Thermoplastic Starch: Current Development and Future Trends

Fengwei Xie*,[1], Paul Luckman[1], John Milne[1], Lachlan McDonald[1], Conor Young[1], Chen Yang Tu[1], Teo Di Pasquale[1], Reinhard Faveere[1] and Peter J. Halley[1,2]

[1]*Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Qld 4072, Australia*
[2]*School of Chemical Engineering, The University of Queensland, Qld 4072, Australia*

ABSTRACT: Starch is a biopolymer that is widely available from agriculture/nature and thus is renewable and cheap. In addition, starch-based materials are biodegradable, offering a great advantage over traditional non-biodegradable synthetic polymers. However, the poor processibility and product performance of starch have greatly impeded the wide application of starch in real applications. This paper reviews the current developments of the production of thermoplastic starch as a commodity renewable material. The biological origins of the feedstock, formulation development, processing requirements, as well as the important aspects that need to be addressed when designing a product from starch are discussed. It is hoped that this paper will provide insights into thermoplastic starch-based materials trends and and inspiration for future research.

KEYWORDS: Starch structure, thermoplastic starch, thermal processing, extrusion, plasticization

1 INTRODUCTION

Starch is a globally available, low-cost renewable commodity that when processed into a thermoplastic has the potential to replace conventional petroleum plastics. This interest has led to decades of investigation into the large-scale transformation of starch into a thermoplastic material [1, 2].

The most common sources of starches produced globally include maize (corn), wheat, rice, potato and tapioca. Starch is produced within plant cells as an energy storage mechanism in the form of spherical granules of size from <1 μm up to 100 μm [3]. The size, amount, and composition of the granules vary between plant species [4].

Starch can be processed by traditional polymer processing techniques, such as extrusion, without significant modification [1]. However, since native starch exists in granules (as a form of energy storage in nature), melt processing of native starch requires thermomechanical treatment, accompanied by a plasticiser (most commonly water—even though some researchers do not consider water as a plasticiser for starch), to produce starch-based materials. During this process, the phase transition ("gelatinisation" or "melting") of starch occurs, which plays a critical role for the plasticisation of starch—indeed this complexity makes the concept of plasticisation of starch different from that of standard synthetic polymers. By plasticisation, raw starch, with structural degradation at multiple levels (molecular, crystalline, and granular) [5], can be transformed into a homogeneous polymeric state, which is known as "thermoplastic starch (TPS)" (in spite of the term, it is noteworthy that plasticised starch is not truly a thermoplastic but more accurately described as a thermomechanoplastic [6]). Figure 1 shows a typical TPS material produced by extrusion. The degree of phase transition can largely determine the processibility and final product properties [2].

Different conditions may also be used for different subsequent processing techniques. For example, starch–polyester blends may be processed in melt state under high shear, 10^2–10^3 s^{-1} in extrusion, and 10^3–10^4 s^{-1} in injection moulding [8].

To understand starch processing in depth, it is necessary to discuss the biological origins of the feedstock,

---

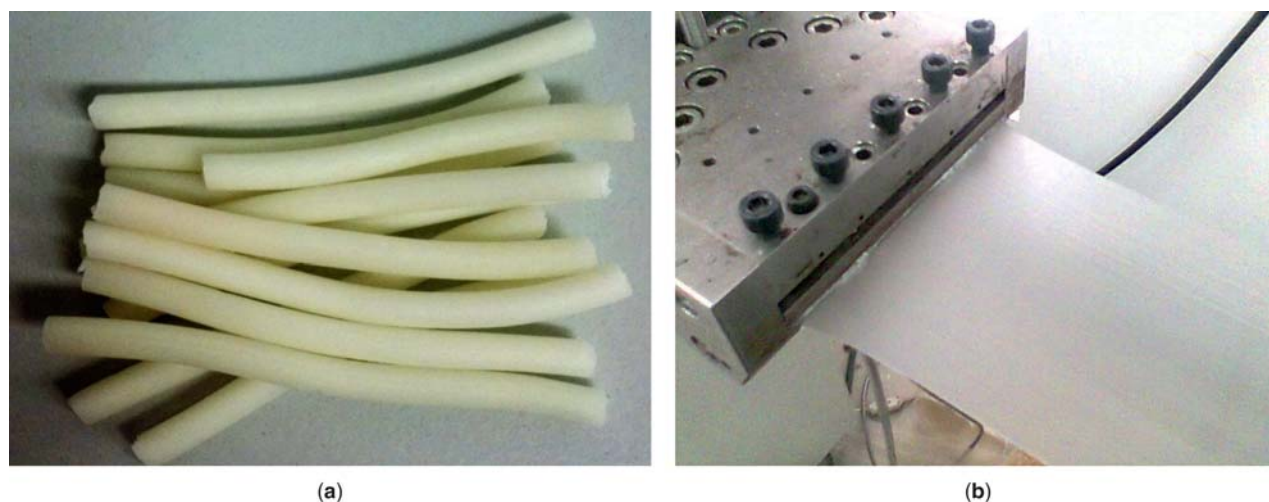*Corresponding author*: f.xie@uq.edu.au; fwhsieh@gmail.com

Figure 1 Typical thermoplastic starch extrudates using different dies: **(a)** rod; **(b)** film. (a) Reproduced with permission from [5]; Copyright © 2013 Wiley Periodicals, Inc.; (b) Reproduced with permission from [7]; Copyright © 2011 Elsevier.

formulation development, processing requirements, and the important aspects that need to be considered when designing a product from starch. These will be discussed in detail in the following sections.

2 FEED MATERIALS FOR THERMOPLASTIC STARCH

2.1 Structural Features of Starch

The extensive varieties of starch sources have significant differences in composition and structure. Starch macromolecules can be classified into two main groups, i.e., amylose and amylopectin (even though there are also some intermediate molecules in between the two main types). The amylose is a linear structure of α-(1→4) linkage of glucose units while amylopectin is a highly branched structure of short α-(1→4) chains linked by α-(1→6) bonds [3]. The ratio of the amylose and amylopectin depends on the source and age of the starch as well as the extraction method from the starch granules [3]. Regular starch cultivars (wheat, maize, potato, etc.) have amylose contents ranging between 20–30% [9], while high-amylose starches (with the amylose content being up to 83% [10]) have long been cultivated and used. Besides this, very small amounts of proteins, lipids and phosphorus are also found in starch granules depending on the botanical resource [11, 12]. These components can interact with the carbohydrate chains during processing (e.g., Maillard reaction) and then modify the behaviour of the starch-based materials. Moreover, starch contains about 10% bound water [13].

Starch occurs in four different polymorphs, the A, B, C and V crystalline forms. Both A and B forms are left-handed double-helices with six glucose units per turn [3]. Their only difference is the packing of the helices, where A-form has a monoclinic unit cell while B has a hexagonal unit cell [3]. The C-type is simply a mixture of A and B. V-type starches consist of a single left-handed helix with a complexing agent (typically lipids) found inside the helix channel [3]. The V-type polymorph exists more in high-amylose starches [10] and is also prone to be formed by thermal processing like extrusion [14, 15].

2.2 Impact of Amylose/Amylopectin Ratios

In spite of the fact that starches with a higher amylopectin content (lower amylose content) have a more ordered supramolecular structure and thus display a higher enthalpy of gelatinisation, as shown from differential scanning calorimetry (DSC) studies [16], the granules of high-amylose content starches are more compactly packed [17, 18], and usually require more energy to be destroyed for the production of TPS [5, 19, 20]. Therefore, poor processibility of high-amylose content starches is encountered. However, compared to those from low-amylose content starches, TPS materials made from high-amylose starches often show more flexibility and superior strength and stiffness, and display less deterioration of the mechanical properties due to ageing [9, 21, 22] (even though their post-processing shrinkage has been reported [9]). On the

other hand, the use of starch with a lower amylose content (higher amylopectin content) could reduce the melt viscosity (improve the processability); but it should be noted that in this case the feed rate into the extruder needs to be increased to keep the torque rate constant and to avoid unstable processing [9]. It has also been reported that a higher amylopectin content could lead to films with a greater elongation-at-break value due to the higher molecular weight of amylopectin [9].

The amylose/amylopectin ratio of starch could largely influence the produced materials. Generally, starch with a higher amylose content has better mechanical properties [7]. Nevertheless, an increase in the amylose content can reduce the transparency of films, due to the materials containing more granules that are not destroyed, suggesting less homogeneity [9]. In addition, examination of 100% amylose or amylopectin TPS substructures has also been carried out. Rindlav-Westling *et al.* [21] reported that pure amylose films had a relative crystallinity of around 30%, while pure amylopectin films were entirely amorphous. Blending of the two polysaccharides would result in variation in crystallinity due to amylose inducing crystallisation of amylopectin [21]. Purified amylose has a higher crystallisation tendency than natural amylose due to the change in molecular weights—a decrease in the molecular weight leads to a decrease in the chain size, allowing for a greater tendency to form continuous networks [21].

2.3   Impact of Chemical Modification

Chemical modification (e.g., hydroxylation [23–25] and acetylation [26–30]) of starch by substituting ester or ether groups for the hydroxyls is an effective way to improve the processing and product properties (mechanical properties, water resistance, etc.). As a typical example, hydroxypropylated starch shows much improved processibility (lower viscosity, specific mechanical energy input (SME), and die pressure) and more flexible mechanical nature of final films [23, 31]. Besides, Thunwall *et al.* [32] observed a more Newtonian behaviour of hydroxypropylated and oxidised potato starch compared to normal potato starch. It is proposed that the modification of groups may weaken the starch intra- and inter-molecular interactions and facilitate the formation of "ellipsoids". Meanwhile, it should be noted that chemical modification often decreases the polysaccharide molecular weight, potentially leading to materials with less mechanical strength, and also that the toxic chemical residues may modify the biodegradability and negatively impact the life-cycle assessment (LCA) of the final products.

3   FORMULATIONS FOR THERMOPLASTIC STARCH

3.1   Plasticisers

The addition of a plasticiser can be used to enable and regulate the degree of melting and disruption of starch granules and change a number of film properties to be more desirable for end use [9]. For a plasticiser to be effective for the production of TPS it needs to be compatible with starch, which means it needs to be hydrophilic [33]. Having a boiling point higher than the processing and drying conditions is also desirable to prevent the evaporation of the plasticiser out of the material both during processing and post processing. A plasticiser can reduce the internal hydrogen bonding while increasing intermolecular spacing, and usually decreases the crystalline-to-amorphous ratio [34]. As a result of the increased mobility of polymer chains, it is common to see a reduction in the glass transition temperature by the addition of plasticiser [9].

The most common plasticisers used in TPS film production include water. However, when water is used as the sole plasticiser, unstable processing could be observed due to the water evaporation. Further, the final products based on starch containing only water usually have poor mechanical properties, especially due to the brittleness, since its final temperature is lower than its glass transition temperature (T_g). Regarding this, polyols such as glycerol, sorbitol and glycol have also been used for the production of TPS [35–45]. It has been found, however, that polyols are less effective plasticisers than water [9], as the gelatinisation of starch becomes less easy with larger molecules of polyols [46]. Nevertheless, polyols are non-volatile plasticisers, overcoming the corresponding drawback of water. More non-volatile plasticisers used for TPS include nitrogen-based compounds (urea, ammonium-derived, amines, etc.) [47–61] and citric acid [62–64]. In particular, citric acid has been regarded as an effective plasticiser for starch as the acidity of citric acid can promote the fragmentation and dissolution of starch granules, as well as the effective interactions with the C–O groups of starch (more than glycerol) and thus the restriction of hydrogen bonds between the hydroxyl groups of TPS. Therefore, citric acid can result in a greater degree of the amorphous state and a low degree of recrystallisation (or "retrogradation", a term specifically for starch) [65].

Along with promoting plasticisation, the addition of a plasticiser like glycerol improves the film's extensibility and reduces elasticity but greatly reduces the tensile strength [34]. However, it is noteworthy that at low concentrations (below around 10–15%) glycerol may exhibit an anti-plasticisation effect due to

its higher affinity with water than with starch [13]. This can increase the gelatinisation temperature of native starch as well as increase the glass transition temperature and brittleness of the corresponding TPS materials [13]. A further consequence of the addition of a plasticiser is the significant increase in water or oxygen permeability of the material [34, 66] (and the permeability depends on water more than on polyols [67]). Also, plasticisers like glycerol and sorbitol were found to allow films to have higher water solubility than other less hygroscopic plasticisers due to their strong affinity with water [34].

3.2 Additives (Including Nanofillers)

In addition to plasticisers, other additives can be introduced to the extrusion feed for various purposes. For example, to reduce the material's tendency to stick to the die and clogging it, lubricants can be used such as magnesium stearate [68], calcium stearate [69] and fluoro-elastomers [70].

Various nanofillers have been used to improve the properties (typically as mechanical properties) of TPS and/or to add functional properties. These include phyllosilicates (e.g., montmorillonite (MMT)), polysaccharide nanofillers (e.g., cellulose nanowhiskers, starch nanocrystals); carbonaceous nanofillers (e.g., carbon nanotubes), and various metalloid oxides, metal oxides, and metal chalcogenides, as having been comprehensively reviewed elsewhere [71–73]. As the most frequently used nanofiller, MMT, as a layered nanofiller, when dispersed homogeneous in TPS, can increase the barrier properties as well as reinforce the material [74]. It is worth noting that unmodified MMT can be dispersed in TPS more evenly than any other modified MMT counterparts, due to the former's stronger hydrophilicity which results in stronger polar interactions, especially hydrogen bonds formed between the –OH groups of the MMT and of the starch molecules [75–78]. This example hints at the importance of considering the nanofiller's hydrophilicity for choosing effective nanofillers for TPS materials.

3.3 Blended Polymers

To improve the performances such as barrier properties, moisture resistibility, mechanical properties, and long-term stability, starch is often blended with other (preferably biodegradable) polymers such as polylactide (PLA) [8, 64, 79–89], polycaprolactone (PCL) [8, 79, 90–96], poly(butylene succinate adipate) (PBSA) [8, 92, 97], poly(hydroxy ester ether) (PHEE) [89, 98] and polyhydroxyalkanoates (PHA) [89, 99, 100]. Blending starch with another biodegradable polymer can maintain the "green" nature of the material;

but, depending on the intended usage, the control of biodegradation of the whole material is sometimes desired, since starch is known to normally have very fast degradation. Moreover, there is always an issue with miscibility between starch and another polymer due to the difference in hydrophilicity/hydrophobicity. Regarding this, the use of a compatibiliser is important. For example, for starch blended with a polyester (PLA, PCL or PBSA), methylenediphenyl diisocyanate (MDI) could reactively compatibilise the two components [84, 92]. Nonetheless, the toxicity of many effective compatibilisers like MDI has forced people to seek more friendly strategies. Huneault and Li [101] claimed that the interface of starch and PLA could be improved by using PLA grafted with maleic anhydride (MA) for the interfacial modification. Besides, it has been demonstrated very recently that chemically modified plant oils (MA-grafted tung oils [102] and expoxidised soybean oil [103]) are also effective in increasing the compatibility between starch (MA-grafted) and PLA.

4 PROCESSING FOR THERMOPLASTIC STARCH

4.1 Characterisation of Native Starch for Design of Starch Processing

As starch undergoes phase transition during thermal processing, it is important to understand the thermal phase transition of starch before practical processing work. This can be done by various techniques such as microscopy with hot-stage, DSC, X-ray diffraction (XRD), and nuclear magnetic resonance (NMR) [1, 104]. Among these, DSC has gained the most popularity due to its convenience of use and accurate results. However, as the thermal phase transition (gelatinisation) of starch occurs only with water (and/or other plasticisers), it is significant to avoid the loss of water during measurement; otherwise the endotherm of water evaporation would largely interfere with the signal of starch phase transition (which is much weaker than that of the former). Regarding this, a stainless steel high-pressure pan was used in DSC for understanding the phase transitions of different starches in pure water [16] or in water–glycerol mixtures [46].

Processing of starch usually involves shear treatment, which is expected to greatly facilitate the phase transition of starch as it can disrupt the multilevel structures of starch granules. This cannot be understood solely by DSC. Regarding this, an attempt was made by Xie et al. [105] to study the phase transition of starch with a low moisture content (45%) and under shear stress by using dynamic mechanical analysis

(DMA). The results showed that the variations in the physical parameter, damp (tanδ) in DMA, occurred both before thermal transition (as indicated by the heat flow in DSC) started and after thermal transition completed. However, the shear treatment in DMA was quite small. By using a twin-rotor mixer (Haake Rheomix®), Xue et al. [106] and Wang et al. [20] investigated the phase transition of starch under a strong shear treatment, just like in an extruder. The torque curve could be used to reflect the viscosity change and to estimate the time needed to achieve the steady molten starch phase, which could provide useful information for designing practical extrusion processing. Nevertheless, more studies are urgently needed to understand the changes of starch under a combined thermomechanical treatment.

4.2 Processing Techniques for Starch

There are a number of techniques used to produce TPS materials, including the most frequently used extrusion, as well as injection moulding, compression moulding, internal mixing, etc. Extrusion can be considered as a core processing technique and is usually coupled with, or prior to, other processes such as injection moulding, compression moulding, and film casting. While solution film casting could be the simplest method for the preparation of starch-based films, it is considered to be much less efficient for industrial-scale production and thus is not discussed in the current paper. More details of thermal processing techniques for the production of TPS can be found in a review paper [1].

4.2.1 General Concept of Starch Extrusion

The main extrusion facility for starch extrusion processing can be a single-screw extruder (SSE) or a twin-screw extruder (TSE). The differences of these two types of extruders have been discussed in detail elsewhere [107]. It is noteworthy that while a SSE can handle the high viscosity of starch and provide a high processing pressure for continuous metering of starch through die shapes, a TSE is much better for the first stage of TPS production from raw starch powder, as its twin screws have a self-wiping ability. Moreover, a TSE has a large operational flexibility (the control of individual barrel zone temperatures, multiple locations for feeding solids and liquids, and versatile screw configurations for different degrees of mixing/kneading) and is useful for intensive mixing and compounding of components into TPS.

A schematic of the twin-screw extrusion process for the production of TPS is shown in Figure 2 [2]. Here, the native starch granules are introduced, preferably by a powder gravimetric feeder, into the extruder in a hungry way (i.e., the feeding capacity is less than the conveying capacity of the screws at the feeding port). Liquids (typically plasticiser) could be introduced in a following location, preferably using a pressure-injection way to ensure uniform mixing between the solid(s) and the liquid(s). The granules undergo exposure to high temperatures and pressures in the extruder, resulting in the disruption, and gelatinisation/melting, of starch granules [16]. After gelatinisation, the TPS will undergo further melting and compression, which may be increased with increased use of high mixing (kneading or reversing) elements
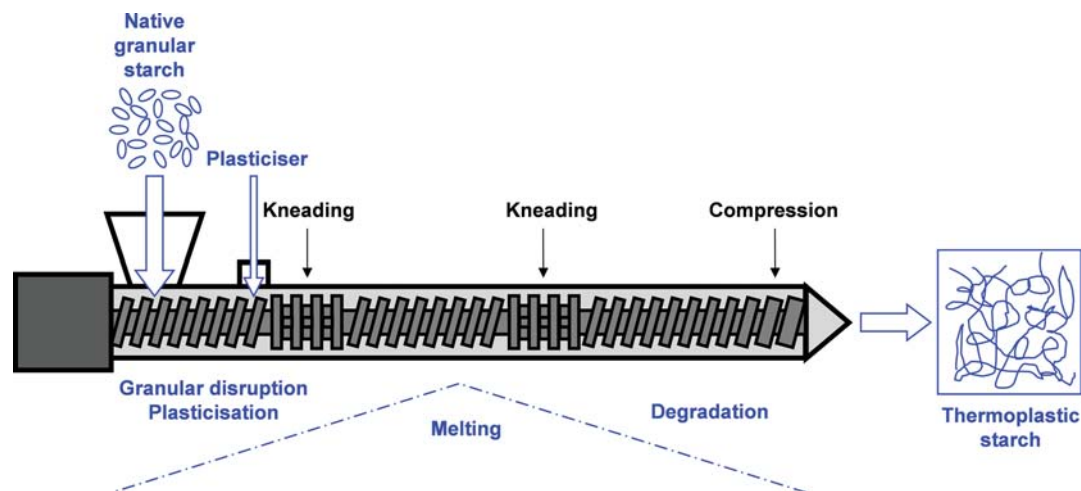

Figure 2 Schematic representation of starch processing by extrusion. Reproduced with permission from [2]; Copyright © 2012 Elsevier.

in the screw. It is important to note that degradation of starch molecules also occurs with the thermal mechanical treatment in the extruder, with amylopectin molecules suffering more than amylose [5, 108]. And the mechanism for scission of the polymer chains is believed to preferentially take place close to the centre of the molecule, causing the size distribution to narrow and converge toward a maximum stable size [108]. The TPS is forced through the extrusion line and finally out of a die at the end of the extruder at a controlled rate (possibly with the aid of a melt pump to further control the flow rate).

It is interesting to note that some special techniques have been used for the production of TPS. For example, Stute *et al.* [109] claimed that starch can be gelatinised by a high pressure (upwards of 800 MPa) alone. However, this high pressure cannot be easily achieved without special equipment, and to date this method of processing has only been applied to starch slurries.

4.2.2 *Characteristics of Starch Extrusion Process*

The primary aim of extrusion is to ensure complete melting and sufficient mixing, while avoiding degradation (to maintain good mechanical properties), to obtain a homogenous TPS melt. This can only be achieved by careful investigation of the key processing parameters, including raw material feed rate, temperature, screw speed, and screw profile.

The temperature profile in extrusion is a vital processing parameter that needs to be established mostly depending on the feed material. A typical temperature profile for all starches will start from a low temperature (e.g., room temperature), ramp up to a highest value at the middle of the barrel, and then is reduced to some extent at the sections near the die and at the die. The use of a low temperature at the sections near the feed port is to prevent the loss of water immediately after the raw starch is fed in, since water is the most frequently used plasticiser. Then higher temperatures at the middle sections, especially coupled with kneading elements there, could provide a strong thermomechanical treatment to destroy starch granules and transform starch into TPS. A reduced, appropriate, temperature at the die could assist stable extrusion of the material from the die (without undesirable foaming if water and/or other volatile substances are used in the formulation) and facilitate the orientation and crystallisation of the material for better properties (in particular mechanical).

It is noteworthy that the different abovementioned parameters can further determine three more important parameters, namely pressure, residence time, and

SME. For example, a change in the screw speed will also modify the pressure, SME, and even temperature. Thus, it is often difficult to isolate the effects of the latter three parameters.

According to Gropper *et al.* [110], SME can be calculated from the following equation:

$$SME = (N \times T \times 60) \; / \; Q \qquad (1)$$

where N is screw speed (rpm), T is torque (N·m), Q is feed rate (kg/h), and *SME* is in unit of kJ/kg. In general, an increased ratio of N/Q can result in a higher SME value and greater macromolecular degeneration, leading to decreased viscosity [2]. Also, it has been found that higher screw speeds can lead to lower gelatinisation of the starch because they decrease the residence time of the starch material in the extruder [111]. However, increasing the screw speed may also lead to a higher mixing torque [112].

4.2.3 *Reactive Extrusion of Starch*

Reactive extrusion (REX) means concurrent reaction and extrusion. It can be used to produce either chemically modified starch or starch-based blends with high conversion efficiency and a rapid rate of production, which has already been extensively reviewed in several papers [113–115]. This technique has recently been used more innovatively. For example, Frost *et al.* [116] created plasticised starch–silica (SiO_2)–poly(vinyl alcohol) (PVOH) composite films by REX using tetraethyl orthosilicate (TEOS) as a precursor. The TEOS-to-SiO_2 conversion efficiencies of up to 41.3% were achieved, and the resulting films had well dispersed SiO_2 particles of size ranging from 20 μm to < 1 μm, which were responsible for the increased tensile strength and Young's modulus. In addition, some of the studies of starch–PLA blends by Xiong *et al.* [102, 103, 117], as mentioned in Section 3.3, could also be considered as involving REX, as the compatibiliser, starch, and PLA reactively interacted with each other during melt processing.

4.2.4 *Impact of Extrusion on Structures and Properties of Thermoplastic Starch Products*

Since extrusion processing is complex, it is not an easy job to design a perfect extrusion process for the production of TPS materials with mostly desirable properties. This needs repeated practical tests with an extruder and improvements in the extrusion process, taking into consideration different technical parameters (type of feed starch, formulation, extrusion processing conditions, and also subsequent environmental

sp

conditions [relative humidity and temperature] of storage or annealing).

It is hoped that native starch granules can be completely transformed into a homogenous plasticised state by extrusion, but unfortunately TPS products, especially those from high-amylose starches (which are preferably used for better properties nevertheless), normally still contain remaining starch granules. This can be detected by various techniques such as microscopy and X-ray diffraction (XRD). Using a light microscope, Li *et al.* [7] showed that granules that were not disrupted still largely exist in extruded films from high-amylose starch. The XRD can also be useful in detecting the granule remnants and its original crystalline structure. As mentioned before about original polymorphs of starch, a strong signal indicating A- or B-type by XRD usually means a large amount of remaining starch granules [5]. Moreover, atomic force microscopy (AFM) can be a good way to image film samples and obtain topographic images of the starch films surface at a micrometre level. It is found that there were granular envelopes with a size of around 10 μm with a surround matrix of amylose, and when films were more gelatinised, the surface contained less granular envelopes [118]. When these envelopes were surrounded by dark regions, it might represent surface tension developed by concentrated amylose solutions in relation to granule remnants as the liquid evaporates during film formation [118].

For reducing the granule remnants in TPS products, a change in parameters such as increased temperature or screw speed may be able to make a more homogenous film. It has been suggested that during extrusion the mechanical shear is more important in disruption of the granules and their crystalline structures than thermal treatment [5]. However, care needs to be taken, as the mechanical shear is also more significant in contributing to the degradation of amylopectin molecules [5], potentially negatively affecting the mechanical properties of the final products.

5 PROGRESS OF STARCH PROCESSING RESEARCH AT UQ

At The University of Queensland (UQ), we have focused on many fundamental aspects in starch processing, including understanding of fundamentals of native starch [10, 119–121], starch degradation during extrusion [5, 108], processing rheology of TPS [122], effects of starch type and chemical modification on the processing and properties [23, 31]; development of new TPS polymer blend products [123–126], optimisation of the related processing [127], understanding

of performance of TPS by post-processing environmental conditions [128–130]; as well as the very recent work on plasticisation of starch using novel plasticisers [131].

Product wise our research has focused on the development of water soluble rigid sheet products and blown films for dry goods packaging and water resistant injection moulding grades for moulding applications [132]. Very recently we have embarked on a new project focusing on thin starch films for barrier packaging. This project, through

- the development of new biopolymers,
- the understanding of barrier properties for biopolymer films and laminates, and
- smart design of films for specific packaging applications,

will enable the robust development of high-performance thin film products with enhanced barrier properties. This technology will greatly expand the product range of current TPS films into attractive markets, such as meat trays and smart packaging, by diminishing reliance on one raw material feed stock, control of novel processing conditions, and by providing possible environmental advantages. An example of a novel thin film is shown in Figure 3.

There is a lack of understanding of processing starch films at low gauge (under 50 microns), as well as the subsequent relationships of processing–structure–properties of these films. A range of film properties such as pH resistance, bacterial resistance, temperature resistance, barrier resistance and changes in these properties over time, have also not been explored.

Figure 3 Thin extruded thermoplastic starch film at 12 micron produced at The University of Queensland.

6 CONCLUSIONS

Clearly starch has always offered a very attractive low-cost base for new biodegradable polymers due to its low material cost and ability to be processed on conventional plastic processing equipment. However, poor processability and product properties narrow the applicability of TPS to niche markets (e.g., edible food packaging, disposable packaging). Thus, the main technological drive in the future will be the engineering of more advanced properties into these kinds of low-cost materials. This development will most probably be in the form of integrating research in parallel from:

a. New TPS formulation (like alternative plasticisation methods, blends, nanocomposites, and reactive modification), and
b. Better fundamental understanding of TPS processing and its effects on extruded starch structure and properties (gelatinisation, plasticisation, retrogradation, degradation, and final material structure and properties).

It is hoped that this paper has addressed key aspects of both these parallel development streams.

ACKNOWLEDGEMENTS

REFERENCES

1. H. Liu, F. Xie, L. Yu, L. Chen, and L. Li, Thermal processing of starch-based polymers. *Prog. Polym. Sci.* **34**, 1348–1368 (2009).
2. F. Xie, P.J. Halley, and L. Avérous, Rheology to understand and optimize processibility, structures and properties of starch polymeric materials. *Prog. Polym. Sci.* **37**, 595–623 (2012).
3. S. Pérez, P.M. Baldwin, and D.J. Gallant, Structural features of starch granules I, in *Starch (Third Edition)*, B. James and W. Roy (Eds.), pp. 149–192, Academic Press, San Diego, 2009.
4. H.F. Zobel, Molecules to granules: A comprehensive starch review. *Starch/Stärke* **40**, 44–50 (1988).
5. M. Li, J. Hasjim, F. Xie, P.J. Halley, and R.G. Gilbert, Shear degradation of molecular, crystalline, and granular structures of starch during extrusion. *Starch/Stärke* in press, 10.1002/star.201300201 (2014).
6. L. Avérous, Biodegradable multiphase systems based on plasticized starch: A review. *Polym. Rev.* **44**, 231–274 (2004).
7. M. Li, P. Liu, W. Zou, L. Yu, F. Xie, H. Pu, H. Liu, and L. Chen, Extrusion processing and characterization of edible starch films with different amylose contents. *J. Food Eng.* **106**, 95–101 (2011).
8. E. Schwach and L. Avérous, Starch-based biodegradable blends: Morphology and interface properties. *Polym. Int.* **53**, 2115–2124 (2004).
9. J.J.G. van Soest and J.F.G. Vliegenthart, Crystallinity in starch plastics: Consequences for material properties. *Trends Biotechnol.* **15**, 208–213 (1997).
10. I. Tan, B.M. Flanagan, P.J. Halley, A.K. Whittaker, and M.J. Gidley, A method for estimating the nature and relative proportions of amorphous, single, and double-helical components in starch granules by ^{13}C CP/MAS NMR. *Biomacromolecules* **8**, 885–891 (2007).
11. J.-l. Jane, Structural features of starch granules II, in *Starch (Third Edition)*, B. James and W. Roy (Eds.), pp. 193–236, Academic Press, San Diego, 2009.
12. S. Pérez and E. Bertoft, The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review. *Starch/Stärke* **62**, 389–420 (2010).
13. R. Shanks and I. Kong, Thermoplastic starch, in *Thermoplastic Elastomers*, P.A. El-Sonbati (Ed.), pp. 95–116, InTech, Rijeka, Croatia, 2012.
14. J.L. Willett, B.K. Jasberg, and C.L. Swanson, Rheology of thermoplastic starch: Effects of temperature, moisture content, and additives on melt viscosity. *Polym. Eng. Sci.* **35**, 202–210 (1995).
15. J.J.G. van Soest, S.H.D. Hulleman, D. de Wit, and J.F.G. Vliegenthart, Crystallinity in starch bioplastics. *Ind. Crops Prod.* **5**, 11–22 (1996).
16. H. Liu, L. Yu, F. Xie, and L. Chen, Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydr. Polym.* **65**, 357–363 (2006).
17. P. Chen, L. Yu, G. Simon, E. Petinakis, K. Dean, and L. Chen, Morphologies and microstructures of cornstarches with different amylose-amylopectin ratios studied by confocal laser scanning microscope. *J. Cereal Sci.* **50**, 241–247 (2009).
18. P. Chen, L. Yu, G.P. Simon, X. Liu, K. Dean, and L. Chen, Internal structures and phase-transitions of starch granules during gelatinization. *Carbohydr. Polym.* **83**, 1975–1983 (2011).
19. F. Xie, L. Yu, B. Su, P. Liu, J. Wang, H. Liu, and L. Chen, Rheological properties of starches with different amylose/amylopectin ratios. *J. Cereal Sci.* **49**, 371–377 (2009).
20. J. Wang, L. Yu, F. Xie, L. Chen, X. Li, and H. Liu, Rheological properties and phase transition of cornstarches with different amylose/amylopectin ratios under shear stress. *Starch/Stärke* **62**, 667–675 (2010).
21. Å. Rindlav-Westling, M. Stading, A.-M. Hermansson, and P. Gatenholm, Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydr. Polym.* **36**, 217–224 (1998).

22. M. Schirmer, A. Höchstötter, M. Jekle, E. Arendt, and T. Becker, Physicochemical and morphological characterization of different starches with variable amylose/amylopectin ratio. *Food Hydrocolloids* **32**, 52–63 (2013).

23. A.L. Chaudhary, M. Miler, P.J. Torley, P.A. Sopade, and P.J. Halley, Amylose content and chemical modification effects on the extrusion of thermoplastic starch from maize. *Carbohydr. Polym.* **74**, 907–913 (2008).

24. D. Lafargue, B. Pontoire, A. Buléon, J.L. Doublier, and D. Lourdin, Structure and mechanical properties of hydroxypropylated starch films. *Biomacromolecules* **8**, 3950–3958 (2007).

25. W. Vorwerg, J. Dijksterhuis, J. Borghuis, S. Radosta, and A. Kröger, Film properties of hydroxypropyl starch. *Starch/Stärke* **56**, 297–306 (2004).

26. C. Fringant, J. Desbrières, and M. Rinaudo, Physical properties of acetylated starch-based materials: Relation with their molecular characteristics. *Polymer* **37**, 2663–2673 (1996).

27. C. Fringant, M. Rinaudo, M.F. Foray, and M. Bardet, Preparation of mixed esters of starch or use of an external plasticizer: Two different ways to change the properties of starch acetate films. *Carbohydr. Polym.* **35**, 97–106 (1998).

28. W. Jarowenko, Acetylated starch and miscellaneous organic esters, in *Modified Starches: Properties and Uses*, O.B. Wurzburg (Ed.), pp. 55–77, CRC Press, Boca Raton, FL, 1986.

29. B. Volkert, A. Lehmann, T. Greco, and M.H. Nejad, A comparison of different synthesis routes for starch acetates and the resulting mechanical properties. *Carbohydr. Polym.* **79**, 571–577 (2010).

30. P.B. Zamudio-Flores, A.V. Torres, R. Salgado-Delgado, and L.A. Bello-Pérez, Influence of the oxidation and acetylation of banana starch on the mechanical and water barrier properties of modified starch and modified starch/chitosan blend films. *J. Appl. Polym. Sci.* **115**, 991–998 (2010).

31. A.L. Chaudhary, P.J. Torley, P.J. Halley, N. McCaffery, and D.S. Chaudhary, Amylose content and chemical modification effects on thermoplastic starch from maize—Processing and characterisation using conventional polymer equipment. *Carbohydr. Polym.* **78**, 917–925 (2009).

32. M. Thunwall, V. Kuthanova, A. Boldizar, and M. Rigdahl, Film blowing of thermoplastic starch. *Carbohydr. Polym.* **71**, 583–590 (2008).

33. H.A. Pushpadass, D.B. Marx, and M.A. Hanna, Effects of extrusion temperature and plasticizers on the physical and functional properties of starch films. *Starch/Stärke* **60**, 527–538 (2008).

34. N. Laohakunjit and A. Noomhorm, Effect of plasticizers on mechanical and barrier properties of rice starch film. *Starch/Stärke* **56**, 348–356 (2004).

35. A.L. Da Róz, A.J.F. Carvalho, A. Gandini, and A.A.S. Curvelo, The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydr. Polym.* **63**, 417–424 (2006).

36. P.M. Forssell, J.M. Mikkilä, G.K. Moates, and R. Parker, Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydr. Polym.* **34**, 275–282 (1997).

37. D. Lourdin, L. Coignard, H. Bizot, and P. Colonna, Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer* **38**, 5401–5406 (1997).

38. A.P. Mathew and A. Dufresne, Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules* **3**, 1101–1108 (2002).

39. S. Gaudin, D. Lourdin, D. Le Botlan, J.L. Ilari, and P. Colonna, Plasticisation and mobility in starch-sorbitol films. *J. Cereal Sci.* **29**, 273–284 (1999).

40. A.R. Kirby, S.A. Clark, R. Parker, and A.C. Smith, The deformation and failure behaviour of wheat starch plasticized with water and polyols. *J. Mater. Sci.* **28**, 5937–5942 (1993).

41. J.J.G. van Soest, D. de Wit, H. Tournois, and J.F.G. Vliegenthart, The influence of glycerol on structural changes in waxy maize starch as studied by Fourier transform infra-red spectroscopy. *Polymer* **35**, 4722–4727 (1994).

42. R. Shi, Q. Liu, T. Ding, Y. Han, L. Zhang, D. Chen, and W. Tian, Ageing of soft thermoplastic starch with high glycerol content. *J. Appl. Polym. Sci.* **103**, 574–586 (2007).

43. J. Enrione, F. Osorio, F. Pedreschi, and S. Hill, Prediction of the glass transition temperature on extruded waxy maize and rice starches in presence of glycerol. *Food Bioprocess Technol.* **3**, 791–796 (2010).

44. Q. Yan, H. Hou, P. Guo, and H. Dong, Effects of extrusion and glycerol content on properties of oxidized and acetylated corn starch-based films. *Carbohydr. Polym.* **87**, 707–712 (2012).

45. X. Qiao, Z. Tang, and K. Sun, Plasticization of corn starch by polyol mixtures. *Carbohydr. Polym.* **83**, 659–664 (2011).

46. P. Liu, F. Xie, M. Li, X. Liu, L. Yu, P.J. Halley, and L. Chen, Phase transitions of maize starches with different amylose contents in glycerol-water systems. *Carbohydr. Polym.* **85**, 180–187 (2011).

47. X.F. Ma, J.G. Yu, and J.J. Wan, Urea and ethanolamine as a mixed plasticizer for thermoplastic starch. *Carbohydr. Polym.* **64**, 267–273 (2006).

48. X. Ma and J. Yu, The plastcizers containing amide groups for thermoplastic starch. *Carbohydr. Polym.* **57**, 197–203 (2004).

49. X. Ma and J. Yu, The effects of plasticizers containing amide groups on the properties of thermoplastic starch. *Starch/Stärke* **56**, 545–551 (2004).

50. X.F. Ma, J.G. Yu, and Y.B. Ma, Urea and formamide as a mixed plasticizer for thermoplastic wheat flour. *Carbohydr. Polym.* **60**, 111–116 (2005).

51. J.-H. Yang, J.-G. Yu, and X.-F. Ma, Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS). *Carbohydr. Polym.* **66**, 110–116 (2006).

52. J.-H. Yang, J.-G. Yu, and X.-F. Ma, Preparation of a novel thermoplastic starch (TPS) material using ethylenebisformamide as the plasticizer. *Starch/Stärke* **58**, 330–337 (2006).

53. J.-H. Yang, J.-G. Yu, and X.-F. Ma, Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). *Carbohydr. Polym.* **63**, 218–223 (2006).

54. H. Dai, P.R. Chang, F. Peng, J. Yu, and X. Ma, *N*-(2-hydroxyethyl)formamide as a new plasticizer for thermoplastic starch. *J. Polym. Res.* **16**, 529–535 (2009).

55. P. Zheng, P.R. Chang, J. Yu, and X. Ma, Formamide and 2-hydroxy-*N*-[2-(2-hydroxy-propionylamino)-ethyl] propionamide (HPEP) as a mixed plasticizer for thermoplastic starch. *Carbohydr. Polym.* **78**, 296–301 (2009).

56. H. Dai, P.R. Chang, F. Geng, J. Yu, and X. Ma, Preparation and properties of starch-based film using *N*,*N*-bis(2-hydroxyethyl)formamide as a new plasticizer. *Carbohydr. Polym.* **79**, 306–311 (2010).

57. H. Dai, P.R. Chang, J. Yu, F. Geng, and X. Ma, *N*-(2-hydroxypropyl)formamide and *N*-(2-hydroxyethyl)-*N*-methylformamide as two new plasticizers for thermoplastic starch. *Carbohydr. Polym.* **80**, 139–144 (2010).

58. J.-S. Zhang, P.R. Chang, Y. Wu, J.-G. Yu, and X.-F. Ma, Aliphatic amidediol and glycerol as a mixed plasticizer for the preparation of thermoplastic starch. *Starch/Stärke* **60**, 617–623 (2008).

59. X. Ma, J. Yu, and J. Feng, Urea and formamide as a mixed plasticizer for thermoplastic starch. *Polym. Int.* **53**, 1780–1785 (2004).

60. X. Ma and J. Yu, Formamide as the plasticizer for thermoplastic starch. *J. Appl. Polym. Sci.* **93**, 1769–1773 (2004).

61. R.L. Shogren, C.L. Swanson, and A.R. Thompson, Extrudates of cornstarch with urea and glycols: Structure/mechanical property relations. *Starch/Stärke* **44**, 335–338 (1992).

62. R. Shi, Z. Zhang, Q. Liu, Y. Han, L. Zhang, D. Chen, and W. Tian, Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydr. Polym.* **69**, 748–755 (2007).

63. J. Yu, N. Wang, and X. Ma, The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch/Stärke* **57**, 494–504 (2005).

64. N. Wang, J. Yu, P.R. Chang, and X. Ma, Influence of citric acid on the properties of glycerol-plasticized dry starch (DTPS) and DTPS/poly(lactic acid) blends. *Starch/Stärke* **59**, 409–417 (2007).

65. J.G. Yu, N. Wang, and X.F. Ma, The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. *Starch/Stärke* **57**, 494–504 (2005).

66. M.A. Garcia, A. Pinotti, and N.E. Zaritzky, Physicochemical, water vapor barrier and mechanical properties of corn starch and chitosan composite films. *Starch/Stärke* **58**, 453–463 (2006).

67. P. Forssell, R. Lahtinen, M. Lahelin, and P. Myllärinen, Oxygen permeability of amylose and amylopectin films. *Carbohydr. Polym.* **47**, 125–129 (2002).

68. J.-P. Onteniente, B. Abbès, and L.H. Safa, Fully biodegradable lubricated thermoplastic wheat starch: Mechanical and rheological properties of an injection grade. *Starch/Stärke* **52**, 112–117 (2000).

69. S. Keszei, A. Szabó, G. Marosi, P. Anna, and S. Nagy, Use of thermoplastic starch in continuous pharmaceutical process. *Macromol. Symp.* **239**, 101–104 (2006).

70. M. Thuwall, A. Boldizar, and M. Rigdahl, Extrusion processing of high amylose potato starch materials. *Carbohydr. Polym.* **65**, 441–446 (2006).

71. F. Xie, E. Pollet, P.J. Halley, and L. Avérous, Starch-based nano-biocomposites. *Prog. Polym. Sci.* **38**, 1590–1628 (2013).

72. F. Xie, Biodegradable starch-based nanocomposites, in *Wiley Encyclopedia of Composites (Second Edition)*, L. Nicolais (Ed.), pp. 102–114, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2011.

73. F. Xie, P.J. Halley, and L. Avérous, Bio-nancomposites based on starch, in *Nanocomposites with Biodegradable Polymers: Synthesis, Properties and Future Perspectives*, V. Mittal (Ed.), pp. 234–260, Oxford University Press, Oxford, UK, 2011.

74. M. Avella, J.J. De Vlieger, M.E. Errico, S. Fischer, P. Vacca, and M.G. Volpe, Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chem.* **93**, 467–474 (2005).

75. H.-M. Park, W.-K. Lee, C.-Y. Park, W.-J. Cho, and C.-S. Ha, Environmentally friendly polymer hybrids Part I: Mechanical, thermal, and barrier properties of thermoplastic starch/clay nanocomposites. *J. Mater. Sci.* **38**, 909–915 (2003).

76. H.-M. Park, X. Li, C.-Z. Jin, C.-Y. Park, W.-J. Cho, and C.-S. Ha, Preparation and properties of biodegradable thermoplastic starch/clay hybrids. *Macromol. Mater. Eng.* **287**, 553–558 (2002).

77. X. Tang, S. Alavi, and T.J. Herald, Barrier and mechanical properties of starch-clay nanocomposite films. *Cereal Chem.* **85**, 433–439 (2008).

78. M.-F. Huang, J.-G. Yu, and X.-F. Ma, Studies on the properties of Montmorillonite-reinforced thermoplastic starch composites. *Polymer* **45**, 7017–7023 (2004).

79. P. Sarazin, G. Li, W.J. Orts, and B.D. Favis, Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer* **49**, 599–609 (2008).

80. E. Schwach, J.-L. Six, and L. Avérous, Biodegradable blends based on starch and poly(lactic acid): Comparison of different strategies and estimate of compatibilization. *J. Polym. Environ.* **16**, 286–297 (2008).

81. N. Wang, J. Yu, and X. Ma, Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion. *Polym. Int.* **56**, 1440–1447 (2007).

82. N. Wang, J. Yu, P.R. Chang, and X. Ma, Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydr. Polym.* **71**, 109–118 (2008).

83. T. Ke, S.X. Sun, and P. Seib, Blending of poly(lactic acid) and starches containing varying amylose content. *J. Appl. Polym. Sci.* **89**, 3639–3646 (2003).

84. F. Xie, T. Xue, L. Yu, L. Chen, X. Li, and X. Zhang, Rheological properties of starch-based materials and starch/poly(lacticacid) blends. *Macromol. Symp.* **249–250**, 529–534 (2007).

85. R. Gattin, A. Copinet, C. Bertrand, and Y. Couturier, Biodegradation study of a starch and poly(lactic acid) co-extruded material in liquid, composting and inert mineral media. *Int. Biodeter. Biodegr.* **50**, 25–31 (2002).

SP

86. J. Guan, K.M. Eskridge, and M.A. Hanna, Acetylated starch-polylactic acid loose-fill packaging materials. *Ind. Crops Prod.* **22**, 109–123 (2005).

87. T. Ke and X. Sun, Effects of moisture content and heat treatment on the physical properties of starch and poly(lactic acid) blends. *J. Appl. Polym. Sci.* **81**, 3069–3082 (2001).

88. M. Mihai, M.A. Huneault, B.D. Favis, and H. Li, Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends. *Macromol. Biosci.* **7**, 907–920 (2007).

89. J.L. Willett and R.L. Shogren, Processing and properties of extruded starch/polymer foams. *Polymer* **43**, 5935–5947 (2002).

90. L. Bélard, P. Dole, and L. Avérous, Study of pseudo-multilayer structures based on starch-polycaprolactone extruded blends. *Polym. Eng. Sci.* **49**, 1177–1186 (2009).

91. S.B. Kalambur and S.S. Rizvi, Starch-based nanocomposites by reactive extrusion processing. *Polym. Int.* **53**, 1413–1416 (2004).

92. F. Xie, L. Yu, H. Liu, and K. Dean, Effect of compatibilizer distribution on thermal and rheological properties of gelatinized starch/biodegradable polyesters blends. *Int. Polym. Process.* **21**, 379–385 (2006).

93. P. Matzinos, V. Tserki, C. Gianikouris, E. Pavlidou, and C. Panayiotou, Processing and characterization of LDPE/starch/PCL blends. *Eur. Polym. J.* **38**, 1713–1720 (2002).

94. P. Matzinos, V. Tserki, A. Kontoyiannis, and C. Panayiotou, Processing and characterization of starch/polycaprolactone products. *Polym. Degrad. Stab.* **77**, 17–24 (2002).

95. O. Myllymäki, P. Myllärinen, P. Forssell, T. Suortti, K. Lähteenkorva, R. Ahvenainen, and K. Poutanen: Mechanical and permeability properties of biodegradable extruded starch/polycaprolactone films. *Packag. Technol. Sci.* **11**, 265–274 (1998).

96. H. Yavuz and C. Babaç, Preparation and biodegradation of starch/polycaprolactone films. *J. Polym. Environ.* **11**, 107–113 (2003).

97. J.A. Ratto, P.J. Stenhouse, M. Auerbach, J. Mitchell, and R. Farrell, Processing, performance and biodegradability of a thermoplastic aliphatic polyester/starch system. *Polymer* **40**, 6777–6788 (1999).

98. P.S. Walia, J.W. Lawton, R.L. Shogren, and F.C. Felker, Effect of moisture level on the morphology and melt flow behavior of thermoplastic starch/poly(hydroxy ester ether) blends. *Polymer* **41**, 8083–8093 (2000).

99. L. Zhang, X. Deng, S. Zhao, and Z. Huang, Biodegradable polymer blends of poly(3-hydroxybutyrate) and starch acetate. *Polym. Int.* **44**, 104–110 (1997).

100. J.L. Willett, M.A. Kotnis, G.S. O'Brien, G.F. Fanta, and S.H. Gordon, Properties of starch-graft-poly(glycidyl methacrylate)–PHBV composites. *J. Appl. Polym. Sci.* **70**, 1121–1127 (1998).

101. M.A. Huneault and H. Li, Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer* **48**, 270–280 (2007).

102. Z. Xiong, C. Li, S. Ma, J. Feng, Y. Yang, R. Zhang, and J. Zhu, The properties of poly(lactic acid)/starch blends with a functionalized plant oil: Tung oil anhydride. *Carbohydr. Polym.* **95**, 77–84 (2013).

103. Z. Xiong, Y. Yang, J. Feng, X. Zhang, C. Zhang, Z. Tang, and J. Zhu, Preparation and characterization of poly(lactic acid)/starch composites toughened with epoxidized soybean oil. *Carbohydr. Polym.* **92**, 810–816 (2013).

104. F. Xie, H. Liu, P. Chen, T. Xue, L. Chen, L. Yu, and P. Corrigan, Starch gelatinization under shearless and shear conditions. *Int. J. Food Eng.* **2**, Article 6/1–29 (2006).

105. F. Xie, L. Yu, L. Chen, and L. Li, A new study of starch gelatinization under shear stress using dynamic mechanical analysis. *Carbohydr. Polym.* **72**, 229–234 (2008).

106. T. Xue, L. Yu, F. Xie, L. Chen, and L. Li, Rheological properties and phase transition of starch under shear stress. *Food Hydrocolloids* **22**, 973–978 (2008).

107. F. Xie, P. Liu, and L. Yu, Processing of plasticized starch-based materials: State of art and perspectives, in *Starch Polymers: From Genetic Engineering to Green Applications*, P.J. Halley and L.R. Avérous (Eds.), pp. 257–289, Elsevier, Amsterdam, Boston, Heidelberg, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, 2014.

108. W.-C. Liu, P.J. Halley, and R.G. Gilbert, Mechanism of degradation of starch, a highly branched polymer, during extrusion. *Macromolecules* **43**, 2855–2864 (2010).

109. R. Stute, R.W. Klingler, S. Boguslawski, M.N. Eshtiaghi, and D. Knorr, Effects of high pressures treatment on starches. *Starch-Stärke* **48**, 399–408 (1996).

110. M. Gropper, C.I. Moraru, and J.L. Kokini, Effect of specific mechanical energy on properties of extruded protein-starch mixtures. *Cereal Chem. J.* **79**, 429–433 (2002).

111. M. Das, Effect of screw speed and plasticizer on the torque requirement in single screw extrusion of starch based plastics and their mechanical properties. *Indian J. Chem. Technol.* **15**, 555–559 (2008).

112. B. Su, F.W. Xie, M. Li, P.A. Corrigan, L. Yu, X.X. Li, and L. Chen, Extrusion processing of starch film. *Int. J. Food Eng.* **5**(1), Article 7/1–12, (2009).

113. S. Kalambur and S.S.H. Rizvi, An overview of starch-based plastic blends from reactive extrusion. *J. Plast. Film Sheeting* **22**, 39–58 (2006).

114. F. Xie, L. Yu, H. Liu, and L. Chen, Starch modification using reactive extrusion. *Starch/Stärke* **58**, 131–139 (2006).

115. G. Moad, Chemical modification of starch by reactive extrusion. *Prog. Polym. Sci.* **36**, 218–237 (2011).

116. K. Frost, J. Barthes, D. Kaminski, E. Lascaris, J. Niere, and R. Shanks, Thermoplastic starch-silica-polyvinyl alcohol composites by reactive extrusion. *Carbohydr. Polym.* **84**, 343–350 (2011).

117. Z. Xiong, L. Zhang, S. Ma, Y. Yang, C. Zhang, Z. Tang, and J. Zhu, Effect of castor oil enrichment layer produced by reaction on the properties of PLA/HDI-g-starch blends. *Carbohydr. Polym.* **94**, 235–243 (2013).

118. R.M.S.M. Thiré, R.A. Simão, and C.T. Andrade, High resolution imaging of the microstructure of maize starch films. *Carbohydr. Polym.* **54**, 149–158 (2003).

119. I. Tan, C.C. Wee, P.A. Sopade, and P.J. Halley, Estimating the specific heat capacity of starch-water-glycerol systems as a function of temperature and compositions. *Starch/Stärke* **56**, 6–12 (2004).

120. F. Xie, W.-C. Liu, P. Liu, J. Wang, P.J. Halley, and L. Yu, Starch thermal transitions comparatively studied by DSC and MTDSC. *Starch/Stärke* **62**, 350–357 (2010).

121. I. Tan, P.J. Torley, and P.J. Halley, Combined rheological and optical investigation of maize, barley and wheat starch gelatinisation. *Carbohydr. Polym.* **72**, 272–286 (2008).

122. S. Tajuddin, F. Xie, T.M. Nicholson, P. Liu, and P.J. Halley, Rheological properties of thermoplastic starch studied by multipass rheometer. *Carbohydr. Polym.* **83**, 914–919 (2011).

123. R.B. Maliger, S.A. McGlashan, P.J. Halley, and L.G. Matthew, Compatibilization of starch-polyester blends using reactive extrusion. *Polym. Eng. Sci.* **46**, 248–263 (2006).

124. M.A.L. Russo, C. O'Sullivan, B. Rounsefell, P.J. Halley, R. Truss, and W.P. Clarke, The anaerobic degradability of thermoplastic starch: Polyvinyl alcohol blends: Potential biodegradable food packaging materials. *Bioresour. Technol.* **100**, 1705–1710 (2009).

125. M.A.L. Russo, R. Truss, and P.J. Halley, The enzymatic hydrolysis of starch-based PVOH and polyol plasticised blends. *Carbohydr. Polym.* **77**, 442–448 (2009).

126. L. Moghaddam, L. Rintoul, P.J. Halley, and P.M. Fredericks, Infrared microspectroscopic mapping of the homogeneity of extruded blends: Application to starch/polyester blends. *Polym. Test.* **25**, 16–21 (2006).

127. P. Halley, R. Rutgers, S. Coombs, J. Kettels, J. Gralton, G. Christie, M. Jenkins, H. Beh, K. Griffin, R. Jayasekara, and G. Lonergan, Developing biodegradable mulch films from starch-based polymers. *Starch/Stärke* **53**, 362–367 (2001).

128. M.A.L. Russo, E. Strounina, M. Waret, T. Nicholson, R. Truss, and P.J. Halley, A study of water diffusion into a high-amylose starch blend: The effect of moisture content and temperature. *Biomacromolecules* **8**, 296–301 (2007).

129. C.M. Chaleat, P.J. Halley, and R.W. Truss, Properties of a plasticised starch blend. Part 1: Influence of moisture content on fracture properties. *Carbohydr. Polym.* **71**, 535–543 (2008).

130. C.M. Chaléat, G. Michel-Amadry, P.J. Halley, and R.W. Truss, Properties of a plasticised starch blend—Part 2: Influence of strain rate, temperature and moisture on the tensile yield behaviour. *Carbohydr. Polym.* **74**, 366–371 (2008).

131. S. Mateyawa, D.F. Xie, R.W. Truss, P.J. Halley, T.M. Nicholson, J.L. Shamshina, R.D. Rogers, M.W. Boehm, and T. McNally, Effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on the phase transition of starch: Dissolution or gelatinization? *Carbohydr. Polym.* **94**, 520–530 (2013).

132. C.M. Chaleat, M. Nikolic, R.W. Truss, I. Tan, S.A. McGlashan, and P.J. Halley, Thermoplastic starch polymer blends and nanocomposites, in *Biobased Monomers, Polymers, and Materials*, Volume **1105**, American Chemical Society, Washington, DC, 2012.