (1 choline chloride and 2 urea) despite the differences in liquid viscosity (Reline *c.a.* 600 cP and Glyceline *c.a.* 300 cP at 20 °C).

3.1.2.2 Measuring Conductivity in the press

Clearly the above results are useful but do not give information about the gelation process under pressure. Many physiochemical changes occur during heating and pressurisation stages and these are difficult to follow in-situ. One property which does change as gelation occurs is the electrical conductivity. When the DES is continuous there will be a relatively high conductivity but as gelation occurs the mobility of the ions will decrease as the viscoelasticity increases. It was decided to devise an experiment to measure the conductivity within the high pressure press.²⁰ Measuring electric resistance of the mixture during the gelation is very important as it can give valuable information about the gelation itself, how plasticisers act and stay within starch chains and the length of time that the mixture needs to convert to thermoplastic. The electric and thermal conductivities of starch are very poor, but the addition of plasticiser to starch increases its conductivity slightly.

Measuring electric resistance during heating and pressing of the starch/ glycerol/ ChCl mixture was done in the compression mould using wood plate as an electrical insulator between the hot plate of the press and the copper plates. By attaching wires to the copper plates the current flow at a set voltage could be measured and hence the resistance could be determined. **Figure 3-5** shows how the mixture of starch/ glycerol/ ChCl was arranged

between the two copper plates of the press. The copper plates were connected to the potentiostat and a chronoamperometry experiment was performed using an applied voltage of 0.5 V, at 140 °C with 100 kN force applied. The data was collected over a five minute period.



(c)

Figure 3-5: *Experimental set up for monitoring conductivity. The mould consist of five pieces, two wood plates and two copper plates and wood plate with a hole in the middle, where wood plates were used to resist the voltage between the copper plates (a) and then the mixture of starch/glycerol/choline chloride pressed at 140 °C with about 100 kN and 0.5 V (b) which is connected to a computer to record the change in currents (c).*

Figure 3-6 shows the resistance changes of the mixture of starch and Glyceline 200 as a function of time at 140 °C with about 100 kN force applied. Initially the conductivity increases as the sample heats up but it does not gel as there is no pressure applied. After about 30 s the sample is rapidly compressed and the rate of increase in Conductivity levels off presumably because ionic migration is limited as the sample is compressed and the medium becomes viscous. After 1.5 minutes gelation occurs and the conductivity decreases markedly. After 2 minutes the conductivity reaches a constant value showing that the sample has completed its gelation.²¹ This is a novel method of following gelation and is the first to study the process under pressure. Comparing these data with those of **Figure 3.4** it is clear that the gelation rate is increased with pressure. The process is complete in approximately 90 s. The main limit is probably the heat capacity of the material and this limits the rate at which it reaches the required temperature. It should also be noted that the sample size in the compression experiment is much larger (28 g) than that used in the QCM experiment (2 g).

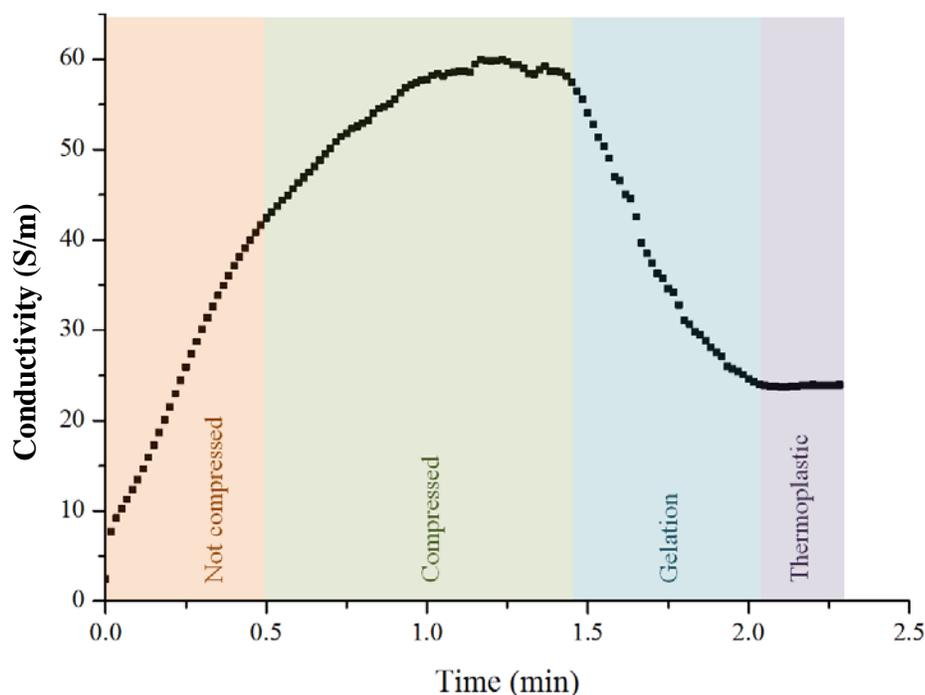


Figure 3-6 : The changes in TPS resistance during the process of producing TPS in the press at 140 °C with about 100 kN and 0.5 V.

3.5. Effect of hydrogen bond donor (HBD)

Pressing a well-mixed starch and plasticiser at 140 °C with about 100-110 kN produce a transparent sheet of TPS, but using different HBDs with choline chloride to plasticise starch results in materials with different mechanical properties. **Figure 3.7** shows the effect of the hydrogen bond donor on the tensile strength of non-extruded TPS. It shows that using glycerol as the HBD produce a material with twice the strength of the other three HBDs. This is probably because glycerol has 3 hydrogen bonding sites and can therefore bond in 3 dimensions.

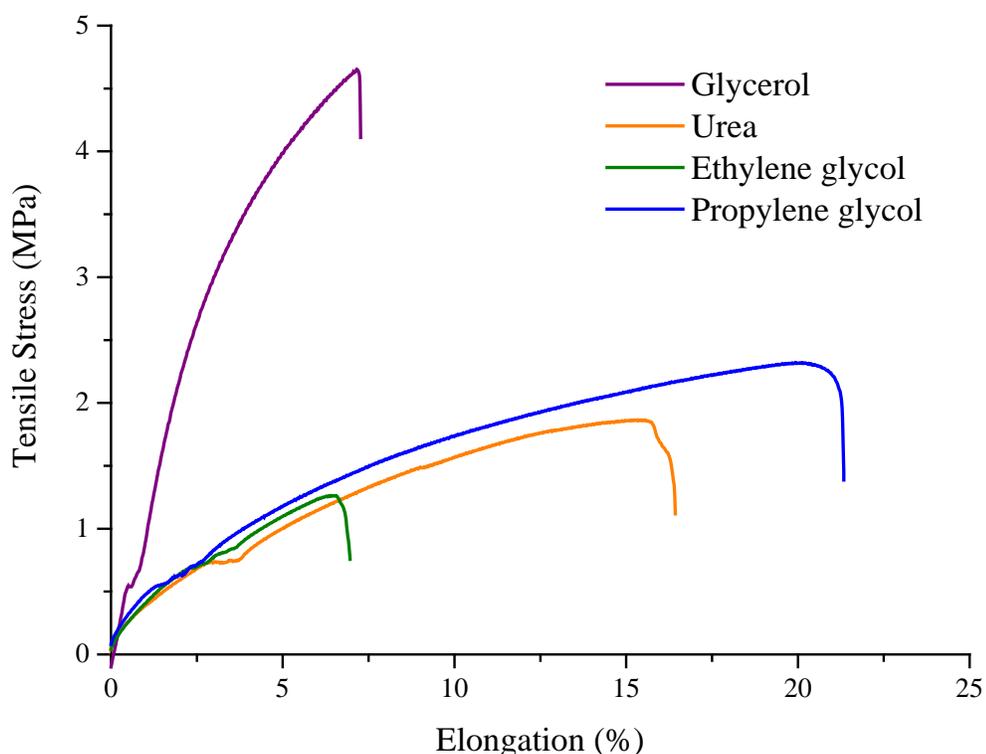


Figure 3-7: Representative stress-strain curves for starch modified with choline chloride with either; urea, ethylene glycol, propylene glycol or glycerol. Samples were being pressed, without extruding, at 145 °C, 110 kN for 10 min without extruding.

The values shown in **Figure 3-7** show that the TPS is relatively weak. This is probably due to the mechanism by which the ingredients are mixed. The tensile strength of pressed TPS samples that were plasticised by a mixture of choline chloride and the four different HBD are in this order: glycerol > propylene glycol > urea > ethylene glycol. **Table 3-2** shows the ultimate tensile stress (UTS), the percentage elongation at break and chordal modulus obtained by measurements taken from 10 samples.

Table 3-2: *Effect of hydrogen bond donor on the strength, ductility and chordal modulus of various extruded thermoplastic starch samples. Samples were extruded at 130 °C, 100 rpm and a die pressure of c.a. 20 bar before being pressed at 140 °C, 110 kN for 10 min.*

Composition Starch: ChCl: HBD	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
HBD = urea	31.39 ± 3.09	1.76 ± 0.11	17.77 ± 1.32
HBD = ethylene glycol	28.52 ± 3.00	1.17 ± 0.07	7.13 ± 0.38
HBD = propylene glycol	13.59 ± 1.80	2.40 ± 0.13	21.70 ± 0.87
HBD = glycerol	87.69 ± 4.87	4.62 ± 0.31	7.54 ± 0.33

As detailed in **Section 1.6** extrusion is a technique which is commonly used to homogenise polymer mixtures. Extruding the mixture of starch and plasticiser has previously been shown to improve the tensile strength of TPS significantly. It was shown that mixtures of choline chloride and urea act as effective plasticisers for corn starch and it was shown that strengths similar to high density polyethylene could be achieved.⁸ In the current study comparisons are made replacing urea by ethylene glycol, propylene glycol and separately with glycerol.

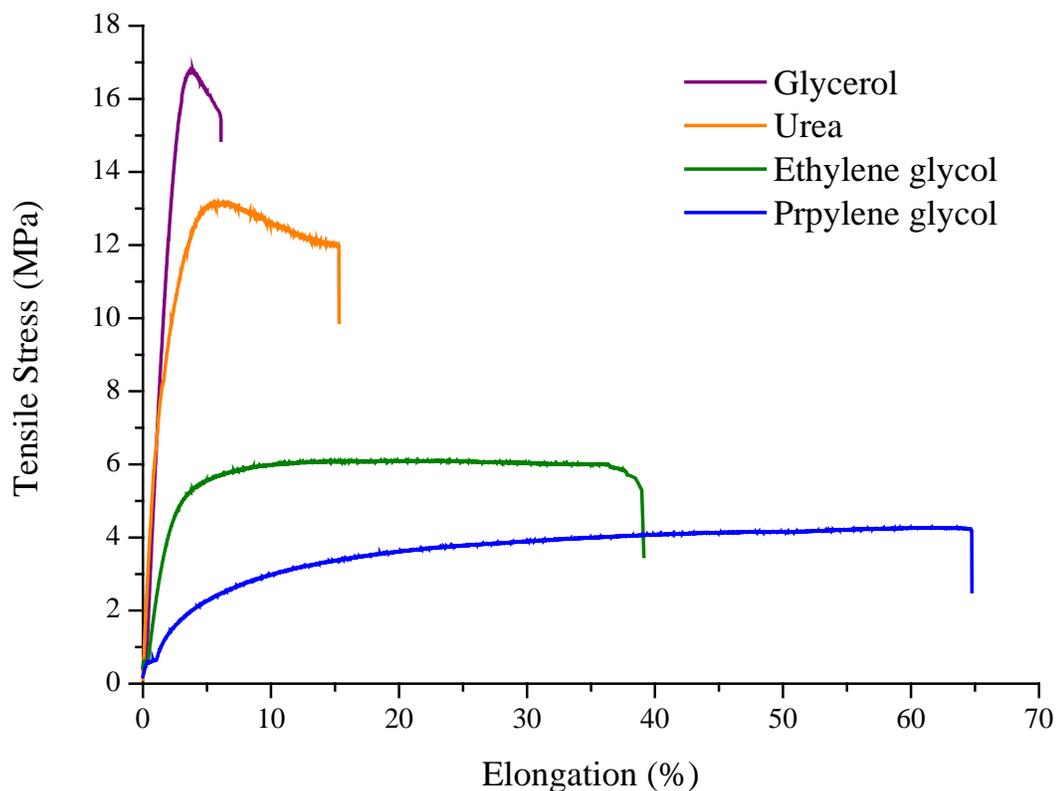


Figure 3-8: Representative stress-strain curves for starch modified with choline chloride with either; urea, ethylene glycol or glycerol. Samples were extruded at 130 °C, 100 rpm and a die pressure of c.a. 20 bar before being pressed at 145 °C, 110 kN for 10 min.

Figure 3.8 shows representative stress-strain curves for these mixtures containing 75 wt% starch and 25 wt% modifier; these compositions were optimised in previous studies.²² **Table 3-3** shows the ultimate tensile stress (UTS), percent elongation at break and chordal modulus obtained by measurements taken from 10 samples.

It can clearly be seen that all three HBDs act as different types of plasticiser. The glycerol-based plastics are stronger, less flexible and more brittle and this is almost certainly due to the ability of glycerol to act as a 3 dimensional hydrogen bond former due to having three functional groups. Ethylene glycol produces plastics which are more ductile but less strong. Glycerol is beneficial as it is a waste by-product from the trans-esterification and saponification of oils and fats which are associated with biodiesel and soap manufacture.²³ In all subsequent experiments the starch plasticiser composition used was 75.0 wt% starch 10.8 wt% choline chloride and 14.2 wt% glycerol. All of the materials described above can

be reground and reprocessed without significant loss of mechanical strength as was previously reported for the urea based salt modified starch.⁸

Table 3-3: *Effect of hydrogen bond donor on the strength, ductility and chordal modulus of various extruded thermoplastic starch samples. Samples were extruded at 130 °C, 100 rpm and a die pressure of c.a. 20 bar before being pressed at 140 °C, 110 kN for 10 min.*

Composition	Modulus	Tensile strength	Elongation
Starch: ChCl: HBD	(MPa)	(MPa)	(%)
HBD = urea	803.3 ± 76.31	13.83 ± 0.25	32.31 ± 1.20
HBD = ethylene glycol	539.3 ± 46.74	9.44 ± 0.41	55.68 ± 4.45
HBD = propylene glycol	36.9 ± 4.80	3.80 ± 0.12	64.72 ± 2.92
HBD = glycerol	1031.0 ± 25.28	17.16 ± 0.58	3.96 ± 0.44
Low density polyethylene	200 - 400	8 - 12	600

There are many factors which could affect the strength of the starch materials and these include the pre-treatment, composition, water content, extrusion temperature, residence time in the extruder, pressing time and pressing temperature.

3.6. The effect of extrusion temperature

The temperatures of zones 2-5 for the extruder shown in **Figure 2-3** were kept constant for each experiment and seven experiments were run between 100 and 160 °C. For each experiment 500 g of starch-DES mix was extruded and the pellets produced were used immediately for mechanical testing. Other samples were sealed in plastic bags to use later for the recrystallization tests. **Figure 3.9 (a)** shows the effect of extruder temperature on the tensile stress and strain of the samples. It can be seen that the extruder temperature significantly affects the physical properties of TPS and UTS shows a relatively linear increase from 100 to 160 °C. Conversely the ductility decreases as the extrusion temperature is increased and the material becomes more brittle. This is partly because water evaporates through the extruder's venting hole but it is also observed that the TPS changes colour due to caramelisation at higher temperatures as the glucose oxidises. **Figure 3.10**

demonstrates that an increase in extrusion temperature also changes the physical appearance of the plastic; both the pellets and the plastic sheet in **Figure 3-10 (g)** are clearly more yellow than those of **Figure 3.10 (a)**. This is potentially due to starch degradation and caramelisation of the sugars as a result of the processing heat in the extruder; however these degradation products were in too low a concentration to be detected by a number of analytical methods (HPLC and NMR).

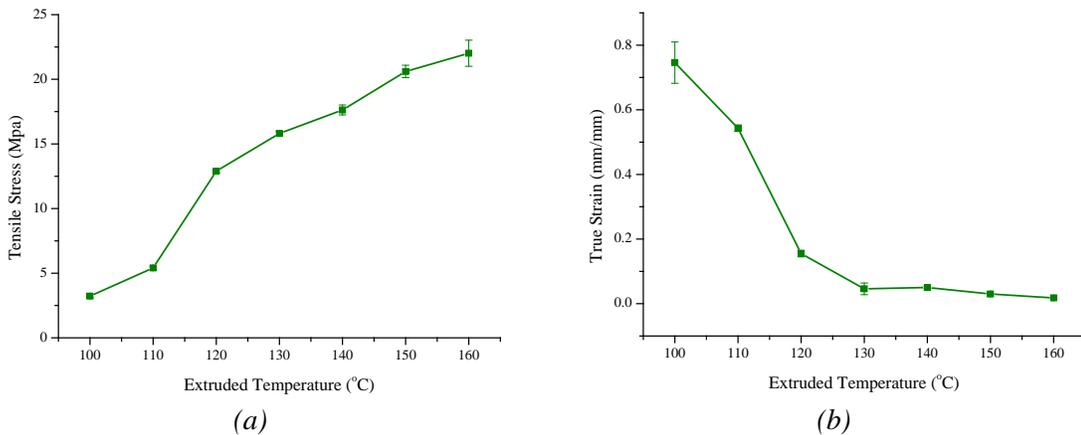


Figure 3-9: The effect of extruder temperature on tensile stress (a) and true strain (b). All samples were extruded at different temperature.

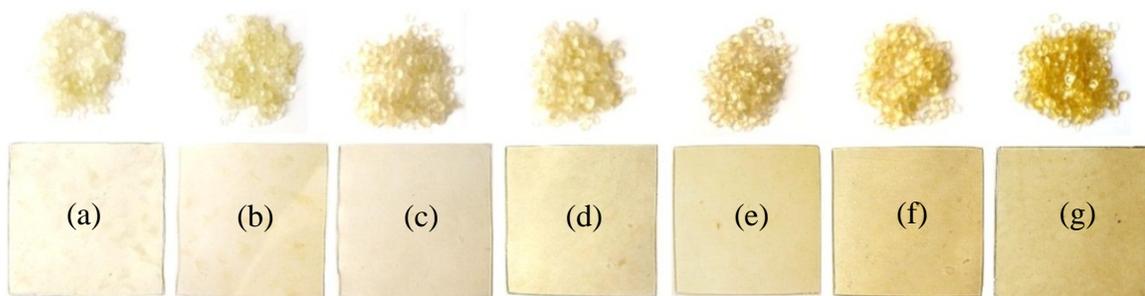


Figure 3-10 : Extruded pellets and sheets samples of starch with glycerol and choline chloride extruded at different temperatures
 $a= 100, b= 110, c= 120, d= 130, e= 140, f= 150$ and $g= 160$ °C.

3.7. The effect of compression mould temperature

Once the sample has been extruded it needs to be reheated in the mould to form the finished shape. **Figure 3.11 (a)** shows the effect of the compression temperature on the UTS and strain at break. TPS pellets that were extruded at 130 °C were chosen to represent the effect of compression temperature by pressing them in variation of temperatures.

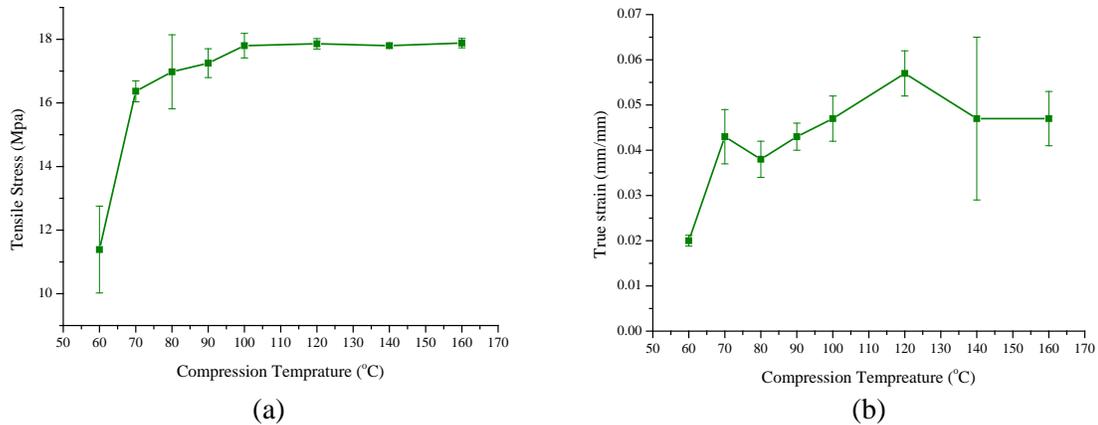


Figure 3-11 : The effect of compression temperature on tensile stress. All samples extruded at 130 °C, 100 screws speed, and then pressed at different temperature with 100 kN and for 10 min.

Figure 3.11 (a) shows that the compression temperature does not impact significantly on the mechanical properties of TPS once compression temperatures above 70 °C are used. TPS pressed at 60 °C is very weak because the pellets do not melt well to form one homogeneous sheet, this can clearly be seen from **Figure 3.12** where the individual pellets can still be seen as they have only partially melted.

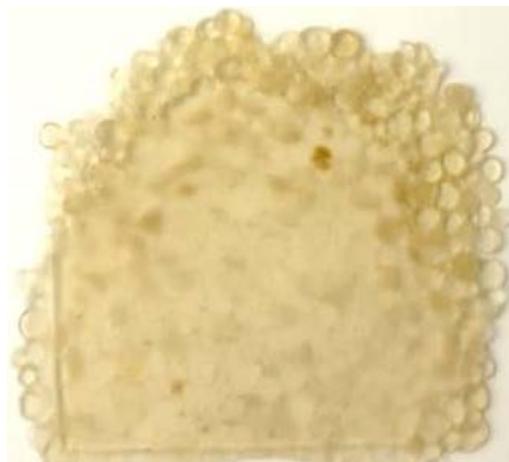


Figure 3-12: Sample extruded at 130 °C then pressed at 60 °C, 100 kN for 10 minutes.

3.8. The effect of extrusion and compression temperature

The starch-plasticiser blends are heated and mixed during both the extrusion and compression-moulding stages. It was previously shown that extrusion increases the strength by up to a factor of 5 however the extrusion conditions will affect the ability of the plasticisers to permeate into the starch structure affecting the water content and hence the crystallinity of the samples.⁸ In this section both the extrusion and pressing temperatures were varied to find the optimum processing conditions. **Figure 3.13** shows the effect of extrusion temperature and compression temperature on the UTS and tensile strain. In most cases the pressing temperature has little effect upon the UTS or tensile strain which demonstrates the importance of the shear mixing of the components during the extrusion process. Once the pellets have been formed, the pressing stage is just fusing the individual grains together. It can be seen from **Figure 3.13 (a)** that increasing the extrusion temperature increases the tensile strength, but the biggest improvement in material properties occurs between 110 and 130 °C.

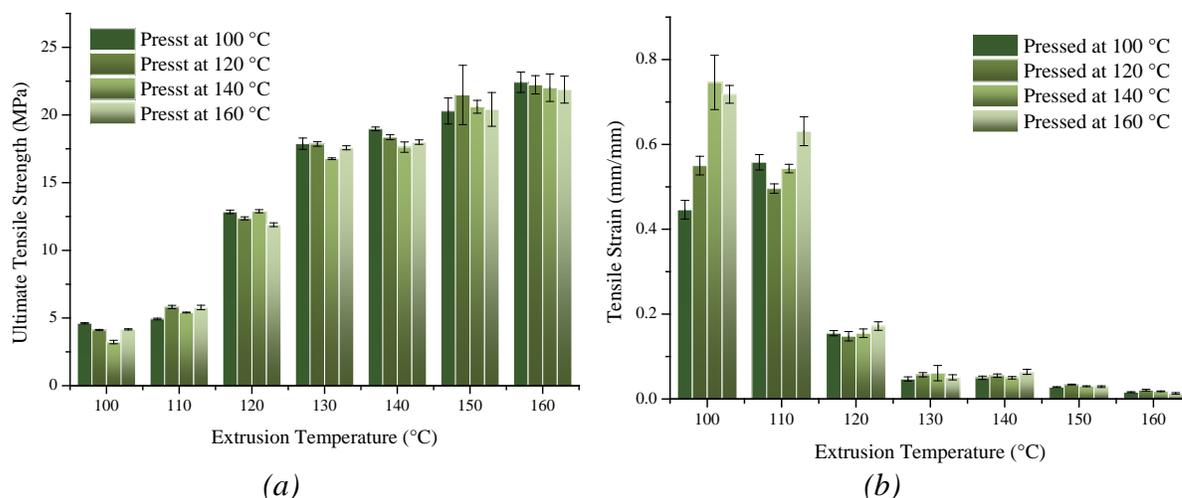


Figure 3-13: The effect of temperature in extrusion and compression mould. (a) tensile strength and (b) tensile strain. All samples in were pressed with 100 kN for 10 minutes.

Dogossy and Cziagany investigated the tensile strength of TPS, modified by glycerol or maltitol (a sugar alcohol, $C_{12}H_{24}O_{11}$) extruded at 90, 105 and 120 °C and found that the UTS was about 4 MPa.²⁴ The results above show that adding the salt to the plasticiser mixture increases the UTS to 6 MPa even for the non-extruded TPS. Extruding the mixture at 120 °C increased the UTS to approximately 13 MPa which is a three-fold increase over pure glycerol. Increasing the extrusion temperature increases the UTS and decreases the tensile strain i.e. materials decrease their flexibility and ductility and become more brittle. This clearly shows that the salt is modifying the structure of the starch and affecting the ways that the polymer chains interact with each other.

3.9. The effect of compression time

The next parameter that needed to be optimised was the time taken for the pellets to melt and form a homogeneous material in the compression mould. From the results in **Figure 3-6** it can be seen that it is likely that gelation should be possible in a few minutes as this is the time when the conductivity is constant. It does not however show whether there are any slower rearrangement processes still occurring which may change the mechanical properties. The results of the pressing time effect on UTS are shown in **Figure 3.14**. The time that the sample spends in the compression mould does not significantly impact the

tensile strength of the sheet. The strength was roughly constant when pressed between one and twenty minutes. This shows that once the sample has been extruded the homogenisation is complete and the pressing (or injection moulding) simply needs to melt the extruded pellets sufficiently to let the sample flow.

One minute is enough to homogenise the extruded pellets to a sheet at 140 °C. However, it is found that the strongest TPS was obtained by pressing for 7.5 minutes which resulted in a UTS of 19.6 MPa. Longer pressing times caused a slight decrease in the UTS.

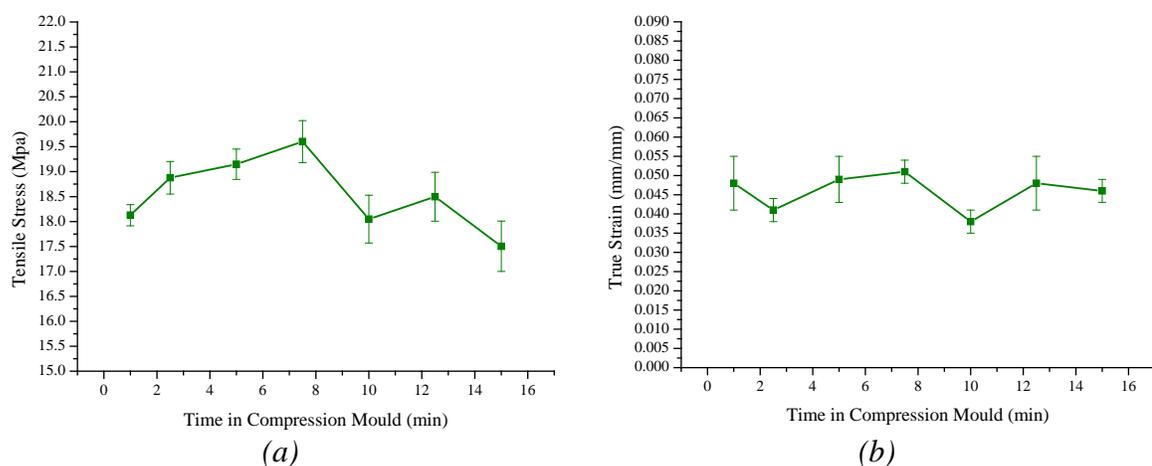


Figure 3-14: The effect of compression time. All samples were extruded at 130 °C with 100 rpm screws speed, and then pressed at 140 °C with 100 kN

3.10. The effect of residence time in extruder

The temperature of the different zones in the extruder is only one parameter influencing the efficiency of the plasticiser to mix with the starch; changing the screw speed which affects both the residence time and the shear mixing. Decreasing of the residence time and increasing shear mixing in the extruder by increasing the screw speed increases the tensile strength of TPS to some extent as shown in **Table 3-4**. However it can be seen from the data at 185 rpm, that treating the material too aggressively results in excessive degradation and the material begins to lose structural integrity.

Table 3-4: *The effect of residence time in extruder.*
All samples were extruded at 150 °C and then pressed at 140 °C with 100 kN

Standard screw speed (rpm)	Real screw speed (rpm)	Tensile Stress (MPa)	True Strain (mm/mm)
100	110	20.61 ± 0.477	0.030 ± 0.001
125	135	21.62 ± 0.398	0.074 ± 0.008
150	160	24.24 ± 0.831	0.047 ± 0.006
175	185	19.74 ± 0.897	0.036 ± 0.003

In addition to the change in strength there is also a change in optical appearance resulting from degradation of the TPS. As the screw speed rises, frictional or shear heating increases and causes the starch granules to degrade to a small extent. **Figure 3.15** shows samples of extruded pellets resulting from extruding the same batch of components at different screw speeds. It is clear that the samples extruded at 185 rpm are darker than those processed at 110 rpm, despite the shorter residence time, and, as with extrusion temperature, this darker colour results in a more brittle material with a higher UTS. These observations and results could provide evidence that an increased rotation rate leads to increased shear heating that results in localised heating of the material beyond its degradation temperature.



Figure 3-15: *The grains and sheets.*
Samples were extruded at 150 °C, with different screws speed
1=100 rpm, 2=125 rpm, 3= 150 rpm and 4=175 rpm.

3.11. Glass transition temperature

The effect of the four plasticiser systems on the physical properties of thermoplastic starch was studied in **section 3.5**, showed that mixture of starch/choline chloride/glycerol gives the strongest TPS. **Table 3-5** shows the effect of these four plasticiser systems on the glass transition temperatures, all non-extruded samples had slightly higher T_g values than the extruded ones. The reduction in T_g after extrusion is due to non-gelled starch granules in the samples after the presence of high mixer and temperature.

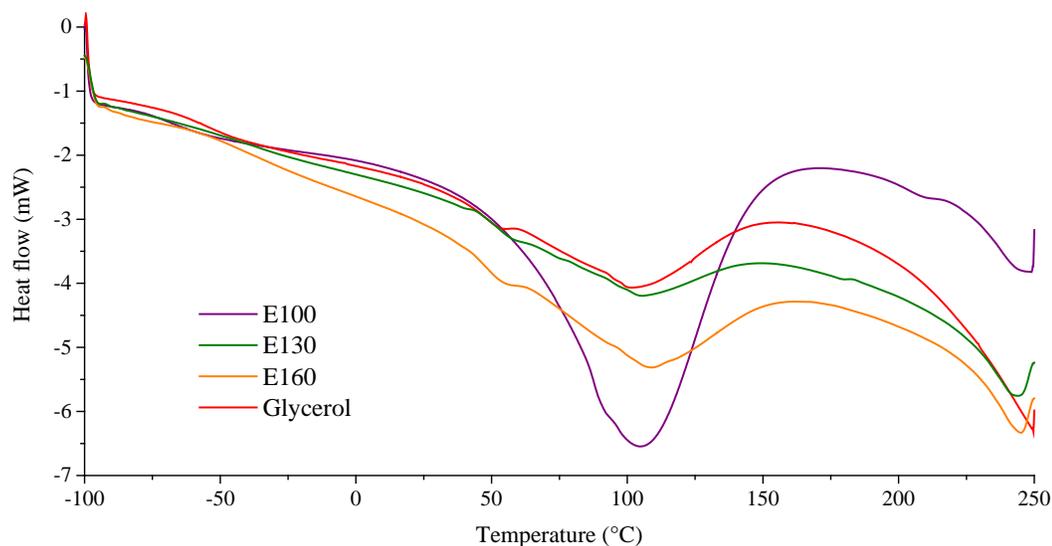
The T_g of glycerol based TPS dropped after extrusion from 65.4 °C to 57 °C. Glycerol based TPS also had the lowest T_g before and after extrusion implying that glycerol/choline chloride is the most efficient plasticiser to modify starch compared to the other systems as glycerol has more hydroxyl groups than the rest that improve the plasticisation.

Table 3-5: *Effect of hydrogen bond donor on the glass transition temperature of various extruded thermoplastic starch samples. The extruded samples extruded at 130 °C, 100 rpm and a die pressure of c.a. 20 bar before being pressed at 140 °C, 110 kN for 10 min. The mixture of non-extruded samples dried for two hours at 50 °C and then pressed at 140 °C, 110 kN for 10 min.*

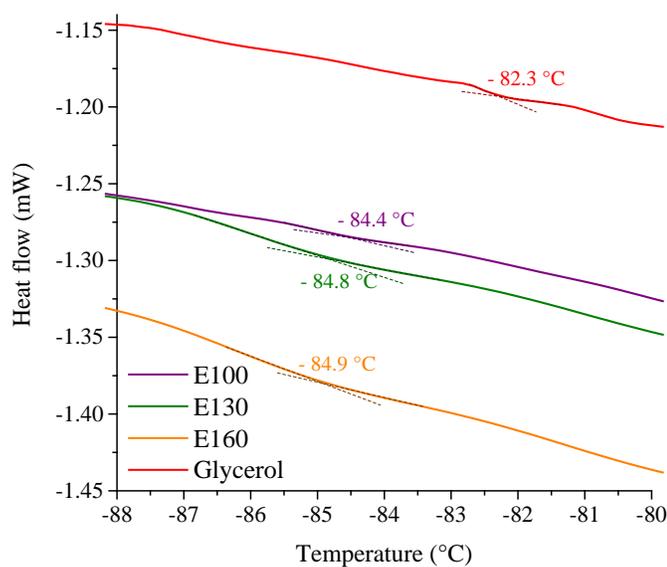
Composition	Non-Extruded	Extruded
Starch: ChCl: HBD		
HBD = urea	72.9 ± 6.5	69.9 ± 8.4
HBD = ethylene glycol	72.0 ± 7.7	71.2 ± 11.8
HBD = propylene glycol	68.6 ± 9.1	68.1 ± 7.8
HBD = glycerol	65.4 ± 6.5	57.0 ± 9.9

Figure 3.16 compares the DSC thermograms of starch/glycerol-TPS (G130) and starch/glycerol/choline chloride-TPS pellets extruded at 100 °C (E100), 130 °C (E130) and 160 °C (E160), all traces demonstrate a characteristic change in heat capacity normally assigned to a glass transition (T_g). The upper and lower glass transition temperature of starch/glycerol-TPS (G130) extruded at 130 °C is 53 °C and -82.3 °C respectively. E100 had a T_g temperature of approximately 92 °C whilst the E130 and E160 have an upper T_g of approximately 57 °C and 55 °C respectively. E100 has the highest glass transition

temperature which was about 92 °C indicating that the mixture has high quantity of non-gelatinised-starch granules.^{25, 26} Also, the endothermic peaks could refer to the gelatinisation of starch which can be slightly affected by glycerol concentration and water content and E100 should have the most amount of water compared to the rest due to the lower extrusion temperature resulting in less water evaporation.²⁷



(a)



(b)

Figure 3-16 : A comparison of DSC results that shows the upper (a) and lower (b) glass transition temperatures of ground TPS pellets extruded at 100, 130 and 160 °C and glycerol-TPS 130 °C without ChCl.

It has previously been shown that DSC traces occasionally exhibit an upper and lower T_g , a phenomenon dependent upon the amount and type of plasticiser; a low glycerol and water content leads to a single phase transition, while more plasticiser gives two glass transition temperatures.^{28, 29} The samples in **Figure 3.16** were also subjected to temperature sweeps down to -100 °C and these showed the second, lower glass transition temperatures which were found to be -84.4, -84.8 and -84.9 °C for E100, E130 and E160 respectively whereas the glass transition temperature for G130 is -81 °C.³⁰

No distinct melting temperatures were observed for any samples although an indication of softening can clearly be seen from the dynamic mechanical analysis, DMA, which is shown in **Figure 3.17**. In all samples evidence of decomposition was observed at approximately 250 °C as a result of decreased moisture content and consequently degradation.³¹

3.12. Viscoelasticity nature

As polymers are viscoelastic materials that have mechanical properties of solids and liquids, thermal analysis is important to determine the properties changes with temperature. Dynamic mechanical analysis (DMA) is the most common technique to measure these characteristics of both solids and liquids. DMA can be used to detect molecular motions or relaxation process and/or to determine viscoelastic and mechanical properties of the tested plastic sample as function of time, temperature, displacement or frequency. DMA characterises the storage modulus (E'), loss modulus (E'') and $\tan \delta$ of the plastic in function of temperature, they related to each other as shown in **Equation 3-1**.³²

$$\frac{E''}{E'} = \frac{\sin(\delta)}{\cos(\delta)} = \tan \delta \quad \text{Equation 3-1}$$

The DMA- T_g occurs at the maximum value of $\tan \delta$, DMA- T_g values were slightly different to the DSC- T_g . **Figure 3.17** shows DMA curves of the extruded TPS samples, and it can be seen that TPS extruded at the higher temperatures had the higher T_g . It was also important to note that the lower temperature extruded plastics had a wide temperature of mechanical relaxation where as those extruded at a higher temperature had a much narrower mechanical relaxation window, **Figure 3.17**.

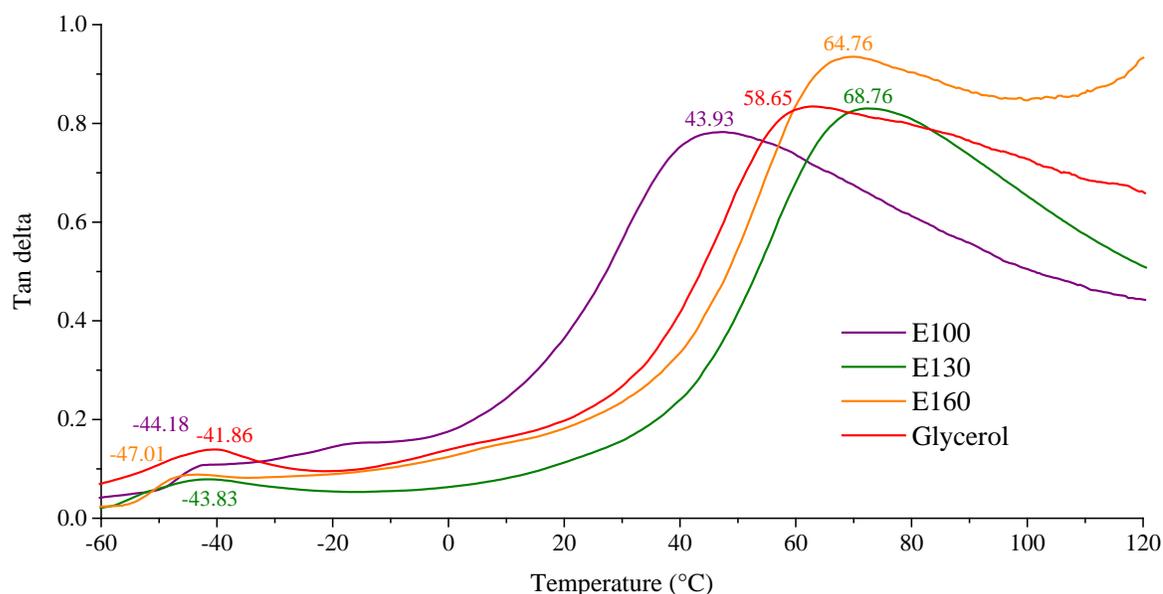


Figure 3-17 : A comparison of DMA results of the extruded blank TP.

DMA reinforces the idea of the two glass transition temperatures in TPS that were suggested by the DSC data above. Low temperature relaxation peaks are observed in the DMA analysis shown in **Figure 3-17** which could signify the phase separation of the glycerol-rich-phase from the starch-rich-phase.^{33, 34} The material extruded at 130 °C (E130) converts from a rigid to a flexible material at higher temperature than that with just glycerol (G130). The glass transition temperature of TPS rises by about 10 °C with the addition of choline chloride to the mixture.

3.13. Homogeneity

The high shear mixing and temperature of the extruder increase the homogeneity of the extruded TPS, and consequently strength and transparency. **Figure 3-18 (h)** shows SEM images of the native corn starch and compares it with the plasticised corn starch samples extruded at different temperatures. The dry starch granules were molten or physically broken up into small fragments.³⁵ It can be seen the notable granular structure becomes less notable after extrusion. At high temperature, glycerol and the small amount of water break

up the corn-starch-granules and disrupt inter- and intra-molecular hydrogen bonds, which change the native starch to a thermoplastic.³⁶ The lower extrusion temperature produce incompletely gelled TPS, **Figure 3-18 (a)**, the higher temperatures produced more uniform and transparent TPS, **Figure 3-18 (b-g)**. The TPS sample extruded at 160 °C, **Figure 3-18 (g)**, is much more transparent than the others and almost no residual granules remain from the corn starch.

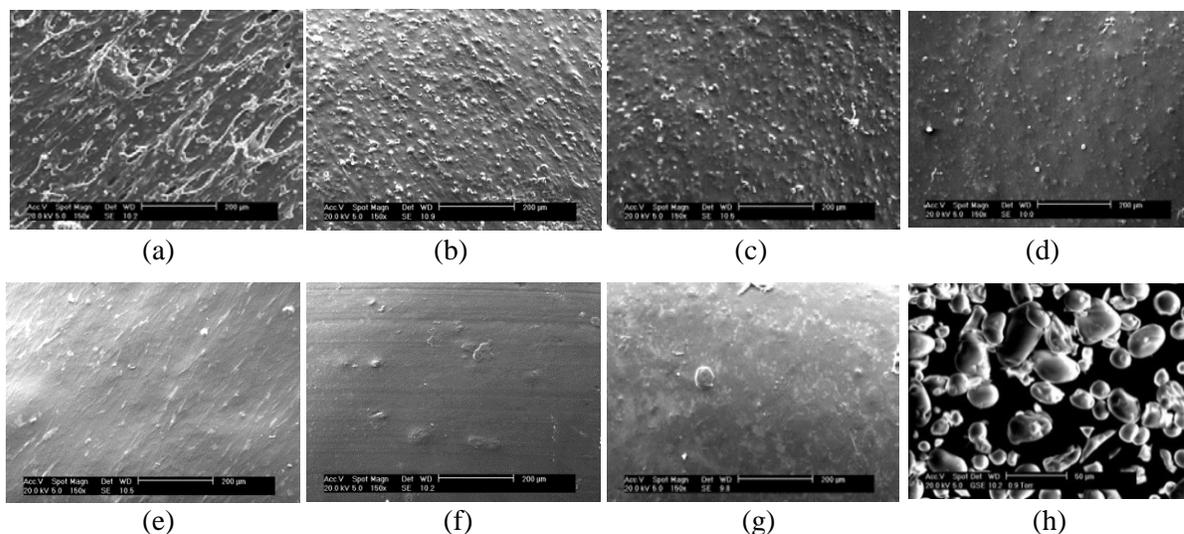


Figure 3-18: SEM image of extruded with screws speed of 100 rpm, and temperature of (a) = 100 °C, (b) = 110 °C, (c) = 120 °C, (d) = 130 °C, (e) = 140 °C, (f) = 150 °C, (g) = 160 °C and (h) = dry corn flour. All images magnified 150 times and scale bar of 200 μm except (h) which magnified 300 times and scale bar of 50 μm .

Extruding with faster screw speeds reduce the expansion of TPS which almost play the same role of higher temperature. Also, the viscosity of the starch mixture declines, and phase homogeneity increases. Subsequently, the tensile strength improves as the bulk density increases.³⁷ **Figure 3-19** shows SEM images of TPS samples obtained at different screws speed; the faster the screw speed the more uniform, the stronger and more transparent the sample, however this also resulted in much more brittle samples as would be expected as brittle failure takes over from ductile failure.

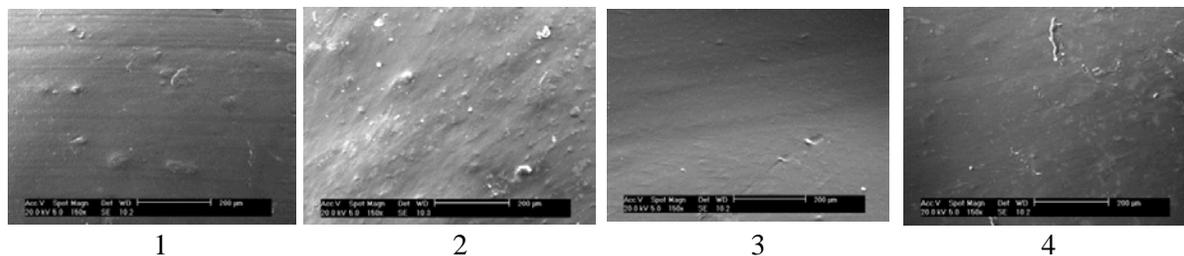


Figure 3-19 : SEM images of extruded at 150 °C with different screws speed are 1=100 rpm, 2=125 rpm, 3=150 rpm and 4= 175 rpm. All images magnified 150 times and scale bar of 200 μm .

3.14. Crystallinity

XRD experiments were carried out to investigate the effect of different extrusion conditions on the crystallinity of TPS. **Figure 3-20 (a)** shows the XRD of samples extruded at 100, 130 and 160 °C (all pressed at 140 °C). It is immediately apparent that all three samples have some crystal structure; the shoulder at 13° is due to V_H -type structure formed by the crystallisation of complexes of amylose and lipids present in corn flour. The level of crystallinity has been determined from the ratio of integrated signal to a crystalline reference. The native starch has about 40% crystallinity whereas the material extruded at 100 °C has 10% with the degree of crystallinity increasing to approximately 15% for 130 °C and 20% as the extrusion temperature increases at 160 °C. It is possible that at higher temperatures, dehydration of the amylose leads to recrystallization and results in a stronger but more brittle material. The material extruded at 100 °C also has a slightly different diffraction pattern; it is possible that this is due to some sort of phase transition between 100 °C and 130 °C during the extrusion process.

The recrystallisation of amylose during TPS processing is due to the lysophospholipids forming complexes with ingredients such as glycerol. Recrystallisation forms the V_H -type which is a single helix crystal and this can be seen at a 2θ of 19.8°. ³⁸⁻⁴⁰ Teixeira⁴¹ *et al.* investigated the effect of glycerol/ sugar/ water mixtures on thermoplastic cassava starch and they have found that the T_g value, hygroscopic nature and V_H -type peak height decreased in the presence of sugar containing glycerol. This is similar to the above

discussed DMA- T_g of E160 which is lower than the one of E130. Comparing Teixeira's research with the result shown in **Figure 3-20 (a)** and with the fact that water evaporates faster at higher temperature could imply that extruding the mixture of starch/glycerol/ChCl at higher temperature separates glucose from starch chains converting some of polysaccharides to mono-saccharides and that is why it TPS caramelises at high temperature giving a darker golden colour to the plastic, **Figure 3-10 (g)**.

The absence of B type crystalline form from all samples is particularly interesting since this type of recrystallization is known to be responsible for the so called retrogradation of starch based plastics which results in progressive embrittlement during ageing or processing.^{42, 43} XRD results in **Figure 3-20 (a)** show that when the TPS was extruded at higher temperature (E130 and E160) there was less B-type starch which probably results from the shortage of water caused by evaporation at higher temperatures. As a consequence the formation of double helices occurs between the shorter outer chains of amylopectin.^{41, 44}

The helical structures in A-type and B-type starch are similar but different in their packing arrangements.⁴⁵ Peaks at 22.5° represent A-type which indicates the presence of some native corn starch in TPSs, signifying that some starch granules were not completely gelled especially for those extruded at low temperatures. This type of crystallinity has been noticed that, by both Leroy *et al.*⁹ who studied TPS that was plasticised with glycerol or glycerol/choline chloride.⁹ Furthermore, A-type, E_H-type and V_A-type are dependent on the water content and the residence time in the extruder. Less water and longer extrusion times weaken the A-type peak but increase E_H and V_A types peaks and vice versa as shown in **Figure 3-20**.^{1, 46} V_H-type and V_A-type represent hydrated and non-hydrated amylose respectively, while E_H-type is unstable and it converts to V_H-type with storage which is expected to be a polymorphous change rather than crystallinity increase.^{1, 15, 43}

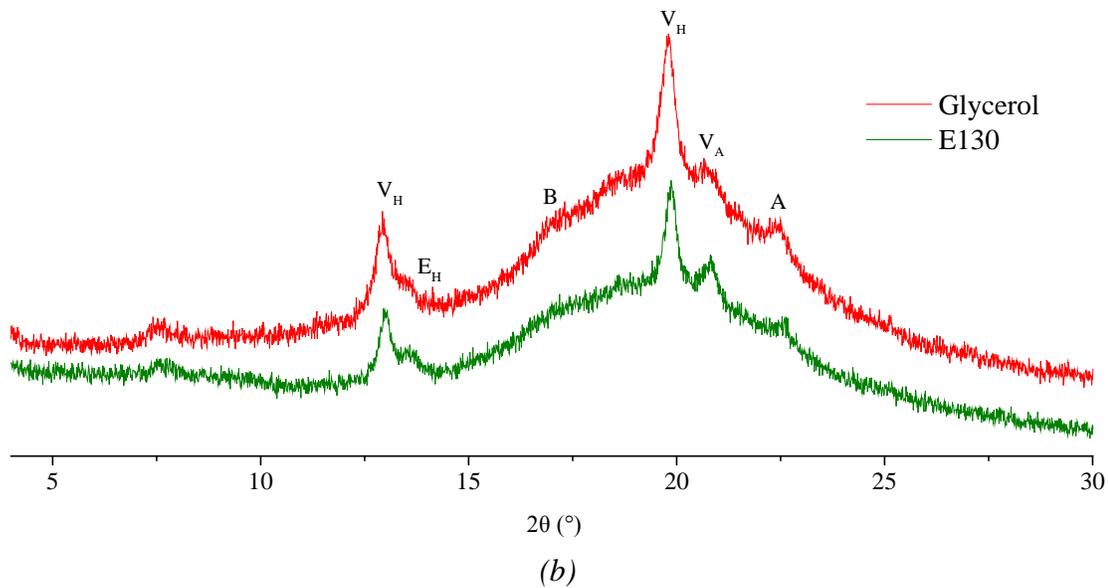
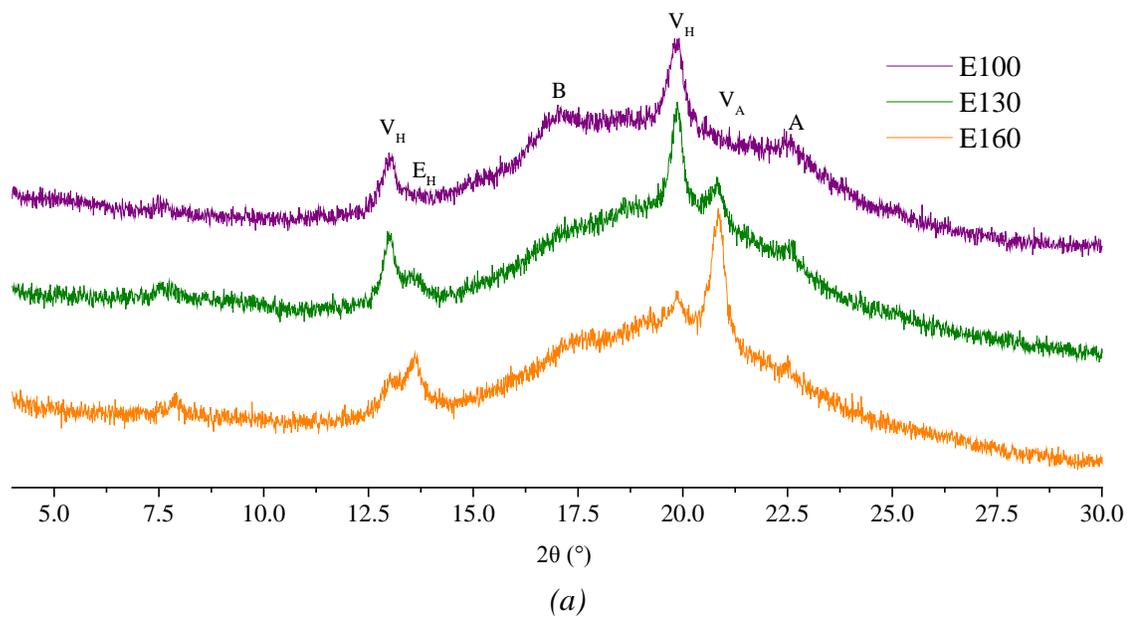


Figure 3-20 : XRD spectra of starch/ glycerol/ choline chloride extruded at 100, 130 and 160 °C together (a) and comparison of starch/ glycerol/ choline chloride and starch/glycerol extruded at 130 °C.

As can be seen in **Figure 3-20** the XRD results show that there is little or no native corn starch present in any of the extruded samples; this is in agreement with visual and physical observations, tensile data and data obtained from the SEM.

3.15. Rheological properties

The ability of a polymer to flow is an important characteristic for polymer processing and can be determined through a parameter called the melt flow rate. It is the amount of material which can flow through a given orifice diameter in a given time and it can be thought of as the opposite of the melt viscosity. The higher flows of thermoplastics under certain conditions, the higher melt mass flow rate (MFR). MFR can indicate the suitability of a polymer to processes such as extruding, vacuum forming and injection moulding.⁴⁷ The MFR was calculated as shown in **Equation 2-1** in **Chapter 2, Section 2.2.11**.

Tajuddin⁴⁸ investigated the effect of glycerol and water in the viscosity of thermoplastic corn-starch by using a multipass rheometer (MPR) and they found that viscosity increased when the glycerol content was more than the water content.⁴⁸ This suggestion does not really clash with other results which signpost the viscosity decreases and melt flow index (MFI) increases with the increase of glycerol content. This behaviour was ascribed to the increase of starch granules mobility.^{49, 50}

The effect of using DES rather than using glycerol on its own is studied in this section. **Table 3-6** compares the melt flow index of thermoplastics plasticised by glycerol with those plasticised by glycerol/choline chloride. It can be seen that the addition of choline chloride to the mixture of starch and glycerol decreases the viscosity of TPS and subsequently increases the MFR. Therefore plasticising starch by DES not only increases homogeneity, transparency, strength and crystallinity, it also makes processing TPS easier by improving the MFI. It is possible that the DES acts not only as a plasticiser but also as a lubricant which would explain the results below. The Abbott group has recently shown that DESs act as extremely effective lubricants which are comparable with mineral based lubricants.⁵¹

Table 3-6: MFR comparison between starch/glycerol and starch/glycerol/choline chloride which extruded at different temperatures. The test was run at 150 °C with load 21.6 kg.

	MFR (g/10 min)	
G130	4.68	± 0.127
E100	15.92	± 0.794
E130	14.35	± 0.168
E160	16.03	± 0.916

3.16. Injection moulded TPS

Thermoplastic starch can be used in many applications specially for the short-term applications, where it can be produced by the same industrial process of current commercial plastics, thus thermoplastic starch can be extruded to produce extruded pellets from a mix of starch flour and the plasticiser which is a deep eutectic solvent in this research that prove glyceline is a very good plasticiser producing comparable plastic to those synthetic plastics in tensile strength. Furthermore, extruded thermoplastics starch can be compressed to produce sheets of plastic that can be vacuum formed as presented in **Figure 3-21 (a)**, it is also can be injection moulded as shown in **Figure 3-21 (b)**.

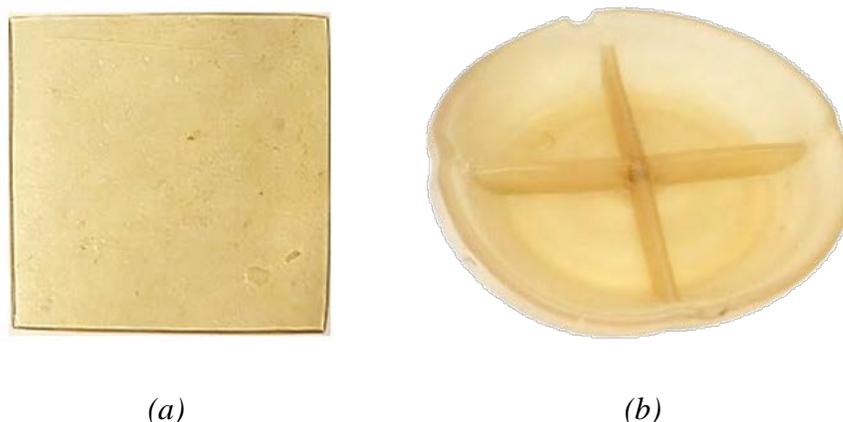


Figure 3-21 : Sample of starch plasticised with glycerol and choline chloride injection moulded into a 10 cm mould (200 °C and 60 Bar)

3.17. Summary

It has been shown that thermoplastic starch, based on corn starch with glycerol and choline chloride as a plasticiser, can be formed and is mechanically comparable to polyolefin-based thermoplastics. TPS has acceptable mechanical properties for many applications especially when used for a short-time. It was found that the physical properties of TPS can be controlled by the processing conditions and that water content is critical as is the extrusion temperature. The pressing time and temperature are relatively unimportant so it can be deduced that the extrusion conditions are vital in controlling the ability of the salt to plasticise the starch/ glycerol mixture. In all processing and composition conditions a small amount (3-4%) of material was still crystalline.

In addition, TPS produced under different processing conditions have been physically and chemically investigated by using variety of methods such as DSC, SEM, QCM, XRD, MFI and DMA.

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Chapter 4: Bio-additives as composites, fillers or water stabilisers

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4. Bio-additives as composites, fillers and water stabilisers

4.1. Introduction

Very few non-metallic materials are used in a pure form; most are composites of a binder, usually polymeric in nature, with a filler. In some cases this can be a waste material such as fly ash which is used in concrete or carbon black from the coking process which is used in a variety of plastics. In some cases renewable, bio-degradable sources are used the most common of which are wood fibres or wood chips which are used in a variety of furniture boards. These fillers reduce the product cost, and can improve the physical and chemical properties of the product.^{1, 2} In this chapter the effect of bio-fillers on the mechanical and chemical properties of thermoplastic starch will be investigated.

The type, content, particle size and shape of the filler play very important roles in changing the physical and chemical characteristics of the final product including the strength, flexibility, crystallinity, morphology, homogeneity, surface finish, glass transition temperature, viscoelasticity, water content and chemical interaction between the matrix, filler and plasticiser.

Many natural types of filler have been tested by several groups, for instance wheat straw,³ flax, cellulose⁴ and hemp⁵ have been used to reinforce thermoplastic starch.⁶ However, in this study some material from natural wastes were used as filler such as banana and orange peels and eggshell.⁷ A previous, unpublished study within the group showed that the optimum ratio of starch to Glyceline which was 2.75:1 respectively that is almost 75 wt% starch and 25 wt% Glyceline. In this project 10 wt% starch was replaced with the fillers including lignin, wood, silk, zein and eggshell.

This chapter will discuss the effect of filler type, and the particle size and shape on the tensile strength, glass transition temperatures, crystallinity structure, homogeneity and the chemical changes of TPS.

4.2. The effect of filler type and content on physical properties of TPS

Grain-like and fibre-like fillers were represented by eggshell and wood-fibre respectively as they were added to TPS with three different content and particle sizes to study their influence on tensile strength and tensile strain. **Figure 4-1** shows how particle shape length can deflect the direction of propagation crack that strengthen the material and delay the break.⁸

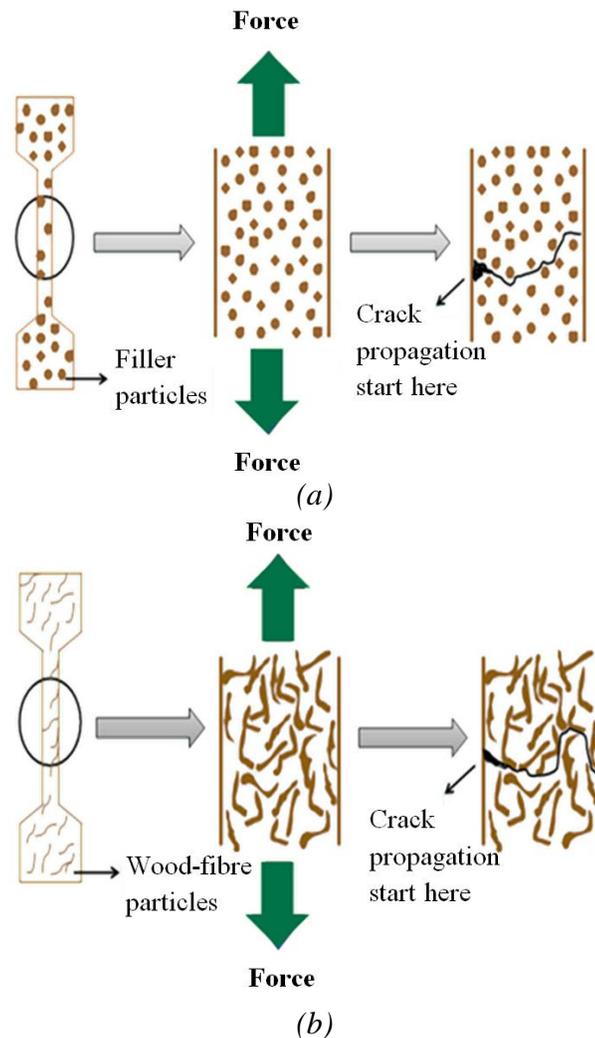


Figure 4-1: Effect of strength and deflecting the direction of propagation when the filler particles are not fibre-like (a), while the direction of propagation is deflected when the filler particles are longer and fibre-like and in very randomly discontinuous orientation (b).

On an atomic level composite materials work by stopping crack propagation. At points where there is a crack or scratch on the surface the stress at the bottom of the crack is accentuated and may increase the local stress by up to 200 times. The local stress can be decreased by a factor of 5 if the direction of crack propagation is deflected at right angles to the direction of crack propagation. In fibre glass, for example, there is a weak adhesive bond between the polymer and glass fibres. In general, if the adhesive bond $> 1/5$ cohesive bond strength then the crack will propagate through the material *i.e.* another brittle material is produced. If the adhesive bond $< 1/5$ cohesive bond strength then the crack will propagate along the interface and the apparent applied stress will be reduced by a factor of 5. This is shown schematically in **Figure 4-2**.

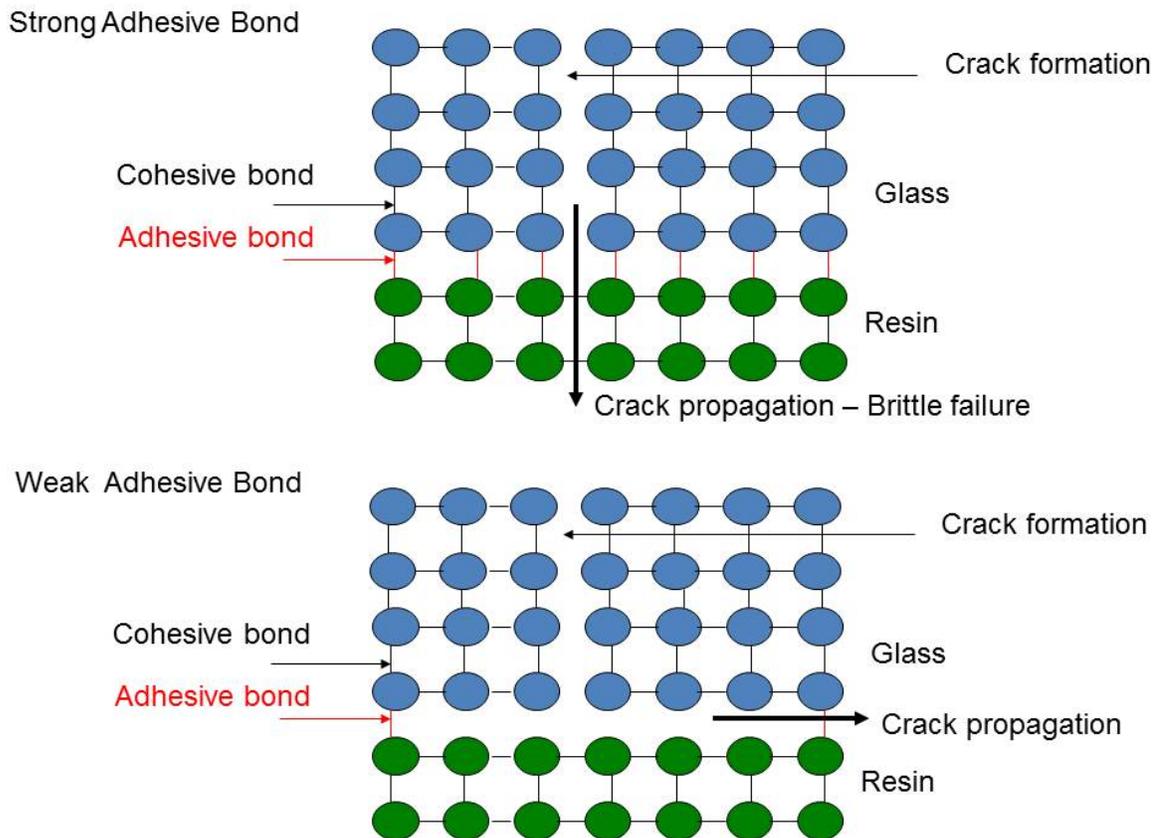


Figure 4-2: Schematic representation of how a composite material changes the direction of crack propagation.

4.2.1. Eggshell-TPS composites

To investigate the effect of grain-like filler and its content, three different particle sizes (100, 200 and 500 μm) of eggshell were tested in three different contents (10, 20 and 30 wt%) in a composite with thermoplastic starch. In all cases the glycerol/choline chloride content was constant at 25 wt% of the total. **Figure 4-3 (a)** shows the tensile strength and strain of non-extruded TPS with the three quantities and three particle sizes. It can be seen that replacing 10 wt% starch with eggshell regardless of particle size reduces the tensile strength of TPS but the larger particle size the weakened the TPS more considerably.⁹

In cases where the composite material decreases the strength of a material this is usually because the packing density is smaller and the particulate incorporates voids into the structure which impart a weakness. Alternatively the polymer can have a strong interaction with the particulate and result in a strong adhesive bond and a brittle composite.

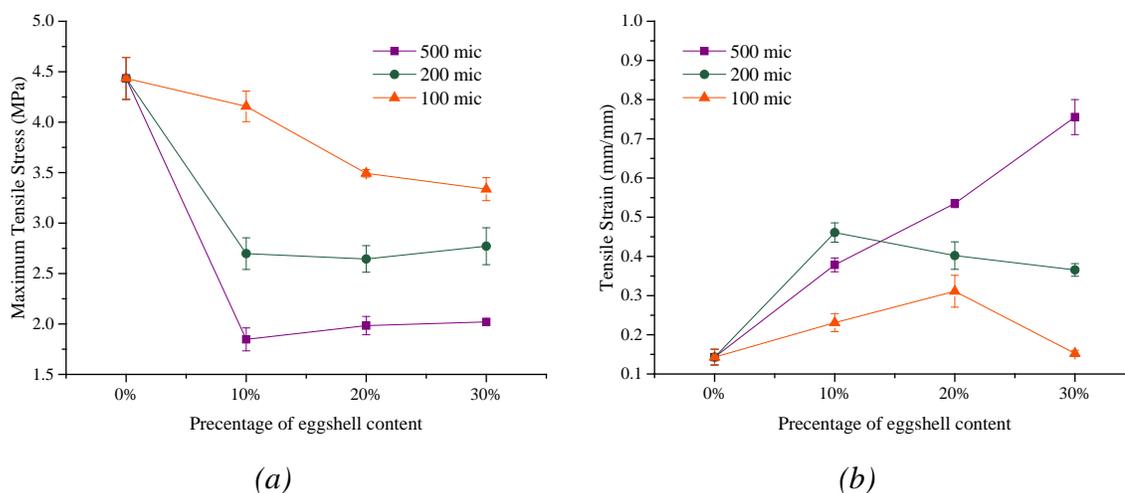


Figure 4-3: The effect of particle size and content of eggshell filler on the UTS and tensile strain data of thermoplastic starch Samples were prepared by mixing all components in the same time then dried in oven at 50 °C for three hours before pressing at 140 °C in 1 mm thick mould.

Adding more eggshell and decreasing the starch content does not significantly change the tensile strength after the first addition. In the only similar study using eggshell as a composite material Supri and Shuhada¹⁰ found that the tensile strength of composites with low density polyethylene fell from 14 to 8 MPa (-43%). These samples were in effect extruded ensuring more homogeneous mixing than that achieved in **Figure 4-3**. In the eggshell-TPS materials there is a significant difference in the strength with the particle and size and loading but the relative changes are similar to those observed with LDPE. The relative decrease in **Figure 4-3** is -22% for 100 μm , -40% for 200 μm and 53% for 500 μm eggshell. The decrease in the current study could be because the particles act collectively to decrease the effect of the polymer between them or they could decrease the density of the polymer by increasing the void volume.

Shakuntala *et al*⁹ studied wood-epoxy composites and found that the strength increased up to 15 wt% and thereafter the strength decreased. It was found that the void volume decreased up to 15 wt% and then increased again. **Table 4-1** shows the density of the components of eggshell-TPS together with those of the composite.

$$\text{The theoretical density of eggshell-TPS} = \sum \rho_i w_i \quad \text{Equation 4-1}$$

Where ρ_i is the density of each component and w_i is the weight fraction.

For the 10 wt% eggshell = $(2.981 * 0.1) + (1.462 * 0.65) + (1.179 * 0.25) = 1.543 \text{ gcm}^{-3}$

Table 4-1: Density (ρ) of extruded eggshell-TPS compared to its components

Elements		Density (g cm^{-3})	
Experimental Theoretical	Eggshell	2.981	± 0.063
	Starch	1.462	± 0.015
	Glyceline 200	1.179	± 0.012
	Eggshell-TPS	1.392	± 0.037
	Eggshell-TPS	1.543	± 0.019

The difference between the theoretical and experimental densities shows that the void volume increases in the composite confirming that the eggshell decreases the packing density. This will increase the number of voids in the structure and potentially weaken the material.

Figure 4-3 (b) shows that the larger particle size with more content of eggshell in TPS increase the ductility of the material. Tensile strength is usually inversely proportional to the tensile strain but with 30 wt% of 100 μm particle size eggshell caused a decrease in the ductility of the samples.⁷ Supri and Shuhada found that the ductility of eggshell-LDPE composites decreased with increasing eggshell loading.¹⁰

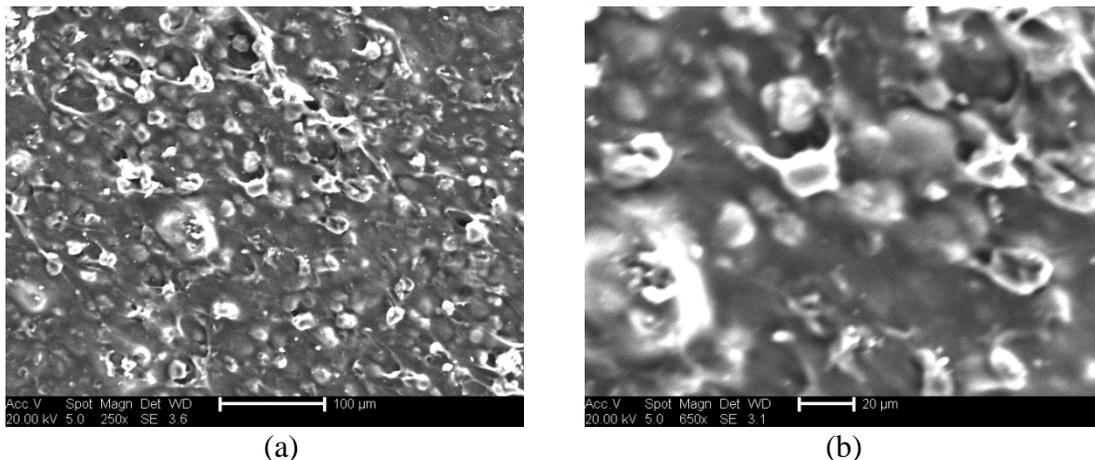


Figure 4-4: SEM images, scale bar of 100 μm (a) and 20 μm (b), of 10 wt% eggshell-TPS samples shows the eggshell particles (c.a. 50 μm)

Figure 4-4 shows an SEM image of an eggshell TPS sample with 10 wt% loading. It is quite clear that the particles are in the main isolated from each other and surrounded by polymer.

Previously in the group Alaysuy measured the properties of eggshell in starch and HDPE as a function of composition. The samples were produced by extrusion and just mechanical mixing. The results are summarized in **Table 4-2**. These results show similar trends to those above and show that there is little difference between the mechanical strength of the extruded and non-extruded composites although there is a significant difference between

the extruded and non-extruded samples without composite material. This shows that the particles themselves are imparting an inherent weakness into the materials.

Table 4-2: Mechanical strength and elongation of eggshell composites with (a) TPS and (b) HDPE

Eggshell/ %	UTS/MPa	Elongation/ %	UTS/MPa	Elongation/ %
TPS	Extruded		Non-extruded	
0	12.00 ± 1.10	41.3 ± 4.16	2.26 ± 0.24	36.37 ± 0.7
10	1.98 ± 0.18	31.3 ± 0.3	3.77 ± 0.32	23.5 ± 0.8
20	1.54 ± 0.05	26.6 ± 0.7	1.87 ± 0.26	39.1 ± 1.2
30	2.24 ± 0.16	11.2 ± 0.3	0.84 ± 0.03	35.2 ± 0.8
HDPE	UTS/ MPa	Elongation/ %		
0%	26.22 ± 0.78	600.4 ± 0.8		
10%	24.37 ± 0.12	9.8 ± 0.1		
20%	21.37 ± 0.29	7.6 ± 0.1		
30%	18.80 ± 0.27	5.4 ± 0.0		

To understand the data above the density of the un-extruded samples were measured and these are presented in **Table 4-3**. It can be seen that at each loading although the amount of each component stays constant the density drops as the particle size is increased which confirms that the void volume is increasing and explains why the strength of the material decreases.

Table 4-3: Density of non-extruded eggshell-TPS in function of eggshell particle size and amount.

Eggshell amount (%)	Density of eggshell-TPS (g cm ⁻³)						
	100 μm		200 μm		500 μm		Theoretical
10	1.252	± 0.027	1.244	± 0.037	1.224	± 0.063	
20	1.371	± 0.031	1.320	± 0.039	1.316	± 0.027	1.62
30	1.523	± 0.032	1.441	± 0.021	1.385	± 0.032	1.79

Comparing the density in **Table 4-1** with that in **4-3** it can be seen that extrusion increases the density from 1.252 to 1.392 which is a decrease in void volume of about 10%. **Table 4-3** also includes the theoretical densities determined using **Equation 4-1**. The differences between the theoretical and measured densities differ by about 15% for the 100 μm particles whereas those for the 500 μm particles differ by 23% at a 30% loading. This clearly explains the results shown in **Figure 4-3**.

Using eggshell as a filler in TPS was achieved in this project by replacing some of the starch and keeping the plasticiser content constant in all cases. Starch granules were gelled by pressing the mixture of the three components in 1 mm thick mould at 140 °C, producing thermoplastic starch sheet containing eggshell filler as shown in **Figure 4-5**. The gelled starch granules here act as a binder between the filler, but at the cost of plastic strength.

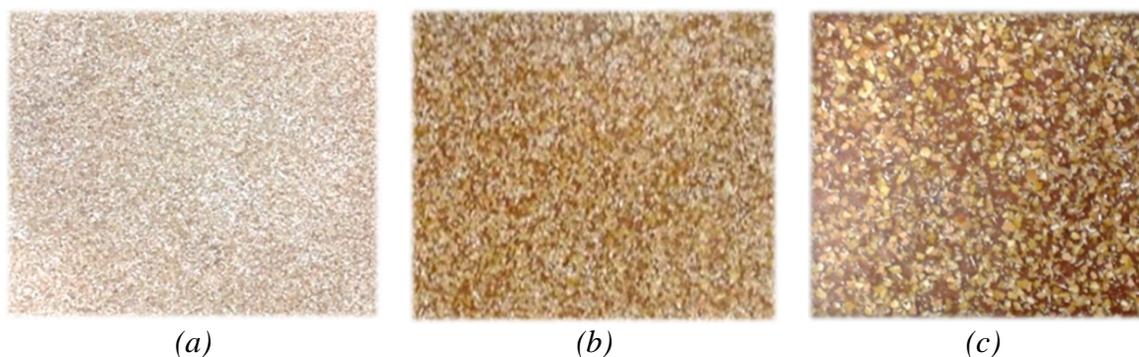


Figure 4-5: Images of the non-extruded TPS sheets pressed at 140 °C and contains 30 wt% eggshell, with particle sizes of 100 μm (a), 200 μm (b) and 500 μm (c).

4.2.2. Wood fibre - TPS composites

Wood fibre or particles (wood flour) are commonly used as a filler and these are usually bound together with a thermoset resin; typically urea-formaldehyde or phenol-formaldehyde. In the current study wood particles has been incorporated with TPS. When 10 wt% of wood-fibre replaces starch in TPS, the tensile strength decreased from about 4.5 MPa to less than 3 MPa in all three different particle sizes as shown in **Figure 4-5 (a)**. This reduction in tensile strength is similar to that observed with eggshell shown in **Figure 4-3**.

Muller *et al.*¹¹ studied the effect of wood content on the strength and density of TPS and they found that increasing the wood content to a certain level increases tensile strength but reduces tensile strain and shrinkage.¹¹ However, in this project it is noticed that the small addition of wood-fibre weakens TPS then it increases with the increase of wood content.

Figure 4-5 (a) shows that replacing 20 wt% starch with wood-fibre increases the tensile strength of 100 μm , 200 μm and 500 μm from *c.a.* 2.3 to 2.7 MPa, 2.4 MPa and 3.2 MPa respectively. Also, replacing 30 wt% starch with wood-fibre improved the tensile strength significantly in TPS samples contain the 100 μm and 500 μm particle sizes as they reach almost 4.75 MPa 5.6 MPa respectively, while 30 wt% of 200 μm particle size of wood only strengthens the material slightly.

The addition of 30 wt% wood-particles can produce stronger TPS than the blank sample, where the plasticised starch works as binders between the fibres, increasing the interface interactions with no significant change in the ductility as shown in **Figure 4-5 (b)**. Tensile strain data show how the TPS samples can be elongated. An increase in wood content decreases the ductility of the sample as would be expected; thus the highest wood content the strongest and least flexible TPS. One advantage of using thermoplastic starch in place of urea formaldehyde is that the material is a thermoplastic rather than a thermoset. This shows that it can be mechanically formed, but also has the advantage that wood-fibre TPS has the ability to be recycled and re-shaped as a thermoplastic.¹²

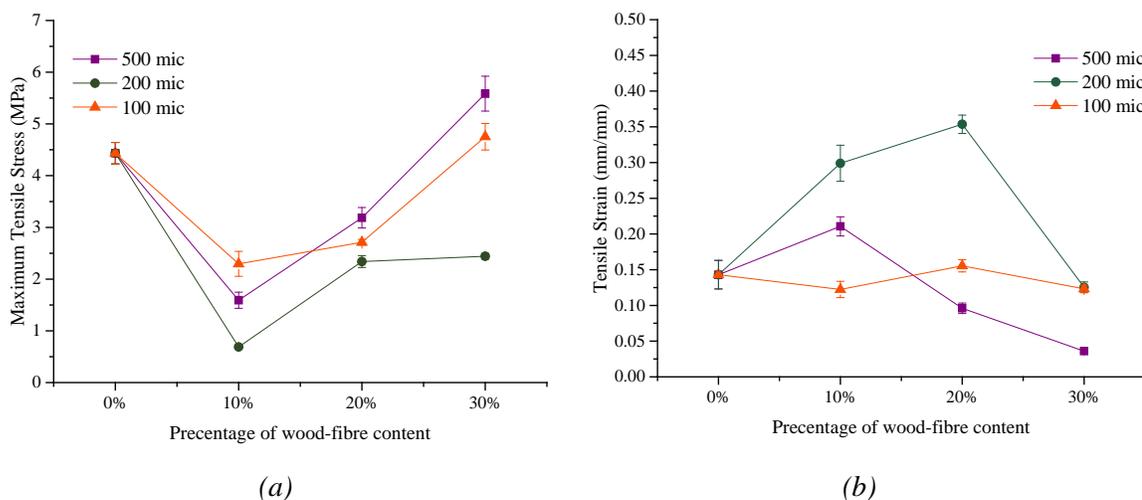


Figure 4-5: The effect of particle size and loading on maximum tensile stress and tensile strain data of thermoplastic starch with three different contents of wood particles. Samples were mechanically mixed and dried in oven at 50 °C for three hours before pressed at 140 °C in 1 mm thick mould and tested in tensiometer.

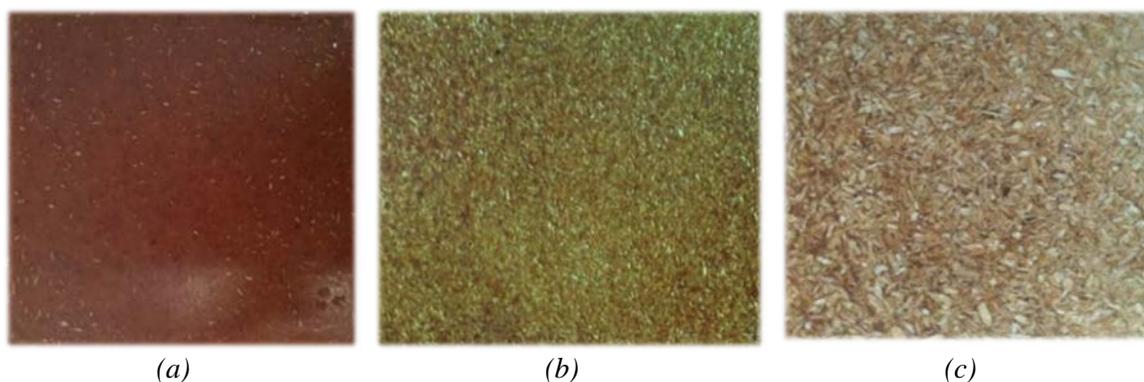


Figure 4-6: Images of the TPS sheets that pressed at 140 °C and contains 30 wt% wood flour, with particle sizes of 100 µm (a), 200 µm (b) and 500 µm (c).

This approach has recently been used to prepared large scale. The boards are useful as they do not contain formaldehyde-based resins, all the components are biodegradable/compostable and come from a renewable feedstock. Probably most important is that because starch is a thermoplastic the materials can be recycled into new boards which have

recently been demonstrated in the literature.¹² The boards can be sanded, routed, sawn, drilled and threaded. And they have been found to be easier to glue, laminate, coat, paint and lacquer than formaldehyde based MDF. It has also been demonstrated that thermoplastic starch-wood can be vacuum formed and injection moulded enabling it to be shaped rather than machined.

Because the wood flour is macro-porous it is compressible and so the density can be changed by increasing the pressing pressure.¹³ This is a factor which has not been optimised in this study but analogy to commercial fibreboard shows that the strength is related to the density of the board.¹⁴ In the following section properties of TPS with various fillers are compared. In each case the same amount of filler by weight is included and the same mixing and pressing conditions have been used in each case; In each case ten percent of filler was used with 65 wt% starch and 25 wt% glycerol/choline chloride. After mixing the three components with the right ratios, the mixture was dried in oven at 50 °C for about three hours before extruding and pressing it at 140 °C for ten minutes in 1 mm thick mould. It was decided for the following study to extrude all of the samples to maximise the interaction between the particulates and the TPS.

4.3. The effect of bio-additives on physical and chemical properties

More investigation of bio-additives effect on the physical properties has been done by using fine powder of five different additives that differ in their structure and properties, these additives are;

- eggshell,
- wood flour,
- zein protein,
- lignin, and
- silk fibres.

Each of these materials has different properties.

Eggshell is a plentiful natural wastes and it is classed as a potential biohazard due to its ability to harbour diseases such as salmonella. It is however simple to sterilise using bleach

and its hardness resulting from its microstructure make it a potentially useful composite material. Each egg contains approximately 15 g of shell and it is estimated that the UK uses 60 million eggs per day (*i.e.* 90 tonnes per day). It is also relatively hydrophobic due to its porous structure. Eggshell is approximately 95% of porous crystalline form of calcium carbonate, calcite, and about 5% organic materials such as sulphated polysaccharides and proteins. The density of eggshell is slightly lower than mineral calcium carbonate.¹⁵ The powder of eggshell has been used as filler in some researches; it has polar groups in its particle surface due to the existence of protein which contains, amine, carbonyl groups.¹⁶⁻¹⁸

Silk is a natural polymer where its structure consists of proteins in continuous repeated sequence form. Silks are bio-degradable, bio-compatible and cheap materials that have notable strength and toughness, it also can be chemically modified and then used in biomedical applications.^{19, 20} The protein structure of silk is built up of peptide links of the amino acids groups with a composition of $(-NH-CHR-CO)$, where R can be H (glycine), CH_3 (alanine) or OH (serine) as shown in **Figure 4-7**. Silk has a secondary structure held by strong hydrogen bonding between the silk chains.^{20, 21} Also, silk have been used in plastics as composites for more reinforcement or cost reductions.^{21, 22}

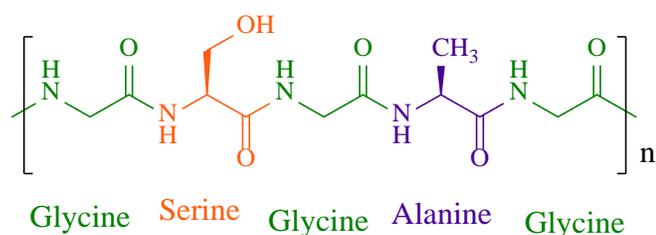


Figure 4-7: The main three components of natural silk linked by peptide bonds.

Zein is a protein that can be found in maize seeds, it is soluble in alcohol and insoluble in water, it can be categorised to four types depending upon their solubility properties.^{23, 24} Zein has high hydrophobic nature due to the amino acids groups that contain hydrophobic

residues such as proline, alanine, glutamine and leucine, **Figure 4-8** shows the structure of the four components.²³

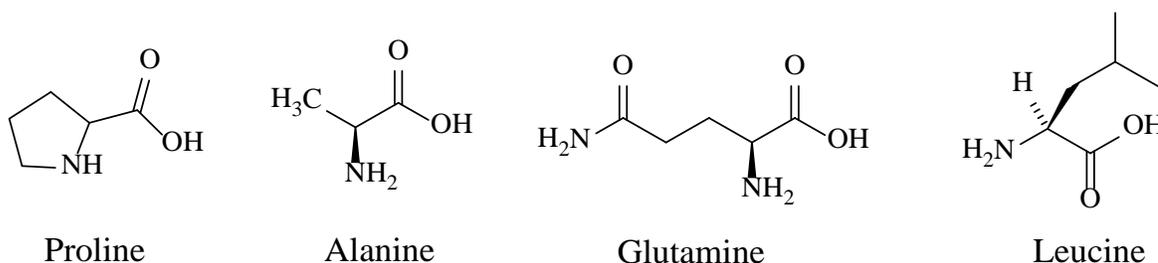


Figure 4-8: The main four components of Zein.

Wood has lignin, cellulose and hemi-cellulose in its structure as three main components of wood, shown in **Figure 4-9**. They all are natural polymers, but they differ in their physical and chemical properties. Cellulose, as defined in **chapter 1**, is highly crystalline polymer consists of D-glucose as the monomer unit. It is the component that gives the strength and structural stability to wood while hemi-cellulose contains about 5 to 6 carbon sugars and it is branched polymer. The chemical structure of lignin relies on its source, but it has amorphous structure. Lignin is considered as cross-linked polymer network, it binds the cellulose fibres in wood.²⁵

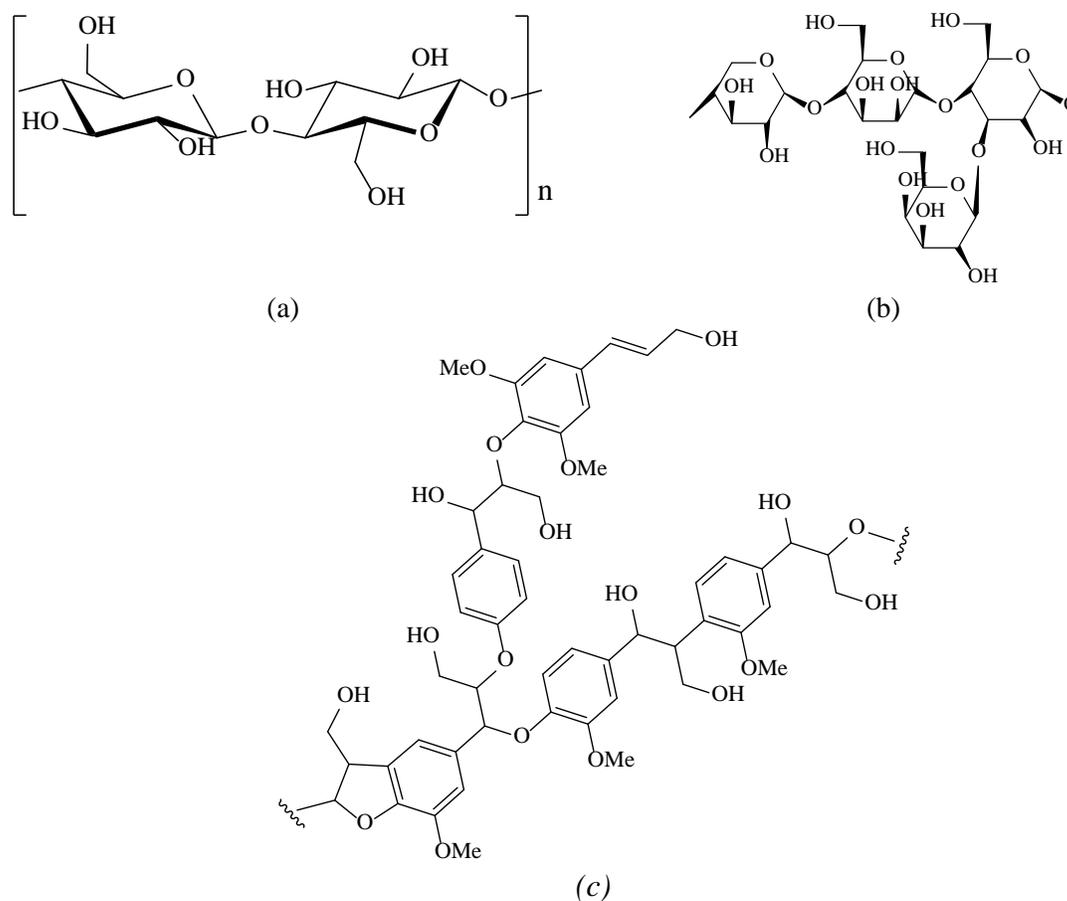


Figure 4-9: The main three components of wood, cellulose (a) hemi-cellulose (b) and lignin (c).

The tensile strength and strain, glass transition temperature, crystallinity, viscoelasticity, homogeneity and chemical interaction will be examined and discussed.

4.3.1. Strength and flexibility

Wood flour, zein protein, silk and lignin all have polar functional groups which are capable of hydrogen bonding to the starch and DESs. When 10 wt% of each of these materials was used as a composite with thermoplastic starch they all became weaker compared to the sample with no composite. Each single type of the fillers showed a markedly different effect on the strength. **Figure 4-10** compares the tensile strength and strain of TPS with and without the bio-fillers, and it is observed that tensile strength decreased with the addition of

the fillers when compared to E130. It should firstly be noted that the strength of the extruded samples is very much higher than those for the non-extruded samples shown in **Chapter 3**.

Wood-flour and zein decreased the tensile strength from 16.7 MPa to almost 14.5 MPa, and the tensile strain ≈ 11 mm/mm to ≈ 9.5 mm/mm. Similar results have been observed by other workers within the group¹² who worked on similar materials.

Some researchers have used starch with sucrose and aqueous sodium hydroxide solutions as a binding agent for the wood, but the tensile strength of their materials were much weaker (less than 4 MPa) than the reported in **Figure 4-10**.^{26, 27}

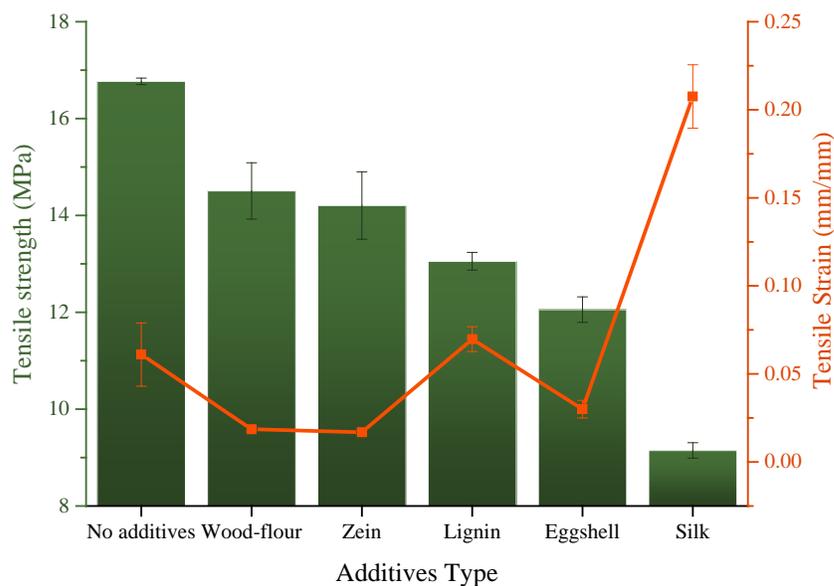


Figure 4-10: The effect of bio additives on physical properties of TPS. Ultimate tensile stress (green) and tensile strain (orange). All samples in this figure were extruded at 130 °C and pressed at 140 °C with 110 kN for 10 min.

However, the addition of 10 wt% lignin or silk decreased strength but increased elongation. Zein, lignin and wood flour (predominantly cellulose) have a much better capacity to hydrogen bond with the DES and this could be one of the reasons that these materials are stronger than silk or eggshell.

Finally, eggshell-TPS is the second weakest TPS with tensile strength about 12 MPa which is still much stronger than blank thermoplastic starch modified by just glycerol with the absence of choline chloride as Dogossy and Cziagany²⁸ reported in 2011 that the tensile strength of TPS, modified by glycerol or maltitol then extruded at 105 °C, is about 4 MPa.

4.3.2. Glass transition temperature

Figure 4-11 compares the DCS thermograms of TPS pellets that contain the bio-fillers with the blank sample, all traces demonstrate a characteristic change in heat capacity normally assigned to a glass transition temperature. The blank TPS had a T_g of approximately 57 °C which was higher T_g than any of the TPS samples that contained a bio-filler. The T_g ranged between 56.3 °C to 46.5 °C after bio-fillers addition as shown in **Figure 4-11**. Lignin-TPS and silk-TPS had T_g at 49.6 °C, while the glass transition temperatures of zein-TPS, wood-TPS and eggshell-TPS are approximately 56.3 °C, 48.3 °C and 46.5 °C respectively. This suggests that the bio-fillers are decreasing the overall crystallinity of the TPS.

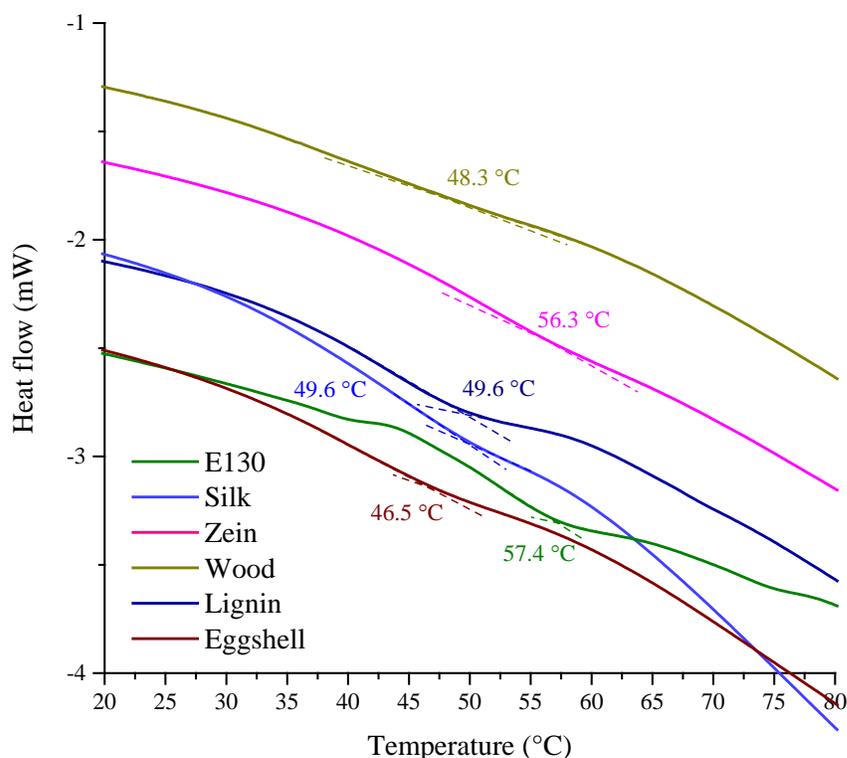


Figure 4-11: A comparison of DSC results of ground TPS pellets with different bio-additives extruded at 130 °C, showing the upper T_g .

It has previously been shown that DSC traces occasionally exhibit an upper and lower T_g , a phenomenon dependent upon the amount and type of plasticiser; a low glycerol and water content leads to a single phase transition, while more plasticiser gives two glass transition temperatures.^{29, 30} The samples in **Figure 4-11** were also subjected to temperature sweeps down to -100 °C and these did not show the second T_g observed in previous studies. No distinct melting temperatures were observed for any samples although an indication of softening can clearly be seen from the DMA data below. In all cases samples show evidence of water loss at about 100 °C and decomposition at approximately 250 °C as shown in **Figure 4-12**.

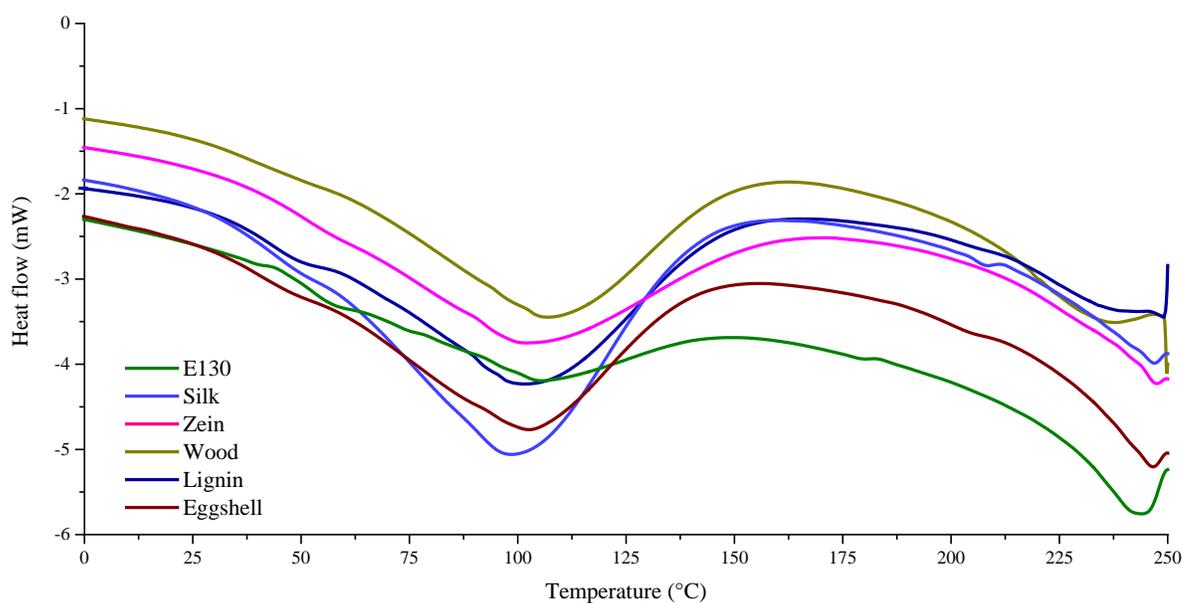


Figure 4-12: A comparison of DSC results of ground TPS pellets with different bio-additives extruded at 130 °C, showing the decomposition temperature.

4.3.3. Viscoelasticity

The main mechanical relaxation T_α associated with the calorimetric T_g was also analysed by dynamic mechanical analysis (DMA) as shown in **Figure 4-13** Whilst the T_α values were marginally different to the DSC data, as is normal when looking at a $\tan \delta$.

Figure 4-13 shows $\tan \delta$ for TPS samples with and without bio-additives where all samples had lower and upper T_g due to the two relaxation temperatures of two phases of glycerol-rich phase and starch-rich phase.^{31, 32} The blank TPS had an upper T_g at about 68.8 °C, however the addition of bio-additives influences the viscoelastic properties of TPS. Zein increases the upper T_g to 105.9 °C and this is due to the stiffness of the material and this can be observed very easily because the zein-TPS is much more brittle compared to the blank sample.³³

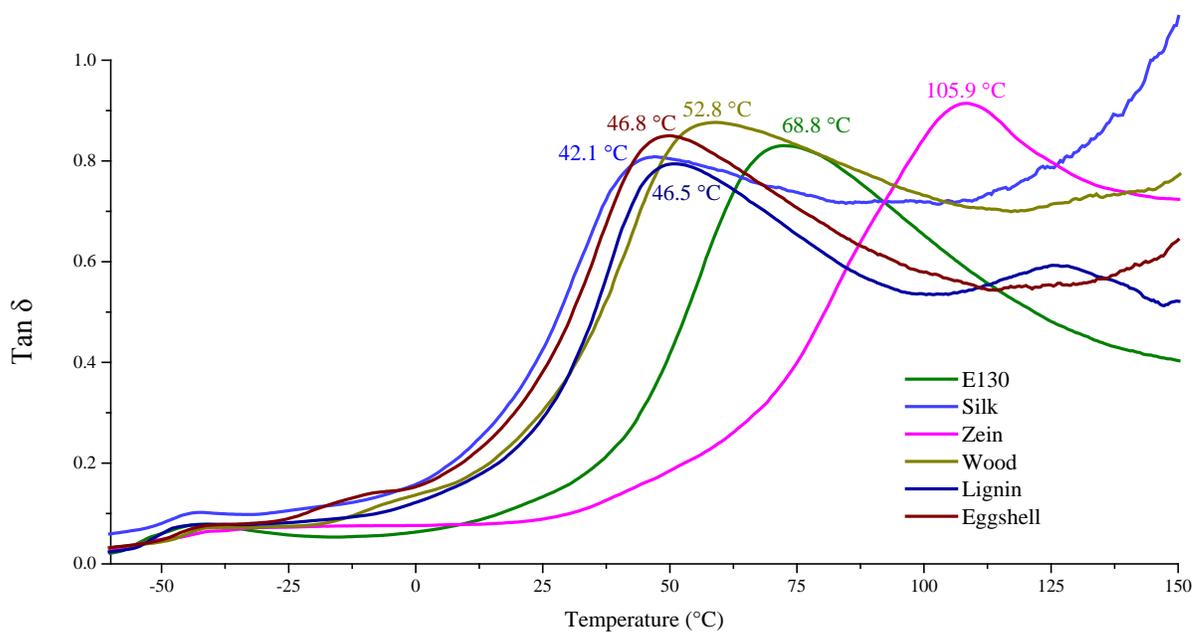


Figure 4-13: A comparison of DMA results of ground TPS pellets with different bio-additives extruded at 130 °C and then pressed at 140 °C, showing the upper T_g temperatures.

Silk and wood-flour reduce the DMA- T_g to 42.1 °C and 52.8 °C respectively. **Figure 4-13** shows that lignin and eggshell TPSs had T_g values which very close to each other at 46.5 °C and 46.8 °C respectively. Angellier *et al.*³⁴ studied the addition of waxy maize nanocrystal as fillers in thermoplastic maize starch plasticized with glycerol. They observed that glass transition temperature rose from 3 to 25.4 °C after the addition of ten percent of the starch nanocrystal. They attributed the change to the mobility of the matrix, and

concluded that the starch interacts with glycerol by hydrogen bonding and as a consequence reduces the mobility. Thus in the case of this project the reduction of DMA- T_g of filler-TPS could imply an increase of the matrix mobility due to either less interaction between starch and the plasticiser or the more water absorbance as will be shown in **chapter 5**.

Increasing the hygroscopic nature of TPS with the addition of bio-fillers is a more convincing suggestion. Lignin-TPS was unlike the other samples in that it displayed a third relaxation temperature as shown in **Figure 4-13**, this may indicate the appearance of a lignin-rich phase due to an hydrogen bonding interaction between lignin and the plasticiser.

Low temperature relaxation peaks are observed in the DMA analysis shown in **Figure 4-14** which could signify the phase separation of the glycerol-rich-phase from the starch-rich-phase.^{31, 32, 35, 36} The lower DMA- T_g of all samples occurs at approximately -45 °C which is the glass transition temperature of a plasticiser-rich-phase of thermoplastic starch which is so close to the glass transition temperature of glycerol.

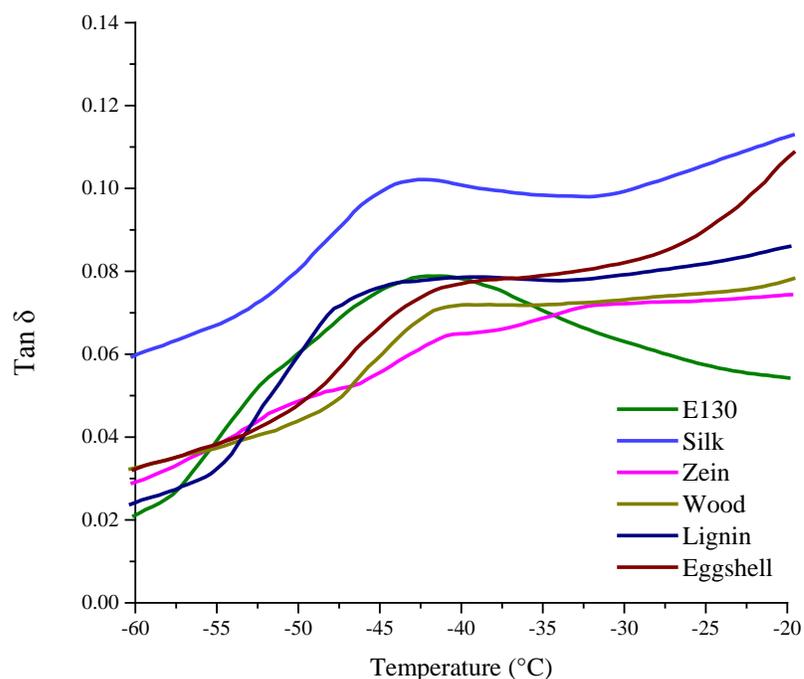


Figure 4-14: A comparison of DMA results of ground TPS pellets with different bio-additives extruded at 130 °C and then pressed at 140 °C, showing the lower T_g temperatures.

4.3.4. Crystallinity

XRD experiments were carried out to investigate the effect of different bio-additives on the degree of crystallinity of TPS. **Figure 4-15** shows the XRD results of all samples prepared in the same conditions and then ground in powder to fit the powder XRD instrument, but they differ in the bio-fillers type. It is obvious from **Figure 4-15** that all samples have crystal structure; the shoulder at 13° which is due to V_H -type starch structure formed by the crystallisation of complexes of amylose and lipids present in corn flour. The level of crystallinity has been determined from the ratio of the integrated signals to a crystalline reference.

XRD data shows that wood-TPS and E130 are almost identical, where they both had peaks at 13° and 19.8° , referring to V_H -type which represents the recrystallization of hydrated amylose.³⁷⁻³⁹ However, the integrated signal of E130 is larger than wood-TPS, indicating that wood-TPS has less hydrated amylose than E130. The shoulder at 21° represents V_A -type starch and proves that, they both had a slight signal for A-type starch at 22.6° . The amounts of A-type, E_H -type and V_A -type are dependent on the water content. When less water is present the signal for the A-type decreases but that for the E_H and V_A types peaks increase and vice versa as shown in **Figure 4-15**. The E_H -type is unstable and converts to V_H -type with storage which is expected to be polymorphous rather than crystalline.⁴⁰⁻⁴²

The disappearance of some peaks or decrease in its signals implies lower degree of crystallinity as can be seen in silk-TPS and lignin-TPS XRD data from **Figure 4-15** compared to E130 sample. They both had smaller peaks of V_H -type at 13° and 19.8° and an increase of V_A -type which means less hydrated and more non-hydrated amylose. At the same time the signal for the A-type disappeared implying that there are less native starch granules in the sample. The shortage of native starch in silk-TPS and lignin-TPS could refer to more hydrogen bonding interaction between lignin and silk separately with starch and the plasticiser than E130 sample.

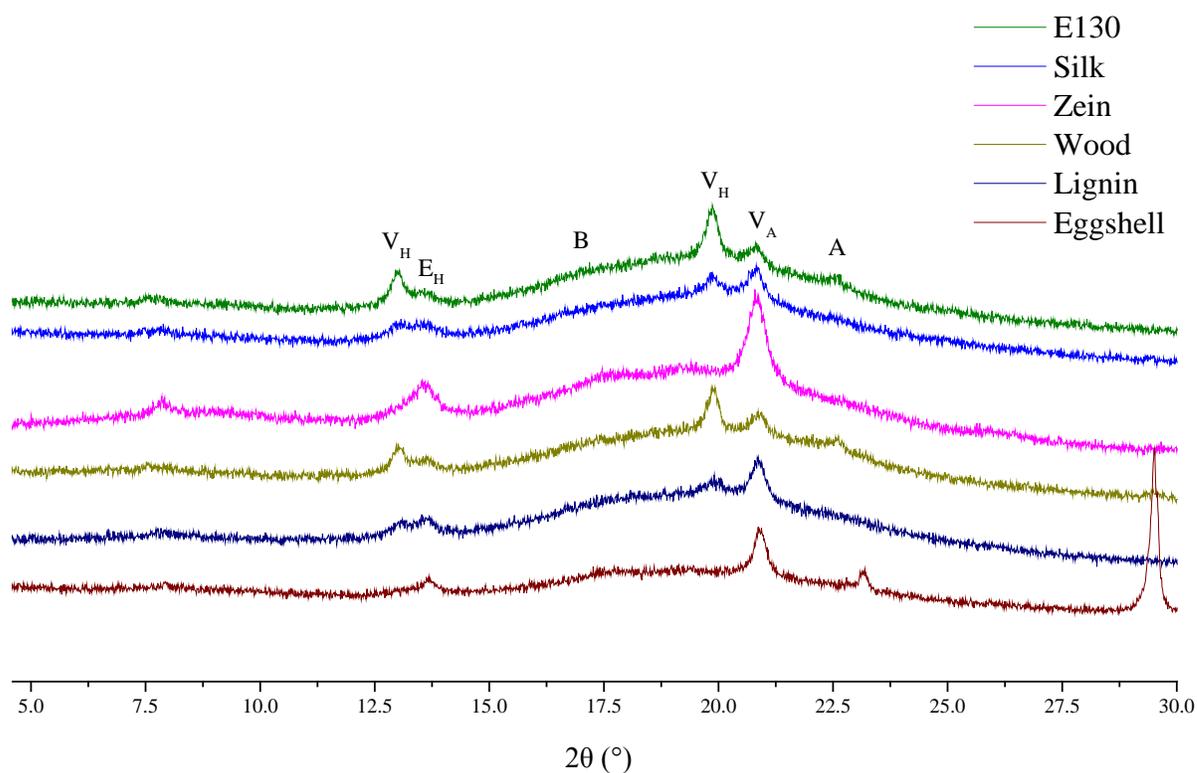


Figure 4-15: A comparison of XRD results of the powder of TPS pellets with different bio-additives extruded at 130 °C. XRD experiment was carried at room temperature

The biggest increase in the degree of crystallinity was in zein-TPS, where it has the highest signal of V_A -type structure which indicates a lower water content and non-hydrated amylose compared to the pure TPS sample. This would explain why the samples are brittle, due to the dehydration of the amylose that leads to recrystallization. Dehydration of the helical structure will remove any resilient (bouncing) properties of the material. It also had no V_H -type hydrated amylose thus proving again the low quantity of water content. According to Teixeira *et al.*⁴³ the V_H -type signal decreases with a decrease of hygroscopic nature which also explains why T_g should decrease in the presence of sugar and glycerol. This matches the result for TPS with less water content, i.e. E160, but as discussed above DMA- T_g of zein-TPS increased significantly. The high crystallinity degree, low water content and brittleness of zein-TPS could refer to strong interaction between zein and starch

granules in the presence of the plasticiser, reducing the mobility of starch and then much higher T_g compared to TPS with no zein.

A-type structures have a peak at 22.5° but this was only observed in eggshell-TPS which is probably due to the lack of chemical interaction between TPS and calcium carbonate which would be expected. However, the signal for V_A -type starch at 21° increases with eggshell filler as a result of the reduction of water: starch ratio. This could be due to the absorbance of water by eggshell. Supri and Shuhada showed that eggshell-LDPE had a good ability to absorb water due to the porous nature of the calcium carbonate. The crystallinity of calcium carbonate can be clearly seen in the XRD data in **Figure 4-16**.¹⁰

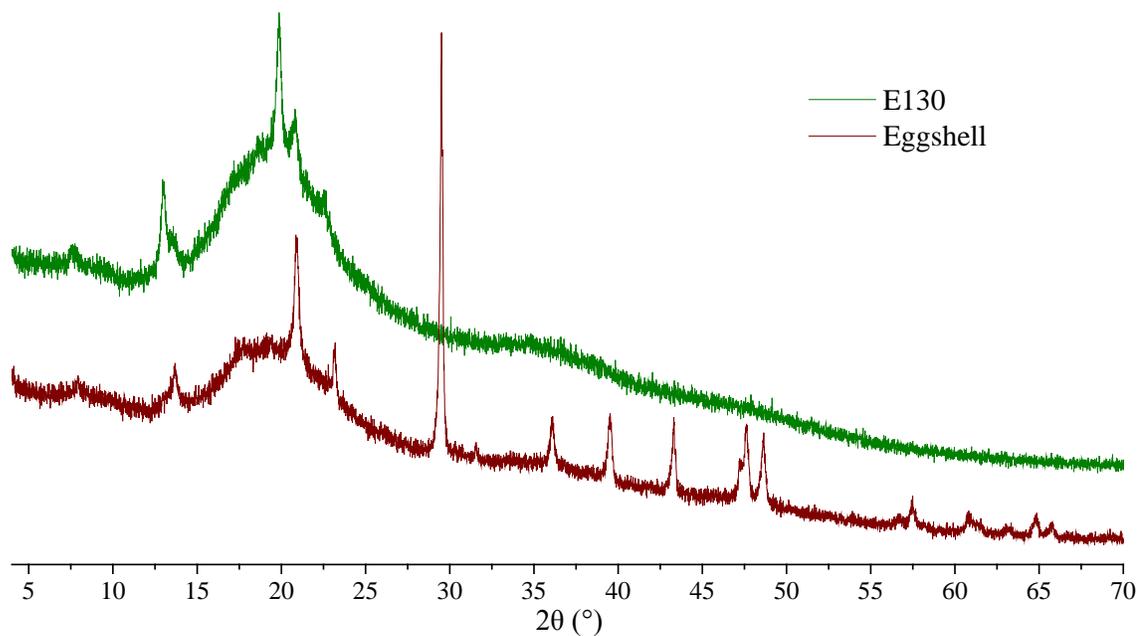


Figure 4-16: XRD results of the powder of TPS pellets with different eggshell extruded at 130°C .

The appearance of A-type starch at 22.5° is due to the formation of double helices occurring in the shorter outer chains of amylopectin and result from the shortage of water in all samples that evaporate during extrusion.^{44, 45} The absence of B type crystalline starch from all samples is particularly interesting since this type of recrystallization is known to be

responsible for the so called retrogradation of starch based plastics which results in progressive embrittlement during ageing or processing.^{31,40}

Figure 4-15 shows the XRD results from the wood flour composite and this shows that wood flour does not change the crystallinity of TPS significantly but increase the water content, and lignin and silk could link to starch and the plasticiser by hydrogen bonding. The crystallinity degree improved remarkably in TPS that contains zein, eggshell-TPS sample has some non-gelled starch granules. The results from the XRD analysis complement those shown in **Figure 4-16** and explain why the different additives change the strength and ductility of the samples.

All TPS samples can be extruded and then pressed to form homogenous thermoplastic sheets, **Figure 4-17** shows photographs of all of the samples tested above and demonstrates that some fillers change the transparency and colour of the composite.

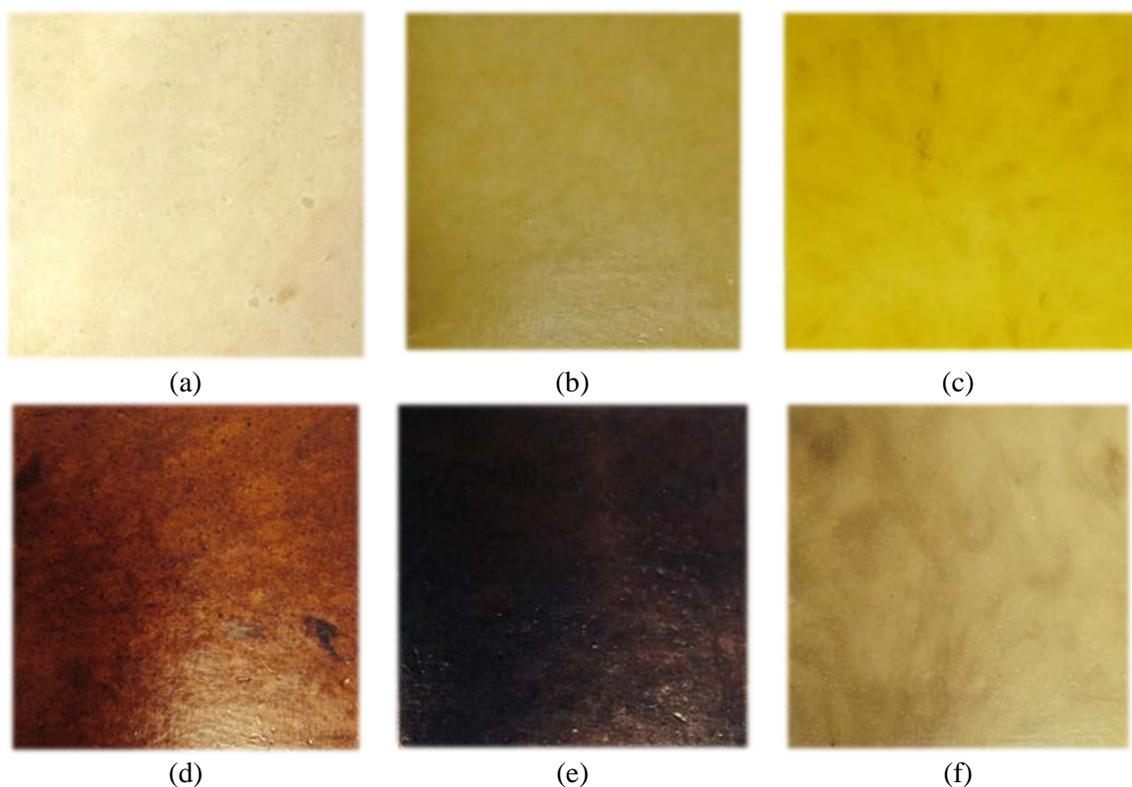


Figure 4-17: Images of TPS sheets with the dimension 91mm x 91mm x 1 mm of the blank TPS(a), and 10% of silk (b), zein (c), wood-flour (d), lignin (e) and eggshell (f).

4.3.5. Chemical changes

To investigate the chemical changes that occur in TPS after the addition of bio-filler, ATR-FTIR experiments were carried on TPS sheets. Analysing FTIR spectra can identify the interaction of hydrogen bond of starch hydroxyl groups. Plasticised starch shows three or four characteristic peaks between 1200 to 900 cm^{-1} . Native starch show a peak near 1160 cm^{-1} and a peak near 1081 cm^{-1} which were attributed to C-O bond stretching of the C-O-H group. Another broad peak appeared, or a combination of two peaks occurs at 1020 cm^{-1} which were ascribed to C-O bond stretching of C-O-C group of the anhydro-glucose ring of native starch.⁴⁵⁻⁴⁹

Modifying starch changes the frequency (wavenumber), the lower peak frequency of the C-O of C-O-C or C-O-H of starch the stronger hydrogen bond interaction.^{49, 50} After plasticisation the peak at 1160 cm^{-1} shifted to lower frequency due to the stretching of C-O in C-O-H of starch, while the hydrogen bonding occurring between the hydrogen in hydroxyl group of glycerol with starch by its oxygen in C-O-C shows two peaks ranged between 1022 and 990 cm^{-1} as shown in E130 spectra from **Figure 4-18**.^{50, 51}

Figure 4-18 illustrates a comparison of the effect of bio-additives on the hydrogen bond interaction in TPS, where the two characteristic peaks at 1156 and 1081 cm^{-1} of native starch which attributed to C-O of C-O-H shifted to lower wavenumber, 1146 and 1078 cm^{-1} respectively, when it was plasticised with glycerol/choline chloride. However, the characteristic peaks at 1020 cm^{-1} of starch was divided into two peaks 1022 and 996 cm^{-1} .⁴⁷ This analysis of FTIR spectra identifies the hydrogen bond interaction between starch and the plasticiser.

Wood-flour had no effect on the interaction when it was used as filler in TPS, while silk and zein show some shift in the peak to slightly lower wavenumber the interaction is negligible.

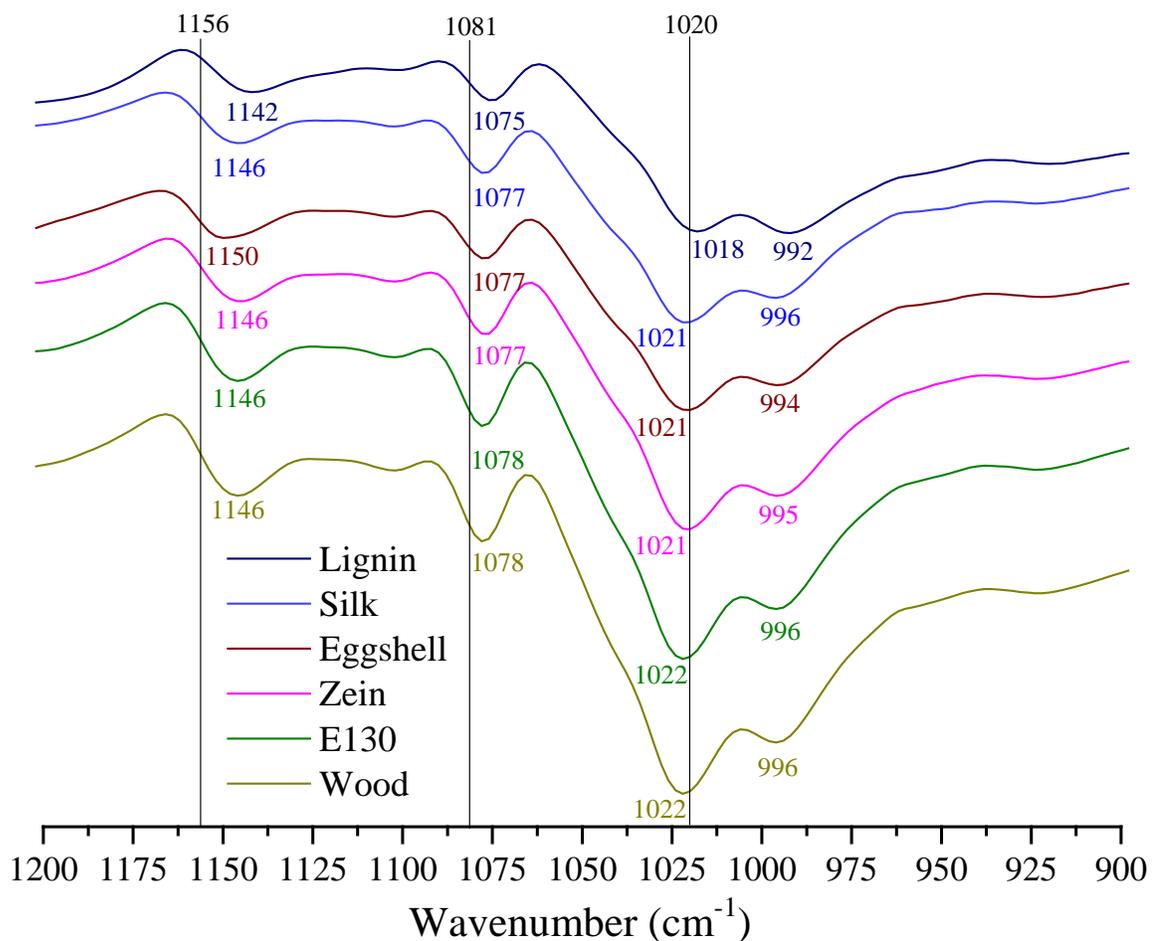


Figure 4-18: The ATR-FTIR spectra of TPS sheets with different fillers compared to the blank one.

The addition of lignin and eggshell had a more significant influence on the hydrogen bond interaction in starch, where lignin strengthened the interaction and eggshell weakened it and more importantly this is an agreement with what determined earlier from XRD results. **Figure 4-18** and **Table 4-4** demonstrate that lignin filler strengthened the interaction of C-O of C-O-H and C-O of C-O-C in starch by shifting all characteristic peaks to lower wavenumber from 1146 to 1142 cm^{-1} , 1078 to 1075 cm^{-1} and 1022 to 1018 cm^{-1} .

On the contrary, the peaks of eggshell-TPS shifted to higher wavenumber from 1146 to 1150 cm^{-1} , referring to weaker interaction of C-O of C-O-H in starch with no significant effect on C-O of C-O-C in the anhydrous ring in starch.

Table 4-4: The vibration wavenumber (cm^{-1})

	C-O of C-O-H in starch		C-O of C-O-C in starch	
Native starch ⁴⁷	1056	1081	1020	
E130	1146	1078	1022	996
Silk	1146	1176	1021	996
Zein	1146	1077	1021	995
Wood	1146	1078	1022	996
Lignin	1142	1075	1018	996
Eggshell	1150	1077	1021	996

The IR data resolution is too low which is about 4 cm^{-1} , as shown in **Figure 4-18** and **Table 4-4**, which could not be considered as results that give reliable information. However, the experiments were repeated three times giving exactly the same wavelength numbers, indicating the existence of chemical changes due to the addition of the filler even if it is negligible.

4.3.6. Morphological characterisation

SEM images of the surface of extruded TPS pellets with 10 % composite materials are shown in **Figure 4-19** for each sample. **Figure 4-19 (a)** shows that the TPS without composite particles has some residual crystalline as confirmed by XRD. The micrographs show a relatively homogeneous distribution of particles in all of the samples which would be expected from the extruded samples. The images also show good adhesion between the fillers and gelled starch, where the plasticised starch act as binding agent.

As suggested from previous analysis of DMA data that lignin-TPS has three phases due to the competition on the plasticiser between starch and lignin, where both can interact with the plasticiser, causing more non-plasticised starch or lignin.

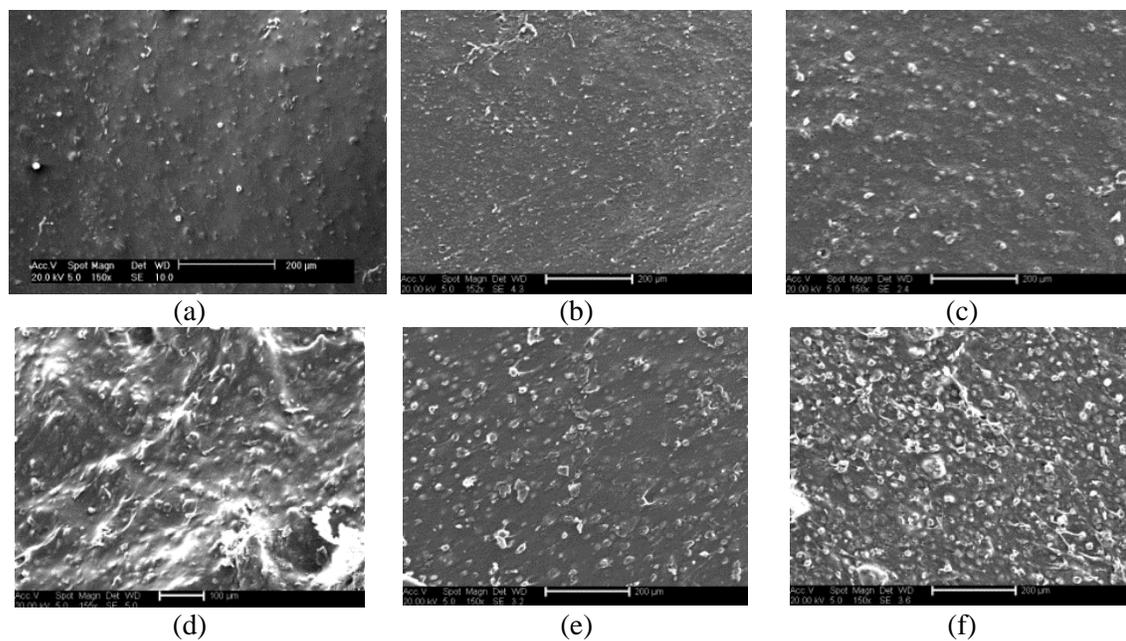


Figure 4-19: SEM images, at 150 times magnification and scale bar of 20 μm , of extruded TPS pellets without filler (a), and with 10 wt % content of silk (b), zein (c), wood (d), lignin (e) and eggshell (f).

4.3.7. Rheological properties

Understanding the rheological properties of polymers is important from a processing perspective as it affects the conditions under which they can be injection moulded or extruded. The rheological properties of thermoplastic starch have been found to depend on the glycerol and water content which influence the viscosity and melt flow index (MFI) due to the mobility of starch granules.⁵²⁻⁵⁴ Also, the fillers type, concentration and shape have an important effect on the rheological properties.⁵⁵ Melt flow rate (MFR) can indicate the suitability of a polymer to processes such as extruding, vacuum forming and injection moulding, where the higher MFR the more plastic that can flow under a given set of conditions.⁵⁶

Other many factors can affect the fluidity of TPS include free volume, flexibility crystallinity, water content, elasticity and chemical interaction, and it is obvious that bio-

fillers can considerably increase or decrease MFR of TPS. **Table 4-5** shows the MFR for TPS with the fillers described above.

Table 4-5: Melt flow rate of TPS samples, the experiment was run at 150 °C with 21.6 kg force.

	MFR (g/10 min)
E130	14.35 ± 0.17
Silk	67.48 ± 2.89
Zein	0.83 ± 0.14
Wood	58.44 ± 2.46
Lignin	17.34 ± 0.53
Eggshell	10.55 ± 0.86

Table 4-5 shows melt flow rate of TPS with and without the bio-fillers, where the MFR of blank TPS is approximately 14.35 g/10 min but the addition of silk and wood-flour increase the MFR significantly to 67.48 and 58.44 g/10 min respectively. The high flow rate of silk-TPS could be a result of its high flexibility and low degree of crystallinity, causing high mobility of starch granules. Wood-flour-TPS, as shown above in the XRD data, has some incomplete gelled starch and/or higher water content which reduce the viscosity and the stickiness to the metal wall of MFI instrument.

Although lignin-TPS has a similar crystalline structure as silk-TPS, its MFR is a little over 25% that of silk-TPS because lignin makes TPS very sticky, particularly at high temperatures. This probably results from the highly hydroxylated structure of lignin.

Eggshell-TPS has a lower MFR than pure TPS, while zein-TPS has almost no fluidity under these conditions when compared to the rest. FTIR illustrated that eggshell powder reduced the chemical interaction between starch and the plasticiser and it is suggested that eggshell absorbs some water from the mixture, and as consequence the flow rate marginally reduced to 10.55 g/ 10 min. The most noteworthy effect on MFR noticed was with zein-TPS, that has the lowest flow rate about 0.83 g/10 min, and that could be due to the high crystallinity and low flexibility of the material.

4.4. Summary

This chapter has shown that a variety of thermoplastic starch composites could be produced with several biofillers. The particle size and filler content were found to have an important effect upon the physical properties of the final product. Eggshell powder can be used as filler in TPS to improve the flexibility, while wood-fibre improve the strength of plastics with 30 wt% content.

Bio-fillers powders with 10 wt% content were found to influence the physical and chemical properties of TPS, such as decreasing the glass transition temperature. This was studied using both DSC and DMA. Additionally, the DMA data showed that all TPS samples with and without fillers have at least two phases: a starch-rich and a plasticiser-rich phase that can be identified by an upper and lower T_g respectively. It is suggested that lignin has the possibility to interact with the hydroxyl groups of the plasticiser, producing a third, lignin-rich phase with T_g at about 125 °C.

The degree of crystallinity and the hydrogen bonding interaction are also affected by the addition of bio-fillers, as the degree of crystallinity was obviously increased in zein-TPS but silk-TPS and lignin-TPS have the lowest degree of crystallinity. FTIR supported the suggestion of the stronger interaction between the mixture of lignin and starch with the plasticiser, but eggshell did the opposite by weakening the interaction.

The morphological and rheological properties of TPS samples have been studied, showing that almost all samples have smooth and flat surface but wood-TPS and eggshell-TPS are less uniform than the rest due to the weak interaction between the filler and the plasticiser. On the other hand, the viscosity and stickiness of thermoplastic starch reduced significantly which by other words increase MFI with the addition of silk and wood but zein had very low MFI.

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Chapter 5: Water effect and applications

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5. Effect of water and applications

5.1. Introduction

Owing to the hygroscopic nature of thermoplastic starch, the mechanical and physical properties can be affected by water.^{1, 2} This chapter discusses the amount of water that can be removed or absorbed from TPS; it also investigates the changes in its tensile strength and flexibility as a function of relative humidity. The variation in water content can be followed using thermogravimetric analysis (TGA) linked to a relative humidity generator to control the moisture content. The absorbance of water will also be monitored using contact angle measurements. The relative humidity (RH) in a sealed environment is controlled using oversaturated solutions of an appropriate salt solution.

Some techniques for protecting TPS products from atmospheric moisture are presented at the end of this chapter. The use of TPS as an adhesive is also investigated.

5.1.1. Relative humidity (RH) and water activity (a_w)

Water activity (a_w) is an important characteristic with food and natural products and affects physical, chemical and microbial properties. It is also responsible for some changes such as stability, texture, colour, aroma and even the flavour of starch products. Water activity is a thermodynamic description of the availability of water in a system, where the activity is defined as³:

$$a_w = \left(\frac{P_w}{P_w^\circ} \right)_T \quad \text{Equation 5-1}$$

Where P_w is the partial vapour pressure of water in the system and P_w° is the equilibrium partial vapour pressure.³

Water activity decreases with decreasing temperature, where lower temperatures at the same a_w level can keep TPS safer from microorganisms. There is also a relationship between water activity and the degree of crystallisation of the product; amorphous products

are usually more hygroscopic than crystalline ones. During storage water can plasticise starch making the material more crystalline due to releasing the adsorbed water.³ The relative humidity (%RH) is a_w expressed as a percentage.^{3,4}

$$\%RH = 100 \left(\frac{P_w}{P_w^\circ} \right)_T \quad \text{Equation 5-2}$$

5.1.2. Contact angle

Wettability and hydrophobicity play very important role in many natural products that could change the physical and chemical properties of a substance. The contact angle is a simple technique that gives a measure of the hydrophobicity of a solid surface by examining its wettability.^{5,6} There are some experimental challenges measuring the contact angle due to the size of the droplet and the nature of solid surface which sometimes hinders the three-dimensional analysis if the surface is very rough or heterogeneous. Surface roughness can affect the contact angle and it is a technique used by nature to achieve superhydrophobic surfaces e.g. on water lillies.^{6,7} In the case of thermoplastic starch these challenges can be easily avoided by using small droplets with a digital camera as will be explained later. In this study smooth, homogeneous sheets of TPS are used to determine accurate contact angles.

Figure 5-1 shows a schematic diagram of how the contact angle of water was determined on a TPS surface. The sample has to be flat and positioned horizontally on a holder that ensures that the only factors which affect the shape of the water drop are interfacial tension and gravity. Above the sample there is a syringe that has pure water in it. The sample should be between a light and the camera but in the same angle, allowing a flat baseline to be determined for the contact angle measurement. After dropping one water droplet and taking an image by the camera which is connected to a computer which saves the image and then calculates the contact angle.

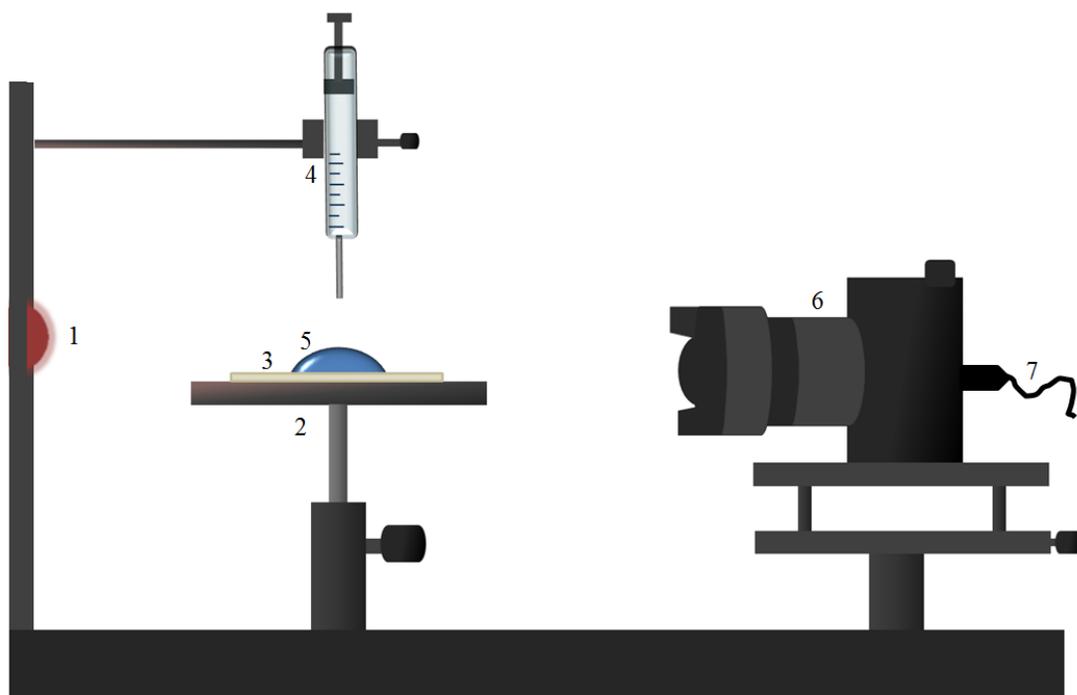


Figure 5-1: Instrumental setup to measure the contact angle of water on a surface. Light source behind the sample and droplet (1), Flat solid substrate to carry the TPS sheets sample (2), TPS sheet (3), microliter syringe of water (4), water drop (5), digital camera (6) and data transfer wire (7).

The shape of the droplet indicates the wettability of the TPS surface as shown in **Figure 5-2 (a)**.⁸ The contact angle range will vary from 0° to 180° depending on the solid material wettability, the more hygroscopic the material the smaller the contact angle. Thus, the contact angle of a very hydrophobic material will be close to 180° with an almost spherical drop on the surface, while the very hydrophilic substrate will give a contact angle of nearly 0° with the drop spreading almost flat on the surface. This is shown schematically in **Figure 5-2 (b)**.

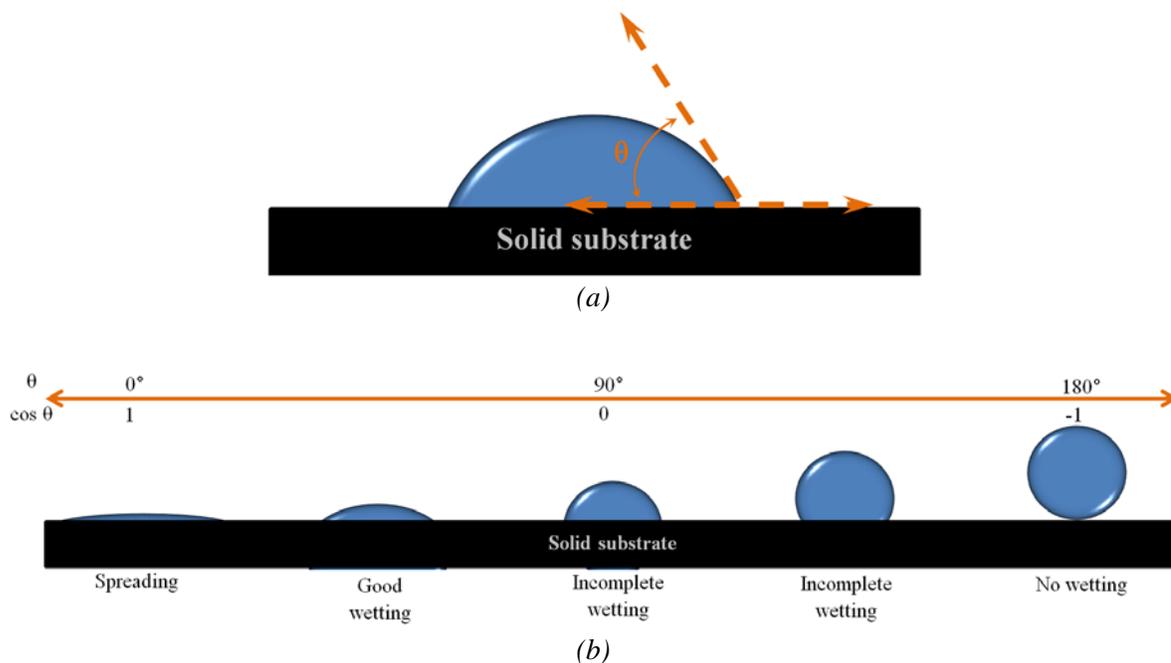


Figure 5-2: The contact angle of liquids on a solid substrate, (a) and the change in droplet shape with surface wettability.

In general, the partial wetting of a substrate gives a contact angle between 0° to 90° , but when the contact angle is more than 90° that means the droplet does not wet the surface completely.^{8,9}

5.2. Water content

Thermogravimetric analysis was carried out on a series of samples made with different DESs under different extrusion conditions. The samples were sealed under nitrogen directly after processing. The water content was determined by heating TPS samples at 100°C until constant mass was achieved (typically 20 minutes). The TGA results are shown in **Figure 5-3** and the water contents are shown in **Table 5-1**. Samples of E100, E130, E160 and G130 were produced with the same ratio of starch to plasticiser and the same conditions except the extruding temperature. Samples E100, E130 and E160 used glycerol/choline chloride as the plasticiser extruded at 100, 130 and 160°C respectively. Sample G130 was plasticised with just glycerol at 130°C . **Table 5-1** shows that the higher

the extruder temperature the less water that is found in the extruded product which is what would be expected as more water can be lost during extrusions through the steam vents. However, G130 contain nearly half the amount of water that E130 has, signifying that choline chloride enables the TPS to hold on to more moisture during extrusion, by preventing it from evaporating.

Chapter 4 discussed the effect of adding 10% by weight of composite materials from biological sources. These will also have hydrophilic and hydrophobic properties and in this chapter the effect of the additives on the water content of the composites will be determined. In all cases the composite materials had the same particle size (200 μm) and they were all extruded at 130 $^{\circ}\text{C}$ using Glyceline as a plasticiser. The results in **Table 5-1** show the percentages of water removed from TPS with bio-based composites.

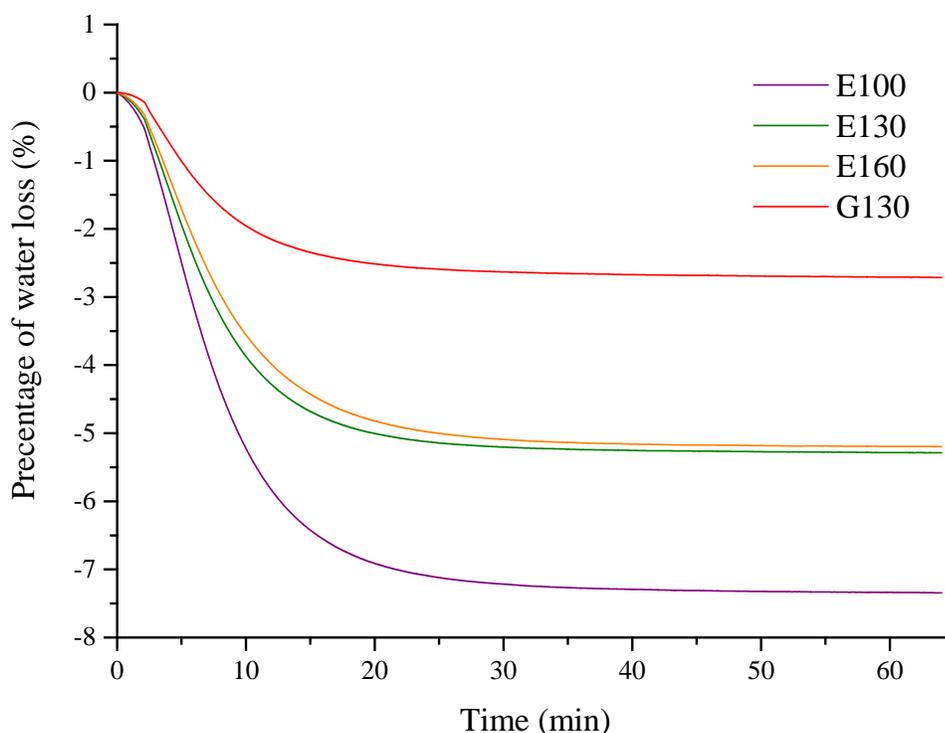


Figure 5-3 : Percentages of water loss of extruded TPS pellets that were ground, sieved to 200 μm particle size and then they were placed in TGA and held at 100 $^{\circ}\text{C}$ for 90 min.

Table 5-1 shows that replacing ten percent of starch flour with zein protein improves the hydrophobicity of TPS (zein-TPS 1.34 wt% water *c.f.* E130 with 5.30 wt%).¹⁰ Lignin also decreases the water content slightly to 3.65 wt% water. To some extent this is not surprising as this is partially the role that these additives play within plants. In contrast, using wood-flour as an additive in TPS slightly increases the hygroscopic nature of TPS, with approximately 5.96% water. Addition of silk or eggshell does not significantly change the water content, with 5.18% and 4.94% water respectively.

Table 5-1: TGA results showing the water content in fresh thermoplastic starch. Samples were held at 100 °C for about 90 min.

	water removal (%)
E100	7.46 ± 0.15
E130	5.30 ± 0.02
E160	5.25 ± 0.04
G130	2.67 ± 0.18
Silk	5.18 ± 0.03
Zein	1.34 ± 0.07
Lignin	3.65 ± 0.13
Wood	5.96 ± 0.31
Eggshell	4.94 ± 0.03

5.3. Water absorption isotherm

The biodegradability of TPS is due in part to its hygroscopic nature. The absorbance of water from the surrounding air makes a good environment for enzymes to digest TPS.¹¹ TPS has been mixed with synthetic polymers to reduce the hygroscopic nature of the starch at the cost of the biodegradability. In the current study a variety of bio-based additives have been incorporated into TPS to improve the hydrophobicity.¹² The water absorbance of these materials was investigated using TGA, but with a relative humidity of 50% at 50 °C, to understand how much each TPS sample can absorb water in these conditions.

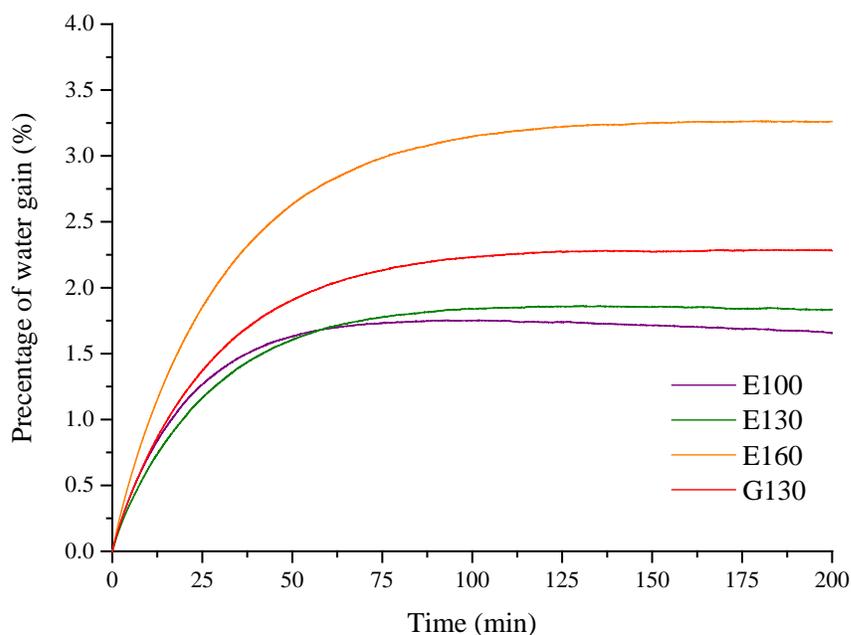


Figure 5-4: Percentages of water gain of the fresh thermoplastic starch. Extruded TPS pellets were ground, sieved to 200 μm particle size and dried at 50°C for 3 hours. TGA experiments were held at 50 °C with 50% RH for 180 min.

Figure 5-4 and **Table 5-2** show the water uptake for the same samples that examined and shown in **Table 5-1**. Since E100, E130, E160 have essentially the same composition once dried it would be expected that they should have similar water uptakes when exposed to the same relative humidity for the same length of time. It may also be expected that the water levels should reach those listed in **Table 5-1** but they did not. TGA results show that the TPS samples all reach an equilibrium mass in less than 2 hours.

Bio-based additives in TPS do show small differences in their ability to absorb water.¹³ **Table 5-2** shows zein-TPS is the least hygroscopic while lignin-TPS is most which is a similar result to **Table 5-1**. In comparison, Gáspár et al.¹⁴ studied the water uptake of TPS made from starch and glycerol with and without the addition of zein as an additive and found that zein reduces the water uptake significantly.

Table 5-2: TGA results showing the water uptake in fresh thermoplastic starch dried at 50°C for 3 hours and then examined held at 50 °C with 50 % RH for 180 min.

	water uptake (%)
E100	1.79 ± 0.29
E130	1.89 ± 0.07
E160	3.16 ± 0.19
G130	2.29 ± 0.05
Silk	3.13 ± 0.10
Zein	1.77 ± 0.07
Lignin	4.12 ± 0.71
Wood	3.40 ± 0.04
Eggshell	2.19 ± 0.32

It is shown that the blank TPS samples that were extruded at higher temperature had less water initially, but they were able to absorb more water as shown in **Table 5-2**. E160 gains water approximately 3.16 wt% which is more than what E130 and E100 absorb, 1.89 wt% and 1.79 wt% respectively. This is because starch has different types of water bound; some stronger.

To study the relationship between water bond and temperature, a TGA experiment was carried on to determine the water loss as a function of temperature. **Figure 5-5** shows that blank samples of TPS, extruded at different temperatures, had different amount of water loss. TPS samples that were extruded at higher temperatures lost less water at the temperature range between 50 to 150 °C, while all samples started to oxidise above 160 °C. E160 sample lost about 2.72 wt% while E100 lost about the double of that, proving that higher temperature during extrusion produces TPS contain less water. This proves that TPS has a variation of weak and strong hydrogen bond interactions between starch chains and water molecules, where the weaker bonds leave at lower temperature during processing and vice versa.

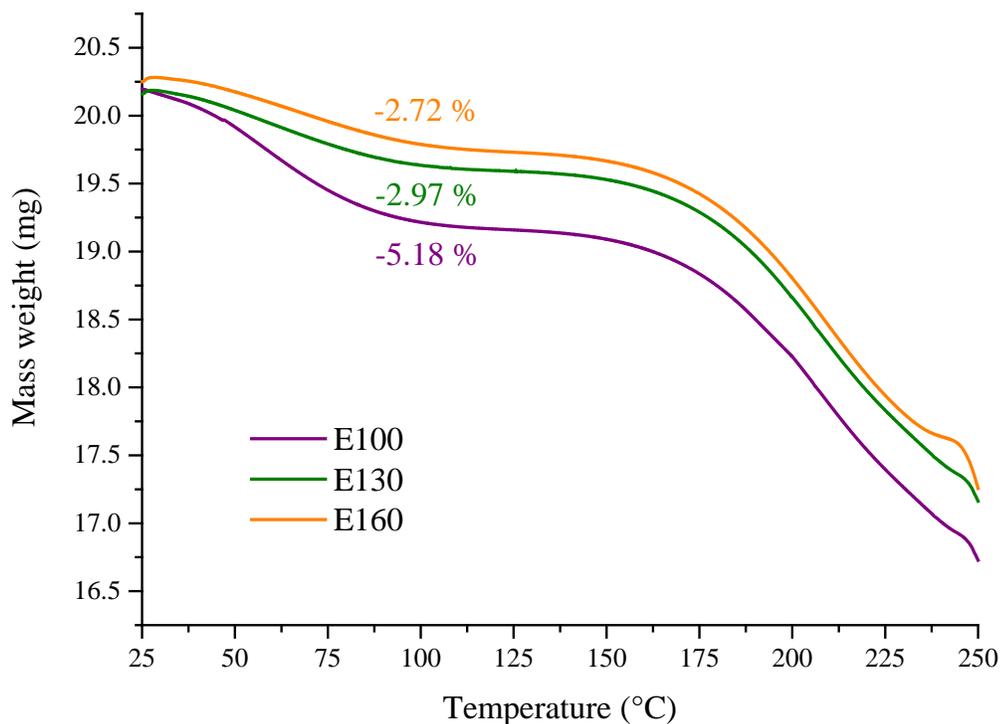


Figure 5-5: TGA curves for fresh thermoplastic starch experiment in function of temperature.

The absorbance of water into TPS is clearly dependent upon the relative humidity of the environment. The effect of RH on TPS has been investigated, where about half gram of powdered TPS, 200 μm particle size, was placed in a sealed desiccator that contained oversaturated solution which controlled the RH. The appropriate salt was chosen as the desire RH, where each solution of a certain oversaturated salt has distinct water activity that control % RH. After the addition of the oversaturated solution the desiccator was sealed for a set period of time. The experimental set up is shown schematically in **Figure 5-6**.

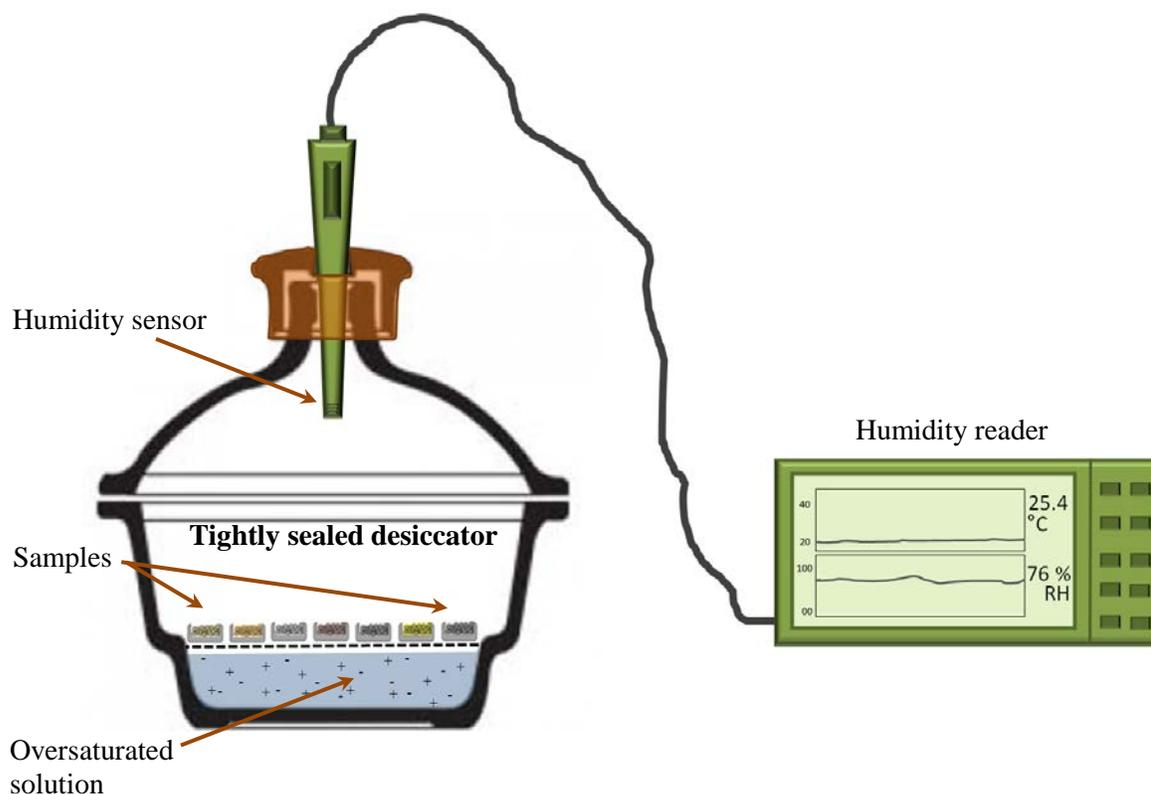


Figure 5-6: Water absorption isotherm experiment diagram.

Humidity reader was connected to a very sealed desiccator that contains the oversaturated salt solution, and TPS samples in small plates. The desiccator was held inside an oven to control the temperature which was constant at 25 °C for 3 weeks for every RH environment.

Table 5-3 illustrates the appropriate salt for each RH, as the relative humidity inside the sealed desiccator depends on the salt source which is in the oversaturated solution. Increasing the relative humidity causes a significant increase in the amount of absorbed water by all TPS samples, as shown in **Figure 5-6**. Bendaoud and Chalamet have reported that there is a relationship between water absorption and plasticiser content in TPS, where at low constant RH the plasticiser ratio increases while the water absorption decreases.¹⁵

Table 5-3: relative humidity of oversaturated salt solutions at 25 °C.

Salt	% RH
LiCl	12
MgCl ₂	35
NaBr	58
NaCl	76
BaCl ₂	98

Figure 5-7 and **Table 5-4** illustrate the effect the relative humidity on the water absorbance in TPS. Small differences are observed for each additive although the results are extensively similar. It is interesting to note that the absorbance of water does not become significant until RH exceeds 50%. Thereafter water absorbance is significant as might be expected. Only zein protein shows any noticeable change in the absorbance of water at high relative humidity.

The Eggshell-TPS is the most hydrophobic sample at $\approx 10\%$ RH, but it became one of the most hygroscopic when the RH increases to $\approx 70\%$.

Table 5-4: Water uptake percentages by weight of TPS samples. All experiments were carried out at 25 °C.

% RH	Water uptake percentage by weight (%)				
	12 %	35 %	58 %	75 %	98 %
E100	0.02	2.27	3.64	11.82	47.96
E130	0.02	3.11	6.22	14.26	51.04
E160	0.03	2.77	5.69	14.24	46.93
G130	0.02	2.65	4.21	12.83	45.78
Silk	0.02	1.96	4.98	12.61	51.91
Zein	0.35	1.59	4.21	9.78	31.89
Lignin	0.75	2.30	5.34	14.21	46.73
Wood	0.02	2.67	6.09	14.04	45.06
Eggshell	0.01	2.58	6.33	14.77	49.66

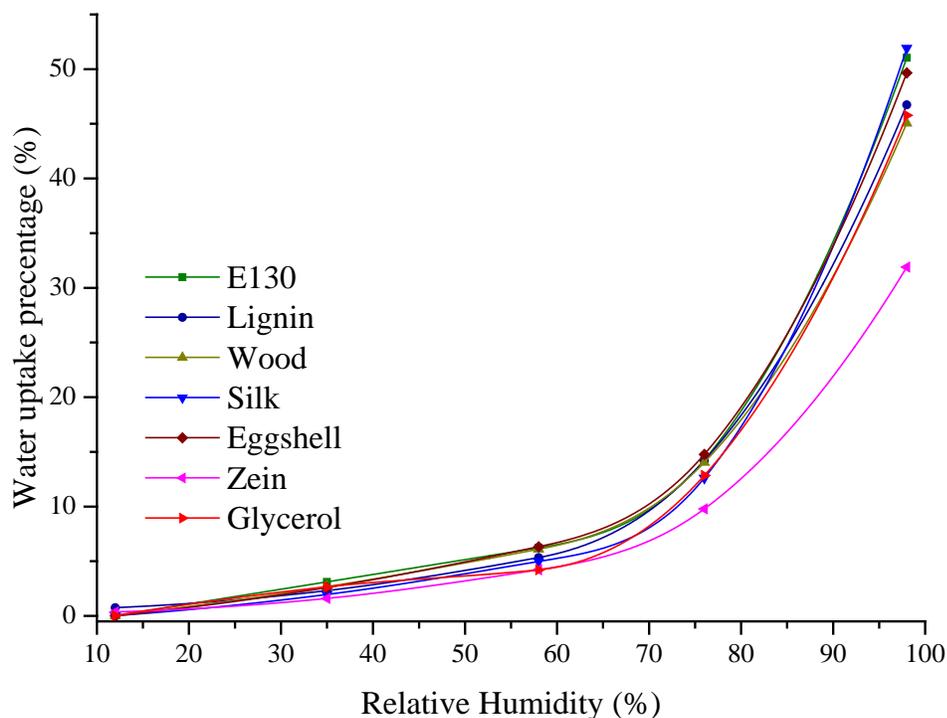


Figure 5-7: Water uptake percentages by weight of TPS samples. All experiments were done at 25 °C, the relative humidity percentages were achieved by using oversaturated salts in a sealed environment.

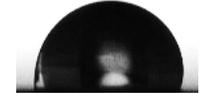
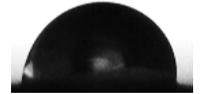
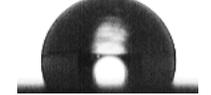
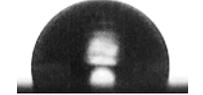
5.4. Contact angle

The contact angle was measured as a function of time to investigate the wettability of TPS samples and to determine whether particulates at the air interface could form a hydrophobic barrier.¹⁶ In this experiment eleven images were taken in function of time, one immediately after adding the droplet and one every minute for the next ten minutes. **Table 5-5** shows the contact angles and their images as a function of time.

The initial contact angle decreases in the order $G130 = E100 > E130 > E160$. It would be expected that the most hydrophobic surface would have the largest contact angle so it is not surprising that G130 has a large value but the rest of the data are not in agreement the results in **Table 5-2**. The most probable reason for these differences is the structure of the TPS. As shown in **Chapter 3** the extrusion temperature significantly changes the structure

of the starch with E160 demonstrating a totally amorphous structure (**Figure 3-18**) whereas E100 retains some globular, crystalline starch structures which will affect surface wetting.

Table 5-5: Contact angle images and data in function of time of TPS samples with and without the bio-additives. One image of water drop on TPS sheet was taken every minute.

	Contact angle (°)		
	1 second	1 minutes	10 minutes
E100	 81.6 ± 2.2	 69.5 ± 1.6	 25.0 ± 2.5
E130	 73.0 ± 3.0	 56.8 ± 3.6	 18.4 ± 2.4
E160	 65.41 ± 1.19	 56.48 ± 1.58	 17.66 ± 2.582
G130	 80.288 ± 5.69	 64.85 ± 8.09	 23.87 ± 3.26
Silk	 65.07 ± 1.33	 52.45 ± 0.73	 18.23 ± 1.68
Zein	 101.54 ± 6.04	 92.91 ± 6.43	 61.64 ± 7.59
Lignin	 75.64 ± 1.45	 63.74 ± 0.59	 25.58 ± 1.17
Wood	 74.62 ± 0.47	 57.12 ± 0.42	 22.69 ± 0.91
Eggshell	 106.67 ± 4.01	 101.19 ± 4.22	 75.25 ± 5.52

It is well known that surface micro- and nano-structures can affect the wettability of surfaces and this is a method employed by many plants and animals to obtain super-hydrophobicity.

When a liquid is in intimate contact with a surface which is microstructured it becomes what is known as a Wenzel state which is shown in **Figure 5-8**.

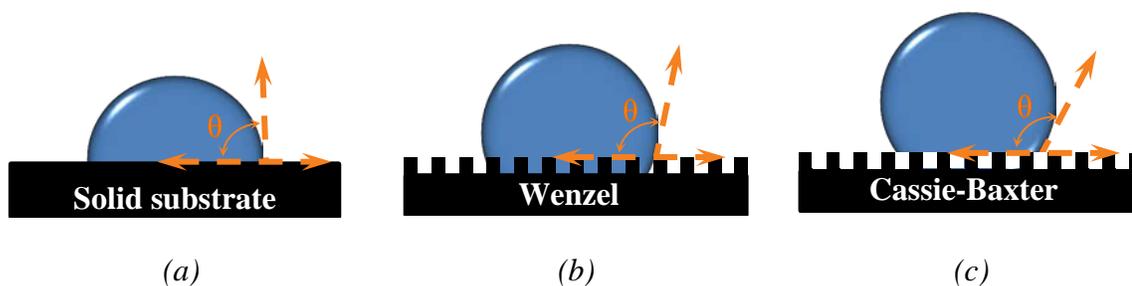


Figure 5-8: The effect micro-structured surface on the contact angle, soft solid substrate (a), Wenzel effect (b) and Cassie-Baxter effect (c).

The contact angle in the Wenzel state θ_w^* can be related to the contact angle on the non-structured surface, θ by;

$$\cos \theta_w^* = r \cos \theta \quad \text{Equation 5-3}$$

where r is the ratio of the actual area to the projected area.¹⁷ The microstructuring tends to amplify the properties of the surface such that microstructuring a hydrophobic surface will make it more hydrophobic whereas doing the same to a hydrophilic surface will have the opposite effect. Surfaces with a contact angle greater than 90° tend to be classified as hydrophobic whereas those with a contact angle less than 90° are hydrophilic. The data presented in **Table 5-5** suggest that TPS is initially slightly hydrophilic but the porous nature of the material makes it easy to soak water into it making it more hydrophilic which is why the contact angle decreases with time.

The only exceptions to this are the samples containing zein protein and eggshell which appear to show Wenzel state behaviour.

Figure 5-8 also shows the Cassie and Baxter state where the liquid is suspended on the tops of microstructures, but no evidence of this behaviour was observed in any of the materials. This could be due to the relatively low concentration of the composite particles (10 wt%). Better surface wetting could be obtained by having a smaller particle size and a higher particulate loading.

Figure 5-9 shows the percentages of reduction in the contact angles after ten minutes, showing the retention of the hydrophobic nature. This again shows the potential for eggshell as a potential hydrophobic coating.

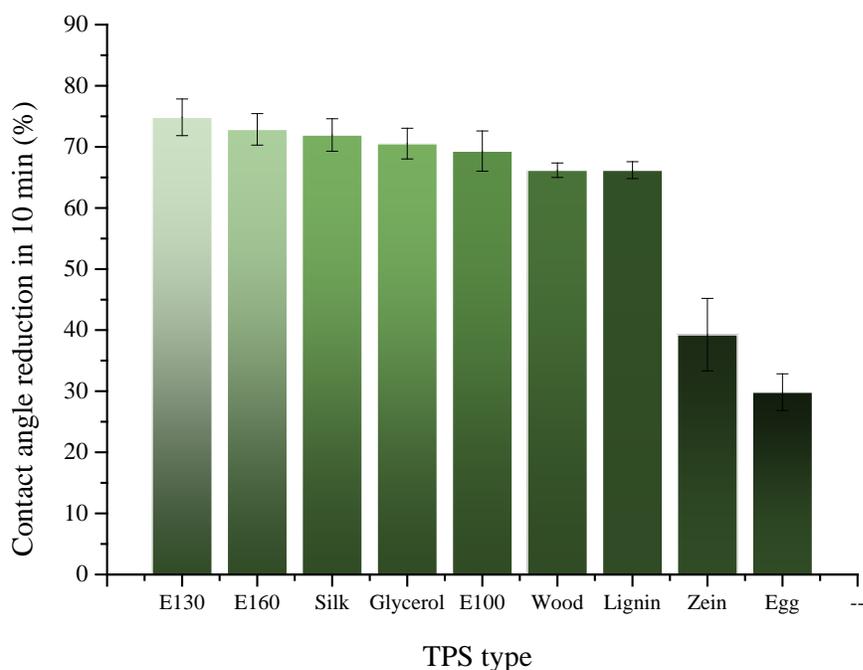


Figure 5-9: percentages of contact angle change in 10 minutes, showing the wettability of each TPS sample and the effect bio-additives in the hygroscopic nature.

5.5. The effect of long-term storage on TPS properties

Even under relatively low humidity levels the absorbance of water can affect the properties of TPS such as tensile strength and strain and glass transition temperature.^{18, 19} Chung and Lim found that when TPS was stored at temperatures lower than its glass transition

temperature for long time, it will reach the thermodynamic equilibrium and as a consequence T_g will decrease.^{20, 21}

Samples of E100 and E160 sheets were stored in sealed bags in the laboratory for about 14 months and their properties were examined using a tensiometer to determine the tensile strength and flexibility which was compared to the fresh samples. **Table 5-6** shows how aging TPS influenced the tensile stress and elongation of the samples, implying the relationship between water content and mechanical properties that scientifically discussed above. Water content in TPS samples would increase when they left in normal environment due to absorbing water from the surrounding air moisture. The storage effect has been studied on TPS sheets that had stored for 90 days at room temperature and about 64% RH, showing that storing TPS decreases the tensile strength with an increase in its tensile strain.¹⁸

It has recently been shown that one of the main advantages of using salts to modify starch is that the material does not significantly recrystallize over time.²² To ensure this is the case with the glycerol/choline chloride samples tests were carried out on freshly extruded pellets and the same pellet batch after storing in sealed bags for 14 months. **Table 5-6** shows the tensile strength of two batches extruded at different temperatures (100 and 160 °C) but all pressed at 140 °C just prior to stress testing. It is evident that the material extruded at 100 °C has not significantly changed its mechanical properties even after a significant length of time in storage. The material extruded at 160 °C is initially brittle but strong but upon storage it loses its strength but it becomes less brittle and it is still stronger than E100. This suggests that the crystalline regions slowly become amorphous with time i.e. the plasticiser is mobile within the material.²²

Table 5-6: Effect of storage for 14 months (bagged in open laboratory) on the tensile strength and elongation at failure for two starch/glycerol/ChCl mixtures extruded at two temperatures. All samples were pressed from pellets at 140 °C prior to measurement.

	Tensile stress (MPa)	Elongation (%)	Water content (wt%)
Extruded at 100 °C			
Fresh	4.1 ± 0.04	65.1 ± 3.2	7.46 ± 0.15
Stored	3.9 ± 0.22	61.9 ± 2.4	10.55 ± 0.44
Extruded at 160 °C			
Fresh	22.2 ± 0.7	3.2 ± 0.1	5.25 ± 0.04
Stored	9.5 ± 0.6	7.4 ± 1.2	7.24 ± 0.23

5.6. Applications

Thermoplastic starch is a renewable, biodegradable and inexpensive raw material which is limited in its application by its strength and water susceptibility. To enable its wider use it need to be able to be stuck to other (generally more hydrophobic materials) or be coated with a naturally degradable material which is more hydrophobic. In nature this is achieved using lignin and starch with water and other salts. Hydrophobic coatings are generally in the form of waxes which are complex mixtures of organic compounds including containing alkyl esters, alkanes, fatty acids, primary and secondary alcohols, diols, ketones, aldehydes. Plant based waxes are already used for furniture polishes and floor wax for exactly this application.²³

5.6.1. Carbohydrate-based adhesives

Various adhesives are starch-based particularly those which have domestic use such as wallpaper adhesives, envelope glues and packaging adhesives. They are used extensively for paper and cardboard manufacture. They are generally supplied as aqueous colloidal dispersions and they cure slowly by loss of water (effectively drying). This produces a bond which is a thermoset so it does not weaken with changes in temperature. They show good adhesion to cellulose and resist fats and oils. The main sources of starch for adhesives are corn, wheat, potato, rice, tapioca, and sago. They form gels when heated in water in the range 50 to 80 °C depending on the plant source as they have different amounts of amylose

and amylopectin. Typically the starch content is less than 7 wt% as thick rubbery solids form when the starch content exceeds this value.²⁴

While lignin based adhesives have been used previously they are by no means common.²⁵ The idea to use lignin as an adhesive came from the unexpected observation that it dissolves effectively in glycerol/choline chloride DESs at 50 °C producing very viscous rubber-like materials when hot and a sticky material at room temperature. Several studies can be found in the literature about dissolving lignin with ionic liquids in different conditions, some use catalyst to depolymerise lignin, and some require temperatures higher than 160 °C.²⁶⁻²⁸ Pinkert *et al.*²⁹ used ionic liquids to dissolve lignin and then extract it, where the anion of the IL play is the most significant part in the dissolution as suggested by Pu *et al.*³⁰ who also used IL to dissolve lignin.

Lignin is a heterogeneous and amorphous biopolymer; it is non-toxic, biodegradable and renewable and is the second most abundant natural polymer. Lignin consists of two main components: aromatic and carbon chains, its structure has numerous hydroxyl groups that can interact with water and glycerol/choline chloride.³¹ Lignin's chemical structure is not a common homopolymer but it has three main structures, with different ratios depending upon lignin source, which are 4-hydroxyphenyl, guaiacyl and syringyl as shown in **Figure 5-10**.³² Lignin is more hydrophobic than starch, but due to the plentiful hydroxyl groups in lignin chains lignin can interact with water or glycerol/choline chloride by hydrogen bonding.³¹

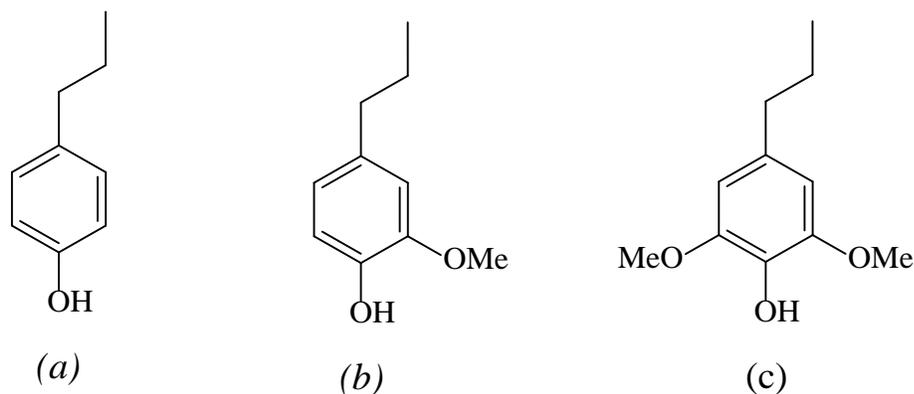


Figure 5-10: Main structures of lignin. 4-hydroxyphenyl (a), guaiacyl (b) and syringyl (c).³¹

To test the strength of the adhesives two pieces of “dog-bone” starch were glued together and the stress required to break the samples was measured with a tensiometer. The experimental set up is shown schematically in **Figure 5-11**. Clearly the samples can fail by two modes, the starch sample can break in which case the adhesive is stronger than the TPS or the two dog-bone sections can separate in which case the adhesive is the weaker element. For each experiment the adhesive was applied to the two halves of the test sample (both made out of E130) and the sandwich was left for 1-3 hours to cure without the application of temperature or pressure.

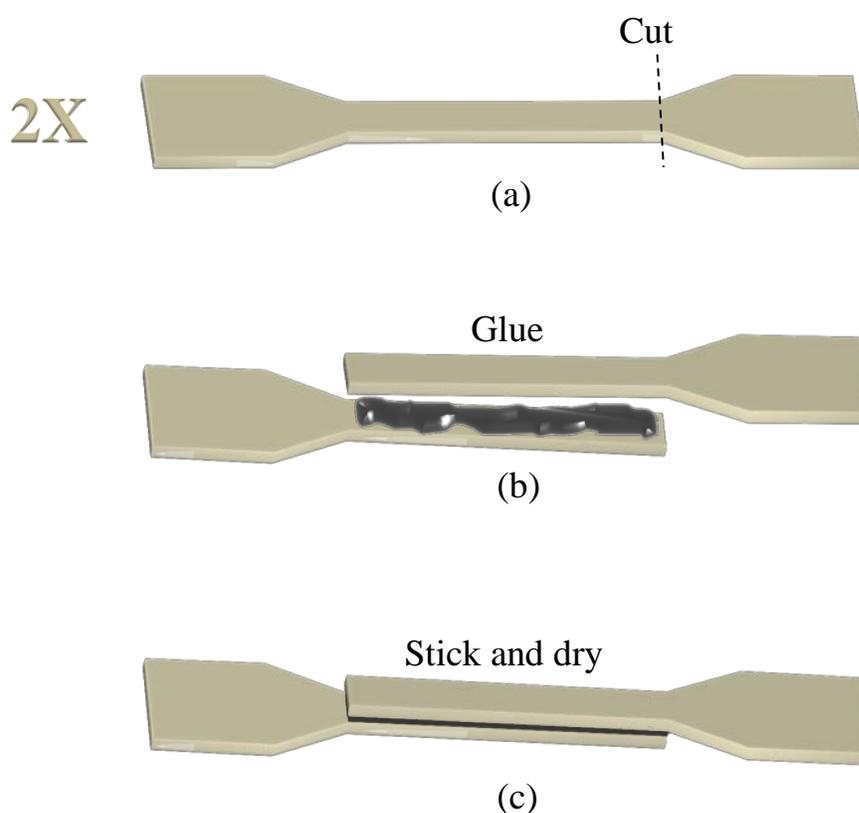


Figure 5-11: Two TPS specimens were cut for each bio-adhesive test (a), the adhesive replaced between the two specimen (b) and then they left to dry before the tensometer test (c).

Initially blank experiments were run with common commercial adhesives. Polyethylene oxide (PEO) was dissolved in a small amount of dichloromethane (DCM) till it became a viscous fluid. **Table 5-7** illustrates the use of dissolved PEO, polyurethane (Impact glue),

butanone spray (SA-90) and cyanoacrylates (super glue) as standard adhesives to be compared with the carbohydrates-based adhesives of the project. It is observed that dissolved PEO had strength about 1.34 MPa, while the other three commercial adhesives were stronger than 3 MPa.

Table 5-7: Tensile strength and elongation results of some common commercial glue.

Adhesive	Chemicals	Tensile strength (MPa)	Elongation (%)	Failing element
Dissolved PEO		1.34 ± 0.12	14.70 ± 2.04	adhesive
Impact glue	Polyurethanes	3.62 ± 0.14	16.93 ± 1.04	adhesive
SA-90	Butanone-spray	3.08 ± 0.59	8.27 ± 2.15	TPS
Super glue	Cyanoacrylates	3.83 ± 0.31	8.50 ± 3.24	TPS

The mixture of starch and Glyceline 200 was examined as a carbohydrate-adhesive with different ratios of 2:1, 1:1 and 1:2. It is found that 1:1 was more viscous than the others and it sticks the TPS dog bones but not strongly enough to be tested in the tensiometer. That could be due to the excess of water content in the mixture and lack of starch plasticisation without water or pressure to bring about gelation. Putting the sample in an oven at 50 °C for 24 hours to get the sample to gel increased the strength to approximately 0.91 MPa, as shown in **Table 5-8**.

Table 5-8: The effect of starch/Glyceline ratios on strength and elongation as adhesives.

**left in oven at 50 °C for 24 hours.*

Composition	Ratio	Tensile strength (MPa)	Elongation (%)
Starch: Glyceline	2:1	Failed to stick	TPS
Starch: Glyceline	1:2	Failed to stick	TPS
Starch: Glyceline	1:1	Sticks but very weakly	
Starch: Glyceline*	1:1	0.91 ± 0.0065	0.53 ± 0.12

It is observed experimentally that lignin can be dissolved in Glyceline 200, and that the presence of heat during mixing lignin with Glyceline accelerates dissolution. Dissolving lignin, **Figure 5-12**, leads to a complex hydrogen bonded structure shown previously by FTIR in **Chapter 4**.

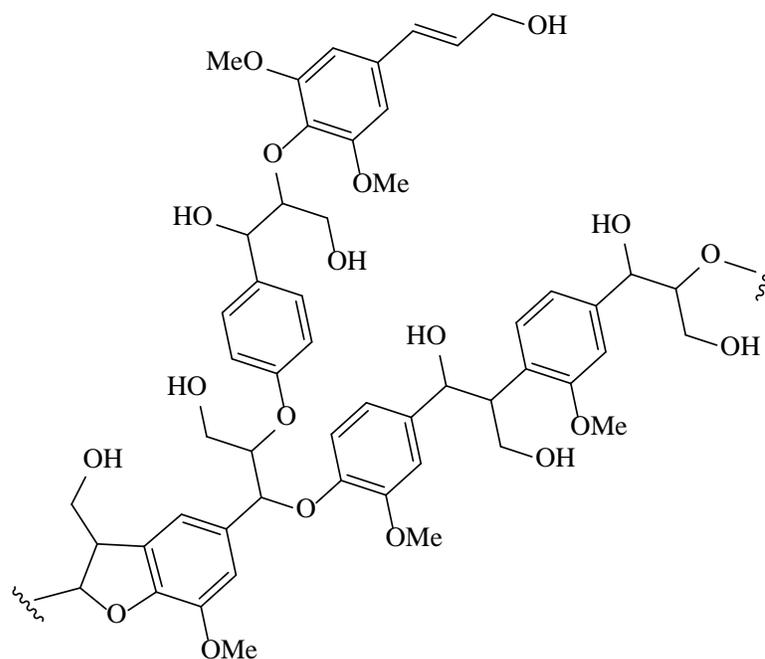


Figure 5-12: Typical structure of lignin.²⁷

Lignin was dissolved in Glyceline 200, the following weight ratios; 1:1, 1:1.5, 1:2 and 1:3 and all mixtures were heated in oven at 50 °C for 12 hours. The adhesive strengths of the different mixtures are shown in **Table 5-9** and it can be seen that the optimum adhesive was obtained at 1:1.5 lignin to Glyceline 200 with a tensile strength about 0.38 MPa.

Table 5-9: Lignin adhesives

The effect lignin/Glyceline ratio and addition of starch on tensile strength and elongation of the adhesive.

Composition	Ratio	Tensile strength (MPa)		Elongation (%)	
Lignin: Glyceline	1:1	Failed to stick TPS			
Lignin: Glyceline	1:1.5	0.38	± 0.013	4.47	± 0.58
Lignin: Glyceline	1:2	0.24	± 0.010	16.80	± 0.15
Lignin: Glyceline	1:3	0.13	± 0.007	8.65	± 0.39

The mixture of lignin/glyceline became more homogeneous, sticky and elastic when kept in the oven at 50 °C for longer times as shown in **Figure 5-13**. To study the effect of heating mixture time on the adhesive strength, the mixture of lignin-adhesive have been examined in function of heating time, **Table 5-10**, showing that the longer heating of the mixture the stronger lignin adhesive will be obtained.

Table 5-10: Lignin adhesives

The effect of heating time at 50 °C in oven on tensile strength and elongation of the lignin/Glyceline adhesives.

Composition	Ratio	Left in oven (hours)	Tensile strength (MPa)		Elongation (%)	
Lignin: Glyceline	1:1.5	0	Failed			
Lignin: Glyceline	1:1.5	6	0.12	± 0.0097	1.52	± 0.19
Lignin: Glyceline	1:1.5	12	0.38	± 0.013	4.47	± 0.58
Lignin: Glyceline	1:1.5	24	0.47	± 0.017	5.85	± 0.61
Lignin: Glyceline	1:1.5	48	0.53	± 0.021	6.96	± 0.68

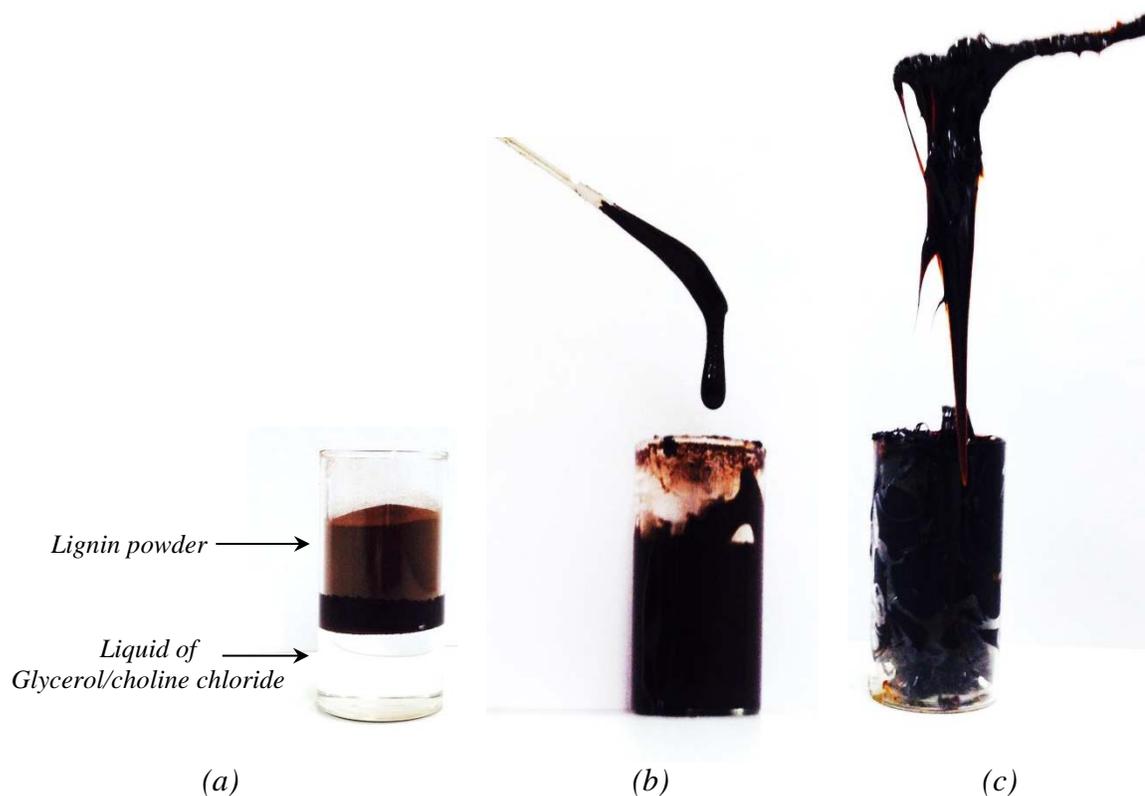


Figure 5-13 : Mixing lignin with Glyceline in the ratio of 1:2 by weight (a), before mixing (b) after stirring (c) after being kept in an oven at 50 °C for 6 hours.

The addition of starch to the lignin-adhesive could gel the mixture quicker and improving the stickiness as a consequence. Many different ratios of the three compositions of lignin/Glyceline/starch mixtures were tested, and it is found that adding starch to lignin/Glyceline adhesive can strengthen it. The optimum strength of 0.77 MPa was obtained with a 1:2:1 mixture of starch: Glyceline: lignin. Furthermore, heating this mixture in oven at 50 °C can also improve the adhesive still further as shown in **Table 5-11**. The lignin/Glyceline/starch adhesive can reach about a third of the strength of some of the commercial adhesives shown in **Table 5-7**.

Table 5-11: The effect of heating time on the tensile strength and elongation of lignin/Glyceline/starch adhesives.

Composition	Ratio	Left in oven (hours)	Tensile strength (MPa)	Elongation (%)
Lignin: Glyceline: Starch	1:2:1	6	0.77 ± 0.050	2.33 ± 0.29
Lignin: Glyceline: Starch	1:2:1	12	0.93 ± 0.041	2.01 ± 0.22
Lignin: Glyceline: Starch	1:2:1	24	1.14 ± 0.048	1.68 ± 0.32

5.6.2. Protecting the surface of TPS from moisture

The main aim of producing TPS starch is its biodegradability and to be used in short term applications. However, the durability of thermoplastic starch or wood based thermoplastic starch can be extended by covering their surfaces with laminate, preventing the surface from the absorbing water from the surrounding air during the use. Laminating TPS by using environmentally friendly adhesive with hot pressing was achieved; **Figure 5-14** shows a sample of the laminated TPS. The sample shown in **Figure 5-14** was immersed in hot water for 24 hours and did not show any signs of warping or delamination.

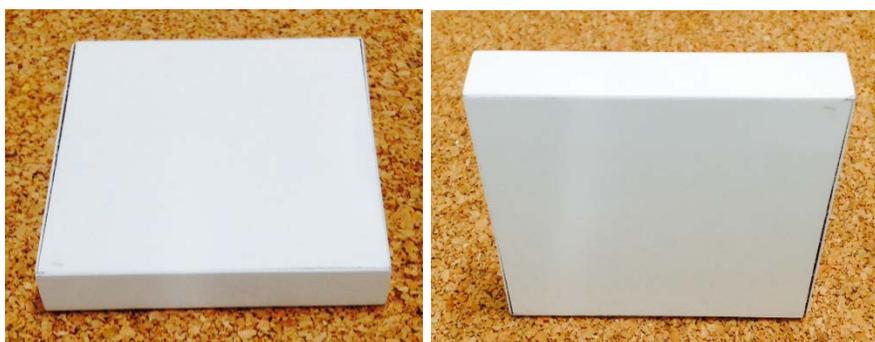


Figure 5-14: Image of laminated TPS.

Protecting the surface of TPS sheets can be achieved by applying a commercial waterproof spray (Woly, 3 x 3 protector) or a thin layer of melted wax on the surface. After covering the TPS surface, water absorption capacity experiments were carried on the thermoplastic starch sheets. The samples of TPS were coated in distilled water for 24 hours at room

temperature with and without interfacial protection for comparison. The mass of the samples were measured before and after coating in water and the percentage mass change is shown in **Table 5-12**.

Table 5-12 shows that the water uptake is reduced significantly when the surface of TPS sheet is protected. The mass increase all of the blank TPS samples increased by about 200%. However, spraying a waterproof spray on the surface of the TPS products reduced the water uptake by more than the half for all samples. Moreover, waxing the prevented the starch based plastics swelling. The advantage of using natural waxes is that wax is removable and keeps the plastic bio-degradable.

Table 5-12: *Water Absorption capacity (WAC) of blank TPS with and without interface protection. TPS samples coated in water for 24 hours at room temperature.*

TPS type	Mass gain (%)					
	Not protected		Sprayed		Waxed	
E100	183.56	± 4.37	85.32	± 12.54	1.15	±0.24
E130	229.89	± 8.76	78.72	± 14.85	1.32	±0.61
E160	238.51	± 9.52	93.84	± 19.78	1.02	±0.33

5.7. Summary

Thermoplastic starch has a hygroscopic nature which can affect its mechanical properties, the amount of water uptake of TPS samples with and without additives have been studied. TGA experiments showed starch has two different types of bound water; weakly and strongly bound. The weakly bound water can be removed at lower temperature than the strongly bound one.

It is also found that using eggshell as a composite material reduced water absorbance at low relative humidity but unfortunately it was the most hygroscopic additives at high relative humidity. Using zein as a bio-additive improve the hydrophobicity of TPS more significantly at any relative humidity.¹⁰

TPS can be protected from surrounding moisture by laminating it, but using non-degradable material to do so will produce a material which is difficult to recycle. Carbohydrate based adhesive have been developed to solve this issue, where this bio-adhesive can be utilised to extend TPS age when it is under use by laminating the biodegradable material of both TPS or wood based TPS. Tensile strength and flexibility of these adhesives have been examined and show that carbohydrate based adhesives can be comparable to the synthetic adhesives. Also, painting the surface of TPS with a natural wax prevented it from swelling in water. The advantage of covering thermoplastic starch with a bio-based adhesive laminate or wax is that they can be removed after use, giving the bio-adhesive, wax and TPS the chance to degrade under the natural conditions.

5.8. References

- 1 A. Al-Muhtaseb, W. McMinn and T. Magee, *J. Food Eng.*, 2004, **61**, 297-307.
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Chapter 6: Conclusion

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6. Conclusion

In the last few decades the fate of plastics in the environment has become a significant issue. The discovery that ocean currents are concentrating water-borne plastics into areas the size of continents is headline news. Stories have hit the headlines about these so-called *Great Pacific garbage patch* and *North Atlantic garbage patch* which have been found to contain about 5 kg km^{-2} of assorted plastic fragments which are a hazard to all forms of aquatic life.^{1, 2} In addition to environmental concerns the use of plastic is using about 6% of the annual oil produced. A report by BP has shown that, based on current usage the majority of oil will be all but exhausted during the next thirty years.³ It is therefore evident that for some applications an alternative material to polyolefin plastics is required.

Many groups are studying environmentally compatible plastics. Most of the commercial alternative plastics involve polylactic acid or cellulose acetate commercial plastics. These materials have found some niche applications but they are expensive and do not degrade under natural conditions. It is also questionable whether these materials are any more environmentally compatible due to their relative environmental stability

This project studied the use of starch as the basis for a bio-degradable plastic using DES as a plasticiser. This research investigated and developed the physical and chemical properties of starch based bio-plastics and attempted to determine if they could be alternative to petrochemical plastics in the near future.

6.1. Summary

Starch was plasticised using four different DES systems, producing TPS with satisfactory properties compared to the literature. The DESs of this project were a mixture of choline chloride as the salt with glycerol, urea, ethylene glycol and propylene glycol as HBD. The mixture of glycerol/ choline chloride improved the mechanical properties of thermoplastic starch better than the other three HBD. The mechanical properties of TPS can be controlled, by altering the processing parameters or plasticiser content. Glyceline produced the strongest plastic and since glycerol is a common, naturally occurring compound and choline chloride is a non-toxic pro-vitamin it was felt that this was the most

environmentally compatible plastic. Previous studies in the group have shown that this material can fully compost in less than 4 weeks.

The gelation of starch was studied using QCM and it was shown that it could be converted from a starch/plasticiser-slurry to a rigid plastic in 1-2 minutes. Studying the gelation of starch by glycerol/choline chloride in QCM followed the procedure of Abbott *et al.*⁴ group research who studied starch plasticisation with the urea/choline chloride. This work also developed a method to study the gelation of starch with DES under pressure. This was done by measuring the conductivity of the starch mixture in the press during gelation. It was rationalised that the conductivity would change as the material gelled and the ionic liquid became incorporated into the starch structure. This was indeed the case and it was shown that the gelation time was also in the region of 1 to 2 minutes. Direct comparison of the two techniques was not possible due to the differences in scale between the two samples but it is quite clear that gelation occurs on the minute time-scale with or without the application of pressure.

Some bio-additives from natural sources were used as fillers such as eggshell, banana and orange peels. Other filler systems were also used to fill TPS including wood-flour, wood-fibre, silk, lignin and zein. The addition of these filler affected the characteristics of TPS including: degree of crystallinity, homogeneity, morphology and glass transition temperature. The degree of crystallinity increased with the addition of zein but it reduced when silk or lignin was added. All fillers reduced the DSC- T_g and DMA- T_g due to the increase of starch: plasticiser ratio except for zein-TPS which had a DMA- T_g much higher than the blank TPS. It is also found that the intra- and inter-molecular hydrogen bond interactions in starch also can be affected by the composite particles, where lignin strengthens the interaction but eggshell weakens it. The composites were found to be weaker than the pure TPS and this is thought to be due to the incorporation of a bigger void volume. The materials are thought to break through crack propagation across the voids. This is probably due to their effect on the packing density. The rheological properties of TPS with the bio-additives vary as zein reduces the fluidity significantly, while silk and wood improve it.

The effect of moisture content on the mechanical properties of TPS was also investigated. Moisture is very important for thermoplastic starch biodegradability but it also decreases the mechanical strength of the material. Water absorption was the focus of last chapter, where contact angle, water sorption isotherm, water absorption capacity and the effect of RH on the absorbance were carried out. It was shown that water absorbance is strongly dependent on the RH, plasticiser content and filler type. The hydrophobicity of TPS was improved with the addition of some fillers such as zein for example. Protecting the surface of TPS can also reduce absorbing water and extend TPS age with keeping it biodegradable. It was shown that lignin and starch can make bio-degradable adhesive that can stick a laminate to the surface. This was shown to protect the underlying starch without difficulty even when the sample was immersed in hot water for a day. For a less durable coating which is probably the most useful for many of the applications in this work, simply coating the surface with a layer of wax was found to be a sufficient barrier to moisture absorption.

6.2. Future directions

One of the most interesting techniques develop in this project was the ability to follow the gelation of starch by measuring the conductivity of the sample. This is a powerful technique for following the gelation process and one of the obvious studies that should be carried out would be the effect of each of the parameters including temperature, applied force, plasticiser content and type and thickness of the mould would affect the kinetics of gelation. The composites if wood with starch is currently being scale up to 1 m x 1 m x 0.018 m and the kinetics of gelation are changing as the sample size increases. This technique could help to work out the mechanism of gelation in the composite. Also, the optimum time that starch needs to gel, at the required conditions, can reduce the energy requirements during processing.

Also, one of the interesting aspects of the research was that lignin dissolved very well in glycerol/choline chloride but not at all in glycerol. Lignin also strengthens the hydrogen bond interactions that occur in starch after the plasticisation, giving a new phase in TPS that has a higher T_g as shown in DMA data. Additionally, 10 wt% with TPS improve the homogeneity of the final product, and it is observed that extruding lignin-TPS is easier and

faster than the blank TPS, as shown by MFR. The next step in this field would be to plasticise pure lignin by the DES and/or increase the lignin content in TPS, and then study the physical and chemical properties.

Dissolving lignin in glycerol/choline chloride with the ratio 1:2 respectively gives very viscous fluid when it is hot and rubbery and sticky when it is cold. This solution was used to laminate TPS with thin board of wood and worked successfully and prevent TPS from moisture absorbance. Studying and improving this natural adhesive would be a good idea, it could also be used to make chipboard or other laminar boards. The future direction in improving this adhesive is by studying its structure by XRD.

The modified starch can work as a binder between wood-fibre and wood-flour as shown in this project and in the previous study (master dissertation). This thermoplastic wood has comparable mechanical properties to medium density fibreboard (MDF) and it is not just that it can replace but it is also reduces the uses of formaldehyde resins. Fine powders of wood can be bound with TPS to form thermoplastic wood which can be re-melted and then re-shaped. This project is ongoing and leading to some interesting results. The use of choline chloride still makes a material which is more expensive than urea-formaldehyde resin so current studies within the group are developing novel formulations which are equally environmentally compatible but at a lower cost. The properties of these resins still need to be fully characterised.

Finally, several researches in the literature have blended bio-degradable and non-degradable plastics to reduce either the cost or improve degradability. Thus, one the most desires that should be done in the future is mixing starch based bio-plastics with polyolefin plastics. The benefit of mixing the powder of synthetic plastics with starch based bio-plastics is that the waste of final product will be powder of the synthetic plastics after the degradation of TPS, reducing the dangerous of plastics wastes. This has been attempted within the group and shown to be a viable approach. These materials still need to be fully characterised.

6.3. References

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