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# Amylose content and chemical modification effects on thermoplastic starch from maize – Processing and characterisation using conventional polymer equipment

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ABSTRACT

A design of experiments was performed on extruded starch based materials studied in a recently published article [Chaudhary, A. L., Miler, M., Torley, P. J., Sopade, P. A., & Halley, P. J. (2008). Amylose content and chemical modification effects on the extrusion of thermoplastic starch from maize. *Carbohydrate Polymers, 74*(4), 907–913] highlighting the effects of amylose content, chemical modification and extrusion on a range of maize starches. An investigation into the effects of starch type (unmodified 0–80% amylose starch; hydroxypropylated 80% amylose starch), screw speed and ageing after moulding on final product properties such as mechanical properties (Young's modulus, maximum stress and strain at break), moisture absorption, morphology and retrogradation are included. A full factorial design was used to study these starch type, processing and final product property relationships. Microscopy was used to observe any morphological difference between the various starch types in thermoplastic starch (TPS) blends and X-ray diffraction (XRD) was used to observe changes in crystallinity over time (retrogradation). The results show that 0% amylose (waxy maize) and hydroxypropylated 80% amylose thermoplastic starches have mechanical properties comparable to that of low density polyethylene (LDPE) and high density polyethylene (HDPE), therefore these materials have the potential to be an environmentally friendly alternative to current polymer resins.

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## 1. Introduction

Plastic packing companies currently using conventional polymers such as LDPE and HDPE plastics are experiencing increasing pressure from existing and proposed environmental and disposal regulations to decrease use and find more sustainability initiatives. Starch is one such initiative, a biopolymer that can be converted into a useful thermoplastic (Nabar, Narayan, & Schindler, 2006; Yu, Gao, & Lin, 1996) and can be safely and effectively disposed of in the soil or by a composting operation (Scandola et al., 1998). However, questions remain as to whether or not starch based thermoplastics (TPS) can provide all the required end-product performance characteristics of: (i) ease of moulding, (ii) thermal stability during moulding, (iii) mechanical properties and (iv) dimensional stability. As a result, research into mouldable TPS resin needs to be continued to meet these performance requirements.

Blends of TPS and synthetic materials have shown that starch based materials have the potential to replace materials such as polyethylene (PE), polypropylene (PP) and polystyrene (PS). The moulding of different amylose content starches blended with a range of non-biodegradable synthetic polymers such as ethylene–vinyl acetate (EVA) and low density polyethylene maleic anhydride (EMA) (Mani & Bhattacharya, 1998), found an improvement with high amylose starch mechanical properties (including a high tensile strength and higher elongation) over blends that contained 25% amylose or less. However, their material properties were unstable, with a significant reduction in elongation when the materials were stored for more than 2 weeks. Another disadvantage to blending starch with synthetic polymers is that biodegradation will simply cause the removal of the starch, leaving a residue of polyolefin (Zheng, Yanful, & Bassi, 2005). In another study it was shown that a wheat based TPS with the addition of magnesium stearate was suitable for injection moulding processing, but the resultant product was brittle with reduced mechanical properties when compared to injection moul-

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ded semi-crystalline polypropylene and amorphous polystyrene (Onteniente, Abbes, & Safa, 2000). Therefore, the current state of thermoplastic starches research has not fully developed a biodegradable product with the required properties to replace non-biodegradable plastics in a wide range of applications.

Dimensional stability over time is of main concern when producing thermoplastic products. Water is required to manufacture TPS to ensure gelatinisation and the formation of a continuous thermoplastic phase however; secondary processes such as compression moulding and injection moulding typically require the elimination of water. Industrial injection moulding resins are often dried using a desiccant drier to reduce resin decomposition during processing. Dry resin reduces the risk of bubbling due steam evolution and ensures dimensional stability over time for the final product (Nabar et al., 2006; Stepto, 2003). Starch in particular is highly sensitive to moisture and more research needs to been done to determine the appropriate moisture content necessary for processing TPS.

In a study of TPS sheet development (Yu & Christie, 2005) it was observed that two factors contributed significantly to TPS shrinkage: loss of moisture and recrystallisation. In TPS research the loss of moisture and the associated dimensional changes is often avoided by storing resin at high relative humidity (Mani & Bhattacharya, 1998; Onteniente et al., 2000; Rosa & Andrade, 2004), even though under ambient conditions moisture loss is likely. Another study (Stepto, 2003) highlighted the importance of moisture control for injection moulding, stating that if high water contents are used in processing of TPS, distortion and shrinkage will occur as the equilibrium water content is naturally achieved after processing. Moisture content control and moisture absorption by the final product during storage has not been yet been properly addressed.

The focus of these experiments was to investigate the effects of starch type (unmodified 0–80% amylose starch; hydroxypropylated 80% amylose starch), screw speed and ageing after moulding on final product properties such as mechanical properties (Young's modulus, maximum stress and strain at break), moisture absorption, morphology and retrogradation. This study extends the understanding of the extrudate that was produced in a previous study (Chaudhary, Miler, Torley, Sopade, & Halley, 2008) by manipulating processing conditions specifically, changes in screw speed. Screw speed is a significant input variable as it translates into frictional heat and thus affects parameters such as shear and extent of mixing of materials within the extruder. A full factorial design was used to study these starch type, processing and final product property relationships. Microscopy was used to observe any morphological difference between the various starch types in the TPS blends as well as give an indication on the degree of gelatinisation for each. X-ray diffraction patterns of the aged TPS were also obtained to observe changes in crystallinity over time (retrogradation).

## 2. Materials

The materials used to manufacture the TPS resin were described in Chaudhary et al. (2008). Plasticisers and emulsifiers were added (in accordance to US Patent No. 7094817) to the starch with an increased level of polyols to produce a thermoplastic starch (TPS) resin suitable for injection moulding applications. A summary of starch type, amylose content and moisture content of the TPS pellets measured after extrusion are given in Table 1.

**Table 1**
TPS description with amylose content and moisture content values.

| Product name | Starch type | Amylose content (%)[a] | Moisture content (%)[b] |
|---|---|---|---|
| Mazaca 3401X | Unmodified waxy maize | 0 | 14.8 |
| Avon Maize Starch | Unmodified regular maize | 28 | 13.7 |
| Gelose 50 | Unmodified high amylose | 50 | 13.5 |
| Gelose 80 | Unmodified high amylose | 80 | 12.9 |
| Gelose 939 | Hydroxypropylated high amylose | 80 | 14.7 |

[a] As specified by Penford Australia.
[b] Moisture content determined using Sartorius Moisture Content Analyser with an error of ±0.0002.

## 3. Methodology

### 3.1. Compression moulding

TPS pellets were compression moulded according to the compression moulding ASTM (D4703-03, 2003). The pellets were moulded at 12–15% moisture content, at 130 °C for 5 min, using 90 Pa of pressure then cooled for approximately 2 min at the same pressure. The stainless steel mould plate was 0.09 × 0.09 m with a thickness of 0.018 m. As compression moulding conditions can affect mechanical properties of the starch material (Thuwall, Boldizar, & Rigdahl, 2006a, 2006b) all sheets were compression moulded under the same conditions.

### 3.2. Conditioning

The moulded sheets were cut into tensile testing bars for mechanical testing and 0.02 × 0.02 m squares for X-ray diffraction (XRD) analysis immediately after compression moulding. The TPS materials were dried to a moisture content of 1% and minimal shrinkage was observed (less than 2%). Once the samples were dried they were placed in the humidity cabinet for conditioning (ASTM D618-05, 2005) at 23 °C and a relative humidity (RH) of 50% ± 5%. The samples were stored for three ageing times, 1, 7 and 14 days.

### 3.3. Mechanical properties testing

All mechanical properties were measured according to the mechanical property ASTM (D638-03, 2003). The tests were performed on an Instron 5584 fitted with a 100 N load cell. The Instron was controlled by BlueHill software (Version 2, Instron Corporation, Norwood, USA), and the same software was used to calculate mechanical properties. The samples were held in small pneumatic grips with a gripping pressure of 40 kN. Tests were performed at a cross head speed of 5 mm/min, which was chosen according to the geometry of the "dog bone" test bar as specified in the ASTM. The tests were conducted in a controlled environment of 23 °C and 45% ± 5% relative humidity. The mechanical properties of a minimum of five test bars were measured and the average calculated.

### 3.4. Moisture content

Samples of compression moulded sheet conditioned at 23 °C, RH 50% for 1, 7 and 14 days were ground under cryogenic conditions into a powder and the moisture content was measured gravimetrically according to the International Standard (ISO 1666, 1996). The samples were weighed, placed into an oven and dried at 130 °C for 24 h then re-weighed. In view of the volatility of glycerol, heating under vacuum was not used (Averous & Fringant, 2001).

### 3.5. Microscopy

The microstructure of raw and extruded TPS was examined using light microscopy. Each of the raw starches and very thin slices of extruded material were placed onto glass slides and exam-

**Table 2**
ANOVA for starch type, screw speed and ageing with interactions (α = 0.05).

| Input variables | Young's modulus | | Maximum stress | | Strain at break | | Moisture content | |
|---|---|---|---|---|---|---|---|---|
| | $P > F$ | Significance | $P > F$ | Significance | $P > F$ | Significance | $P > F$ | Significance |
| Starch type | <0.001 | ** | 0.002 | ** | <0.001 | ** | 0.02 | * |
| Screw speed | 0.22 | NS | 0.62 | NS | 0.86 | NS | 0.11 | NS |
| Replicate | 0.04 | * | 0.38 | NS | <0.001 | ** | 0.0005 | ** |
| Ageing | <0.001 | ** | <0.001 | ** | 0.014 | * | <0.001 | ** |
| Starch type * Screw speed | 0.69 | NS | 0.57 | NS | 0.55 | NS | 0.87 | NS |
| Starch type * Ageing | <0.001 | ** | <0.001 | ** | 0.42 | NS | 0.46 | NS |
| Screw speed * Ageing | 0.41 | NS | 0.48 | NS | 0.79 | NS | 0.11 | NS |
| Starch type * Screw speed * Ageing | 0.39 | NS | 0.58 | NS | 0.95 | NS | 0.56 | NS |

F: variance ratio between variable mean square.
*p*: probability of the event not being random.
**$p < 0.01$ very significant.
*$0.01 < p < 0.05$ significant.
NS no significant difference ($p > 0.05$).

ined with an Olympus AX70 Provis microscope fitted with a Universal Photo System camera using transmitted light at magnifications of 50×. The images were analysed with Spot digital software (Version 4.5, Diagnostic Instruments, Stirling Heights, USA).

### 3.6. X-ray diffraction

XRD tests were performed on compression moulded samples after being conditioned at 23 °C, 50% RH for 1, 7 and 14 days, respectively. These samples were placed in the sample holder of the X-ray diffractometer (D8 Advance X-ray Diffractometer, Bruker, Madison, USA) equipped with a graphite monochromator, copper target and scintillation counter (detector). XRD patterns were recorded for an angular range ($2\theta$) of 2–40°, with a step size of 0.01°, step rate of 1 s per step and for a scan time of approximately 1 h. The radiation parameters were set at 30 kV, 40 mA with a variable slit of 20 mm. Traces were processed using the Diffrac$^{plus}$ Evaluation Package (Version 11.0, Bruker, Madison, USA) to determine the X-ray diffractograms for each specimen.

### 3.7. Experimental design and statistical analysis

The experimental design used to prepare the thermoplastic starch was selected to systematically determine the effect of the extent of mechanical treatment (by varying screw speed) on the extrusion of different starches (Chaudhary et al., 2008). The current study also examines the effect of ageing time on thermomoulded samples made from extruded thermoplastic starch pellets.

Starch retrogradation is scientifically and technologically important since it leads to significant changes in mechanical properties (Lionetto, Maffezzoli, Ottenhof, Farhat, & Mitchell, 2005) thus affecting the final TPS product characteristics. Storing TPS samples and analysing its ageing properties (i.e. mechanical properties at various storage times) can provide valuable insight into starch retrogradation. Therefore, three ageing times (1, 7 and 14 days) were studied to monitor changes in microstructure and mechanical properties.

A multivariable random block design was devised to analyse the relationships of input variables to outputs and to quantify the significance of each. The factors studied were: starch type (unmodified starch containing 0%, 27%, 50% and 80% amylose; hydroxypropylated starch containing 80% amylose), screw speed (250, 300 and 350 rpm) and ageing time (1, 7 and 14 days). The whole design was done in triplicate, giving a total of 135 trials. SAS for Windows (Version 9.1, SAS Institute Cary, North Carolina, USA, 2003) and JMP6 (SAS Institute Cary, North Carolina, USA) software were used to analyse data.

## 4. Results and discussion

### 4.1. Statistical analysis

The analysis of variance (ANOVA) from these experiments can be seen in Table 2. These results show that starch type significantly affected Young's modulus, maximum stress, strain at break and absorption moisture content. Screw speed had no significant effect on any of the output variables. Ageing, like starch type, had a significant effect on all of the outputs. The interaction between starch type and ageing significantly affected the Young's modulus and maximum tensile stress. There were no significant interactions between starch type and screw speed or the interaction between screw speed and ageing. The three way interaction of starch type, screw speed and ageing also had no significant effect on any of the output variables.

Although screw speed had a significant effect on extrusion variable (Chaudhary et al., 2008), the extrudate analysis showed that screw speed did not significantly effect on mechanical properties or moisture studies. This is consistent with earlier studies of starch extrusion where screw had an effect on variables such as expansion and pasting properties (Blanche & Sun, 2004) but had a lesser effect on bulk density and water absorption (Guha, Zakiuddin Ali, & Bhattacharya, 1997). In another example, in a study of extruded high and low amylose potato starches, it was shown that starch type rather than screw speed had a significant influence on mechanical properties (Thuwall et al., 2006a, 2006b).

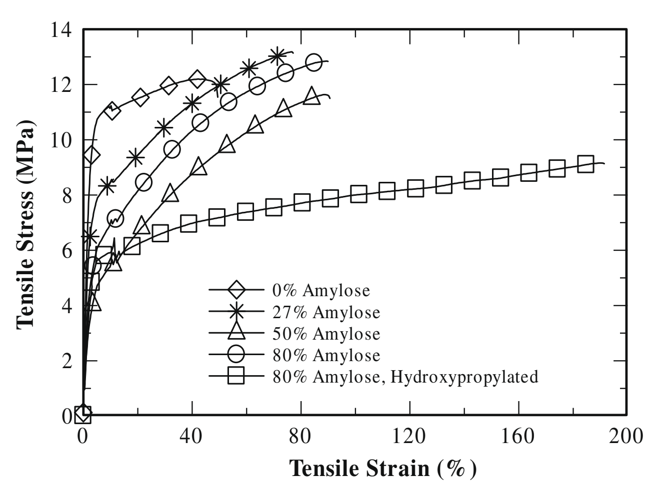


**Fig. 1.** Typical stress–strain curves for the TPS materials. Note that for clarity, only every 25th point has been plotted.

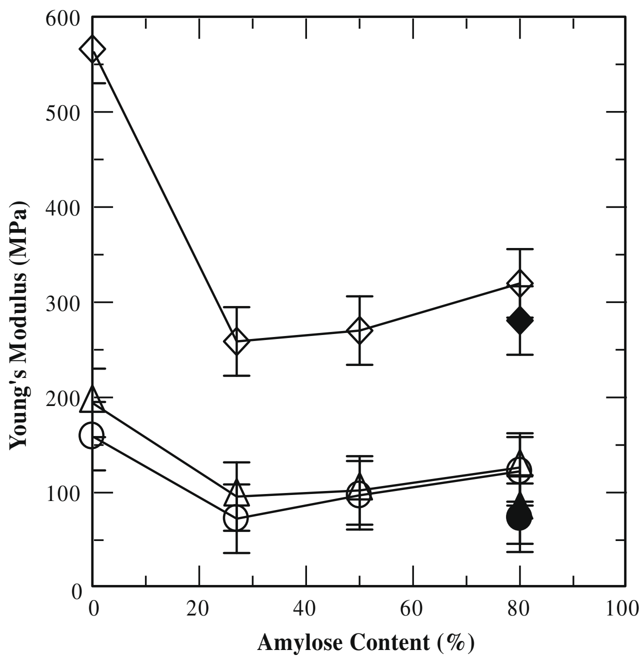


**Fig. 2.** The interaction between starch type and ageing on Young's modulus. Legend: Day 1, ◇◆; Day 7, △▲; Day 14, ○●; unmodified starch, ◇△○; hydroxypropylated starch, ◆▲●. Error bars represent the least significant difference.

### *4.2. Young's modulus*

Typical stress–strain curves for different thermoplastic starches are shown in Fig. 1. The Young's modulus for the TPS materials ranged from 56 to 606 MPa with a mean value of 112.7 MPa. Statistical data showed that starch type, ageing and the interaction between the two (Fig. 2) had a significant effect on Young's modulus. Screw speed and all other interactions (starch type and screw speed, ageing and screw speed and starch type, screw speed and ageing interactions) had no significant effect.

A comparison of starch type shows that the Young's modulus of waxy maize starch is significantly higher than all the other starches, particularly on Day 0 (Fig. 2). On the opposite end of the scale for unmodified starches, 28% amylose TPS had the lowest modulus on all days, though the difference between it and the 50% and 80% amylose starches was relatively small. This may be a result of several factors. First, the high modulus of waxy maize TPS may be due to the amylopectin molecules being more branched in structure, less ordered and having a greater degree of entanglement (De Graaf, Karman, & Janssen, 2003). The entangled chains limit the molecular movement thus increasing the stiffness (De Graaf et al., 2003). Second, for TPS containing amylose, an increase in modulus with an increase in amylose content occurs due to entanglement of long amylose chains (Van Soest & Borger, 1997). The entanglement of the amylose chains and the formation of strong hydrogen bonding results in higher glass transition temperatures of the amorphous materials (Hulleman, Kalisvaart, Janssen, Feil, & Vliegenthart, 1999; Thuwall et al., 2006a, 2006b) thus increasing modulus. However, the higher modulus for waxy maize starch suggests that the branched amylopectin chain entanglement is stronger than the hydrogen bonding found in the higher amylose content samples. More research should be done to confirm this conclusion.

The modified 80% amylose TPS results (145 MPa) showed a reduction in modulus compared to unmodified 80% amylose TPS (190 MPa). This is expected as hydroxypropylation is known to influence the interaction between starch chains by steric hindrance, preventing close association of chains thereby restricting formation of inter-chain hydrogen bonds (Liu, Ramsden, & Corke, 1999). The weaker hydrogen bonding between starch chains within the hydroxypropylated starch matrix produced a material with a lower stiffness.

Ageing also had a pronounced effect on the modulus, with a marked decrease between Day 1 and Day 7 for all samples, and a further small decrease between Day 7 and Day 14. The most marked decrease with ageing occurred in the waxy maize sample, though the relative decrease was similar to the other starch (28% decrease for waxy maize; 28% for 27% amylose; 36% for 50% amylose; 38% for 80% amylose; and 26% for hydroxypropylated 80% amylose). This is due to the high level of plasticiser (30%) interacting with moisture in the system, which increases the free volume of the starch matrix, bringing the material closer to its glass transition (Benczedi, 1999) thus, over time, Young's modulus is reduced.

It is interesting to observe that both unmodified and modified 80% amylose samples showed no difference in modulus at Day 7 and Day 14, while the modulus of the lower amylose starches (0% and 28% amylose content) showed a slight decrease over time (indicating that the low amylose starches had not reached moisture equilibrium). This behaviour suggests that high amylose starches reach equilibrium at a faster rate compared to the lower amylose starches for the same temperature and relative humidity. In contrast, when potato starch with different amylose contents (27%, 55%, 70% and 87%) was compression moulded, it took 6 days for all compression moulded starches to reach moisture content equilibrium (20 °C, 60% RH) (Van Soest & Borger, 1997). However, in their study, the potato TPS mixture did not undergo extrusion prior to compression moulding (the raw materials were premixed then applied to the mould). Thus, the TPS material may not have a well structured starch matrix allowing moisture to move into the system more easily than the materials produced in this study.

### *4.3. Maximum stress*

The maximum stress values from the design of experiments ranged from 4.6 to 13.3 MPa with a mean value of 6.5 MPa. As with the Young's modulus results, maximum stress was significantly af-

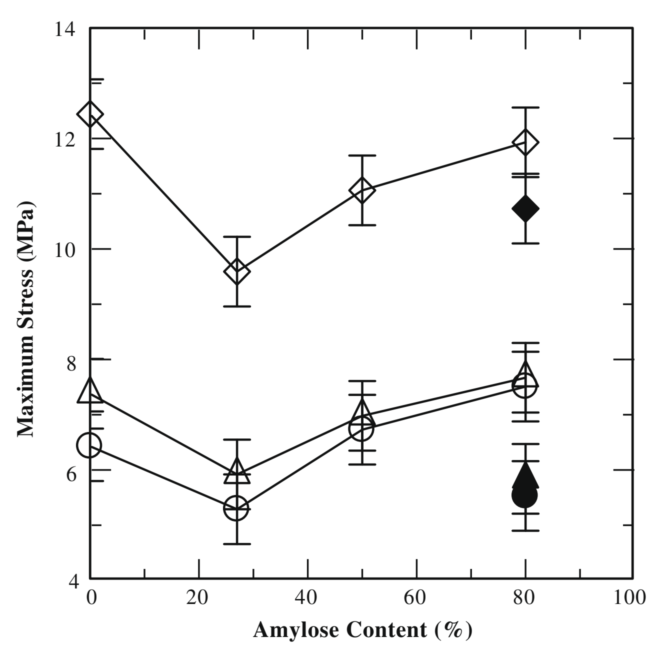


**Fig. 3.** The interaction between starch type and ageing on maximum stress. Legend: Day 1, ◇◆; Day 7, △▲; Day 14, ○●; unmodified starch, ◇△○; hydroxypropylated starch, ◆▲●. Error bars represent the least significant difference.

fected by starch type, ageing and the interaction between starch type and ageing (Fig. 3) but was not affected by screw speed or by any other interactions between the input variables.

Again, the maximum stress for the waxy maize TPS (8.8 MPa) does not follow the general trend of the amylose TPS indicating that there the behaviour of amylopectin chains is different from the combined amylose/amylopectin network. Similar to observations seen with Young's modulus the 28% amylose samples had low strength (6.9 MPa) compared to the waxy maize samples, and then maximum stress progressively increased with increasing amylose content (Fig. 3). The yield strength of the modified 80% amylose sample was also less than that of the unmodified 80% amylose sample. The variation in maximum stress (and also modulus) with amylose can be explained by the amount of amylose and structure of amylopectin molecules. High amylose TPS materials tend to be tougher than low amylose, as amylose interactions with branched amylopectin molecules increases, leading to entanglements of double helix structures of amylose and the outer chains of amylopectin (Van Soest & Borger, 1997) strengthening the TPS. Higher amylose contents have a higher degree of interactions, hence the increase in strength.

Again, similar to the Young's modulus results, the maximum stress for Day 1 is significantly more than Days 7 and 14 (Fig. 3). The decrease in maximum stress over time for waxy maize TPS and 28% amylose TPS, shows that equilibrium had not been achieved. However, the higher amylose TPS (50% and 80% amylose) values remain constant from Day 7 through to Day 14. Overall this indicates that higher amylose starches reach equilibrium sooner.

### 4.4. Strain at break

The strain at break results showed that the TPS materials could withstand 57–204.3% strain prior to failure, with an average strain at break value of 110.8%. Starch type and ageing significantly influenced strain at break whereas screw speed and all other parameter interactions had no significant effects.

Fig. 4 shows that the waxy maize starch had a statistically significantly lower strain at break (74%) compared to the all other unmodified starches (90–95%). The modified 80% amylose sample had a markedly higher strain at break (183%). The higher strain at break of the hydroxypropylated starch is because the hydroxypropyl group gives the starch molecule greater flexibility as there is steric hindrance preventing close chain association and restricting inter-chain hydrogen bonding (Liu et al., 1999). This allows for the starch chains to slide past each other more easily hence the increase in elongation. This is a significant result as some products made by thermoplastic forming (e.g. disposable plates) require a certain amount of flexibility which the hydroxypropylated 80% amylose TPS provides.

The effect of ageing at 23 °C, 50% RH on strain at break can be seen in Fig. 4. Strains at Day 1 (100%) are significantly lower than at Days 7 (108%) and 14 (113%). It is also interesting to note that strain values for Days 7 and 14 are not statistically different. The result from strain at break negatively correlates to the reduction of Young's modulus with time. Therefore, this plasticiser/moisture interaction results in a decrease modulus as well as an increase in percent elongation.

### 4.5. Moisture absorption

Sorption behaviour in the presence of polyol plasticisers has a significant effect on shelf life and mechanical properties of the thermoplastic starch products. An investigation of starch–moisture–plasticiser interactions (Enrione, Hill, & Mitchell, 2007) found that glass transition ($T_g$) of extruded starch samples showed a dependency on moisture and polyol concentrations. Increasing levels of both water and glycerol decreased the $T_g$, with the effect of glycerol level decreasing with increasing water level (Enrione et al., 2007). It is also well understood that properties of a glassy polymer approaching its $T_g$ tend to be time dependent. Because water/polyol interactions significantly affect the $T_g$, understanding the diffusion of water into the system can give information related to the structural mobility of the solid (Enrione et al., 2007).

The moisture absorption results showed that at 23 °C, 50% RH for periods of 1, 7 and 14 days, the TPS sheet moisture content ranged from 3.3% to 5%. The mechanical testing results (Figs. 1–4) have already shown that ageing can significantly affect final product properties possibly due to changes in moisture content. Starch type and ageing significantly affect sample moisture content, however, screw speed and all interactions had no significant effect (Table 2).

Fig. 5A shows the difference of starch type on moisture content of the TPS. There is a slight, but significant, increase in moisture content with increased amylose content. This trend contradicts observations by Mani and Bhattacharya (1998) where starches with different amylose contents were blended with EVA or LDPE. They reported that low amylose starches (waxy maize) absorbed more water than higher amylose contents (25% and 70%) due to increased gelatinisation and degradation of the amylopectin. The dif-

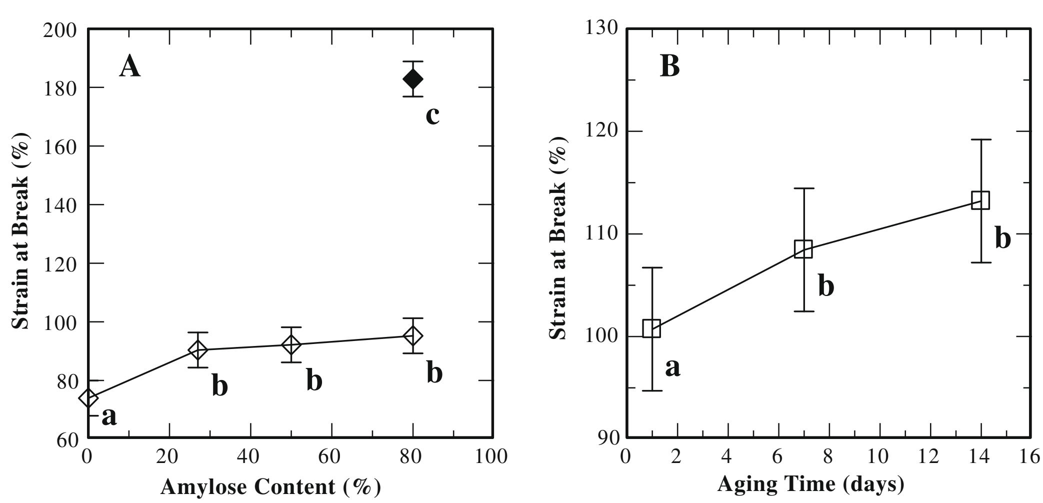


**Fig. 4.** The effect of (A) starch type and (B) ageing time on the strain at break of thermoplastic starch. Legend: Unmodified starch, ◇; hydroxypropylated starch, ♦; a, b, c – means with the same letters are not significantly different ($p > .05$). Error bars represent the least significant difference.

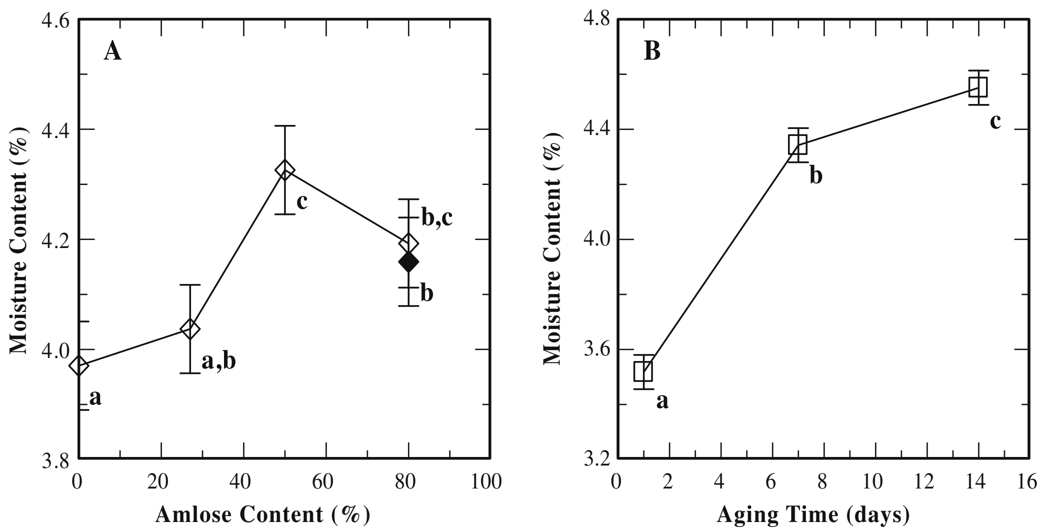


**Fig. 5.** The effect of (A) starch type and (B) ageing time on moisture absorption by thermoplastic starch. Legend: Unmodified starch, ◇; hydroxypropylated starch, ♦; a, b, c – means with the same letters are not significantly different ($p > .05$). Error bars represent the least significant difference.

ference in moisture absorption behaviour between this study, and the present study could be the presence of plasticisers interacting with amylose increasing its ability to re-absorb moisture at a faster rate (Benczedi, 1999; Enrione et al., 2007).

Both the unmodified and modified 80% amylose TPS attained the same average moisture content of approximately 4.2%. The modified TPS was initially lower than the unmodified TPS indicating that over the 14 day period the modified TPS absorbed water at a faster rate. This is indicative of hydroxypropylated starch, that is, increased hydrophilicity (Liu et al., 1999). Also, the torque and specific mechanical energy (SME) results (Chaudhary et al., 2008) showed that hydroxypropylated starch was markedly lower than that of 80% amylose unmodified starch. This too was an indication of the increased hydrophilic nature of the modification.

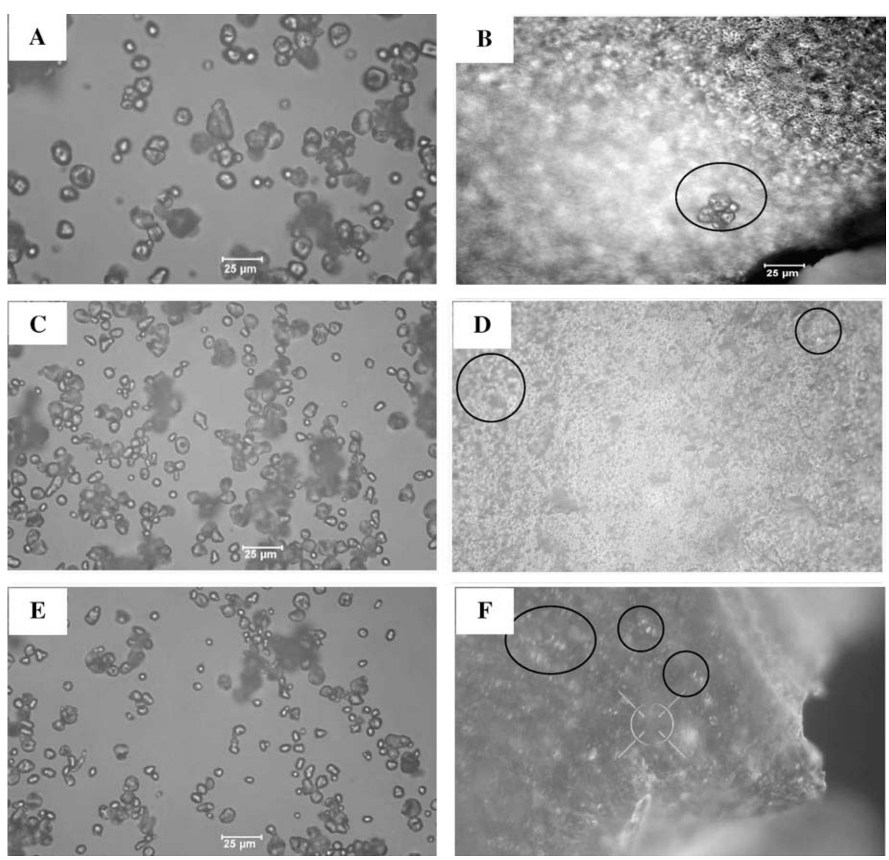


**Fig. 6.** Light microscopy images taken at 50× magnification of (A, C and E) raw starches and (B, D and F) thermoplastic starch. Legend: (A) unprocessed and (B) extruded and thermoformed 27% amylose starch; (C) unprocessed; (D) extruded and thermoformed 50% amylose starch; (E) unprocessed; (F) extruded and thermoformed hydroxypropylated 80% amylose starch. Samples B and D show the thermoplastic starch matrix with gelatinised granules (circled). Sample F shows a high level of ungelatinised starch granules (circled).

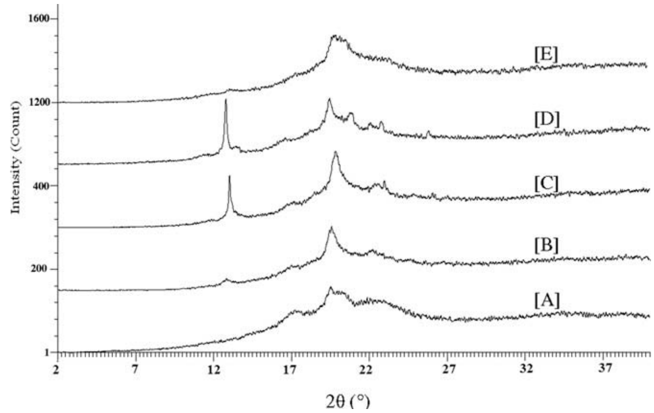


**Fig. 7.** Typical X-ray diffraction scans for TPS Day 7. [A] Waxy maize, [B] 28% amylose, [C] 50% amylose, [D] 80% amylose and [E] hydroxypropylated 80% amylose thermoplastic starch.

As shown in Fig. 5B, moisture content increased progressively during ageing, with each of the three ageing times significantly different from the others. Since the moisture content increased between Day 7 and Day 14, it is not possible to say if the samples have reached equilibrium moisture content by Day 14. A study of the environmental stability of injection moulded TPS at 30 °C, 90% RH (Liu, Yi, & Feng, 2001) showed a similar trend of moisture sorption with time. The higher relative humidity accounts for the faster rate of absorption when compared to the results in the current study.

### 4.6. Microscopy

Unprocessed starch granules are birefringent, and when observed with polarised light show a characteristic Maltese cross. A loss of birefringence within the granule indicates a change in morphology and crystallinity. Fig. 6 shows that the 0% and 28% amylose starch raw granules are rounder and have a higher average particle size than the 50% and 80% amylose starches. The 50% and 80% amylose starches have less regular shaped smaller granules and have no bright Maltese crosses, which is consistent with other literature observations (Van Soest & Borger, 1997).

The TPS samples differed in the number of starch granules and granular ghosts (partially gelatinised granules) that were found. The unmodified high amylose TPS (50% and 80%) showed a relatively large number of ungelatinised starch granules compared to the low amylose TPS (0% and 28%) and modified starch. This indicates that the process may not have been adequate, either too low moisture content or too low in screw speed, to fully gelatinise the high amylose starches.

In contrast to the unmodified high amylose starches, it appears that the modified high amylose TPS showed a more uniform TPS phase. This is an indication that the hydroxypropylated starch being almost completely gelatinised. The changes to granular and molecular structure induced by hydroxypropylation appear to have facilitated penetration and adsorption of the starch granules more readily than the unmodified starches, which ultimately lead to more swelling of starch and leads to a great degree of gelatinisation (Pal, Singhal, & Kulkarni, 2002).

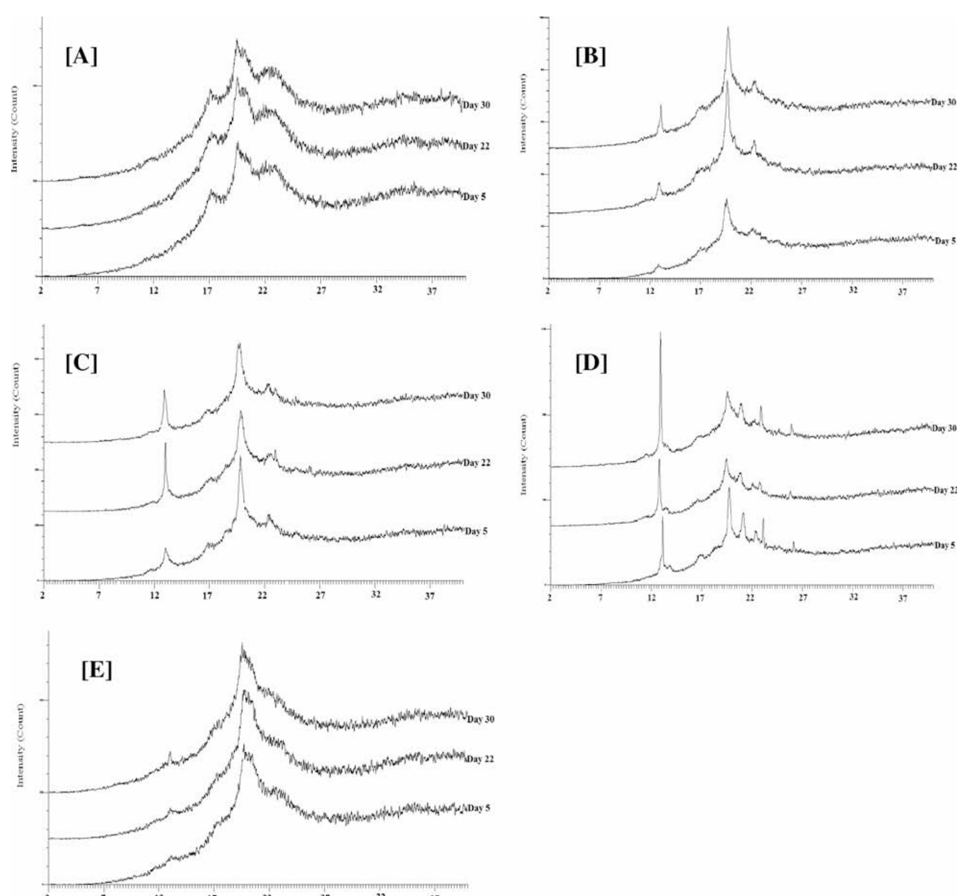


**Fig. 8.** Changes in X-ray diffraction patterns for 1 day conditioning (XRD taken on Day 5), 7 days conditioning (XRD taken on Day 22) and 14 days conditioning (XRD taken on Day 30) [A] waxy maize, [B] 28% amylose, [C] 50% amylose, [D] 80% amylose and [E] hydroxypropylated 80% amylose starch.

Overall, despite evidence of residual starch granules, the TPS phase was largely uniform indicating a relatively high degree of gelatinisation for all materials.

### 4.7. X-ray diffraction

Retrogradation is a term used to describe the physico-chemical changes of starch with time, specifically, the rearrangement of polymeric chains into crystalline domains after it has gone through the gelatinisation process (Yu & Christie, 2005). Such recrystallisation limits the practical use of starch based polymers, as starch based polymers become rigid and brittle during long term storage, which means their industrial value is lost (Huang, Yu, & Ma, 2005).

Amylose and amylopectin have different roles in retrogradation: amylose is responsible for short term changes (the formation of $V_H$-type single helix crystals) and amylopectin for the long term rheological and structural changes (formation of B-type crystals) (Jaillais, Ottenhof, Farhat, & Rutledge, 2006; Yu & Christie, 2005). Fig. 7 compares XRD patterns for each of the thermoplastic starches conditioned for 7 days (23 °C, 50% RH). It appears from these diffractrograms that retrogradation is taking place due to the presence of $V_H$-type and B-type crystallinity. The weak 12.6° and 23° and strong 21° pattern (28% amylose, 50% amylose, 80% amylose TPS) is usually attributed to the $V_H$ polymorph where the amylose recrystallises with lipids in simple helices during storage (Hulleman et al., 1999). For high amylose starches the 12.6° peak was significantly stronger. As mentioned earlier, amylopectin chain length distribution has a close relationship to crystalline structure within the starch granule (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005). Due to longer chain lengths (waxy maize) combined with the increase in number of double helices (amylose) accounts for the higher level of crystallinity. $V_H$-type polymorph was expectedly absent with the waxy maize TPS, however, this type of crystalline structure was noticeably absent with the modified 80% amylose TPS. This indicates that hydroxypropylation of starch retards the crystallisation of amylose, leaving these chains in an amorphous state. This behaviour is also reflected in the material's mechanical properties with a significantly high strain at break (183%) and a reduction in the modulus from 190 MPa (unmodified) to 145 MPa (hydroxypropylated).

Fig. 8 shows the change in crystallinity over time for each TPS. The waxy maize diffractogram showed the characteristic B-polymorph associated with amylopectin recrystallisation. The main peak shows a slight increase with time, indicating that retrogradation has occurred, however not to any great extent. This is due to the presence of plasticisers such as glycerol which, leads to a beta relaxation for the slightly hydrated starch therefore causing a depression in the retrogradation of waxy maize starch in the presence of water (Liu et al., 2001). Unmodified 28%, 50% and of 0% TPS also showed the combination of $V_H$ and B polymorphs. The main peak as well as the well-defined peak at 12.6° increased significantly during the 14 days of ageing, showing that the materials had not yet undergone full retrogradation over this time period and hence, like absorption moisture content, had not yet reached equilibrium. However, the modified high amylose starch shows little change over time. It has been reported that hydroxypropylation decreased amylose leaching, therefore preventing amylose recrystallisation (Perera, Hoover, & Martin, 1997). These results, once again, indicate that hydroxypropylation has great influence over the final product characteristics.

### 4.8. Feasibility of replacing conventional plastics

For comparative purposes the mechanical properties of polymers currently used in injection moulding applications has been included (Table 3). The values shown in here are an average of a wide range of commercially available materials and can be used to give an indication of whether or not the TPS materials in this study have the required mechanical properties for the purpose of injection moulding.

**Table 3**
Comparison of TPS mechanical properties with conventional polymers used for injection moulding grade resin.[a]

| Material | Young's modulus (MPa) | Maximum stress/ ultimate tensile strength (MPa) | Strain at break (%) |
|---|---|---|---|
| Low density polyethylene (LDPE) | 237 | 11 | 314 |
| High density polyethylene (HDPE) | 100 | 20.1 | 511 |
| Polypropylene (PP) | 1790 | 33.1 | 148 |
| Poly(ethylene terephthalate) (PET) | 2950 | 82.2 | 63.2 |
| Waxy maize TPS, Day 14 | 160 | 6.5 | 75 |
| 80% Amylose TPS, Day 14 | 120 | 7.5 | 95 |
| Hydroxypropylated 80% Amylose TPS, Day 14 | 75 | 5.5 | 180 |

[a] Averaged values supplied by manufacturers' data from www.matweb.com (Updated 23 June 2009).

This study has shown that the waxy maize TPS behaved very differently to any other starch type as it did not follow the same trend in mechanical properties relation to amylose content. The results of waxy maize TPS agree with those by Mani and Bhattacharya (1998) showing that waxy maize (0% amylose) starch has high modulus and low strain at break when compared to other unmodified starches. Due to the highly branched nature of amylopectin it therefore has distinct properties such as increased stiffness which is comparable to the modulus for LDPE and HDPE.

The unmodified starches containing 28–80% amylose showed several trends relating to an increase in amylose content. These properties included increased stiffness and strength as well as a lower extent of gelatinisation.

The modified high amylose starch results from this study, however, are largely expected. This was because hydroxypropylated starch allows for efficient interactions to take place between the plasticisers and PVOH that increases the bonds in the matrix therefore reducing the modulus and strength and increasing the strain at break (Perera et al., 1997). When compared to conventional polymers the modified TPS blend had better elongation properties than PP and PET, but similar to that of LDPE (Table 3).

## 5. Conclusion

The effect of starch type, screw speed and ageing on thermoplastic starch properties were studied showing the potential or replacing conventional plastics with a more sustainable alternative. It was found that starch type and ageing times significantly affected properties such as Young's modulus, maximum stress, strain at break and re-adsorption moisture content as well as morphology and retrogradation. However, the statistical analysis showed that the operating variable, screw speed, did not significantly affect the final product properties.

The results showed that waxy maize starch and modified 80% amylose starch were the TPS materials with the best properties. With a Young's modulus value close to LDPE, waxy maize was the strongest and stiffest material with the lowest strain at break. Modified 80% amylose starch had exceptional strain at break, higher than PP and PET but comparable to LDPE.

It was also found that mechanical properties were influenced by changes in moisture over time, more so than the retrogradation observed. Retrogradation was evident in the XRD results as the crystalline peaks increased in intensity over time. This behaviour is known to increase modulus and strength as well as decrease elongation, however, the opposite trend was observed. It has been reported that moisture content has a significant influence on the ageing of TPS (Ma & Yu, 2004) and this aspect needs further investigation to determine the complex relationship of retrogradation and moisture in ageing TPS.

The moisture absorption and XRD (retrogradation) results clearly show that a minimum of 7 days is required for the TPS product to reach equilibrium with its surroundings of 23 °C, 50% RH, especially for waxy maize and 28% amylose maize starches.

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## References

ASTM D4703-03. (2003). Standard practice for compression molding thermoplastic materials into test specimens, plaques, or sheets. ATSM International.

ASTM D638-03. (2003). Standard test method for tensile properties of plastics. ASTM International.

ASTM D618-05. (2005). Standard practice for conditioning plastics for testing. ASTM International.

Averous, L., & Fringant, C. (2001). Association between plasticized starch and polyesters: Processing and performances of injected biodegradable systems. *Polymer Engineering and Science, 41*(5), 727–734.

Benczedi, D. (1999). Estimation of the free volume of starch–water barriers. *Trends in Food Science and Technology, 10*(1), 21–24.

Blanche, S., & Sun, X. (2004). Physical characterization of starch extrudates as a function of melting transitions and extrusion conditions. *Advances in Polymer Technology, 23*(4), 277–290.

Chaudhary, A. L., Miler, M., Torley, P. J., Sopade, P. A., & Halley, P. J. (2008). Amylose content and chemical modification effects on the extrusion of thermoplastic starch from maize. *Carbohydrate Polymers, 74*(4), 907–913.

De Graaf, R. A., Karman, A. P., & Janssen, L. P. B. M. (2003). Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. *Starch/Staerke, 55*(2), 80–86.

Enrione, J. I., Hill, S. E., & Mitchell, J. R. (2007). Sorption and diffusional studies of extruded waxy maize starch–glycerol systems. *Starch/Staerke, 59*(1), 1–9.

Guha, M., Zakiuddin Ali, S., & Bhattacharya, S. (1997). Twin-screw extrusion of rice flour without a die: Effect of barrel temperature and screw speed on extrusion and extrudate characteristics. *Journal of Food Engineering, 32*(3), 251–267.

Huang, M., Yu, J., & Ma, X. (2005). Ethanolamine as a novel plasticiser for thermoplastic starch. *Polymer Degradation and Stability, 90*(3), 501–507.

Hulleman, S. H. D., Kalisvaart, M. G., Janssen, F. H. P., Feil, H., & Vliegenthart, J. F. G. (1999). Origins of B-type crystallinity in glycerol-plasticised, compression-moulded potato starches. *Carbohydrate Polymers, 39*(4), 351–360.

ISO 1666. (1996) Starch – Determination of moisture content – Oven-drying method. International Organization for Standardization.

Jaillais, B., Ottenhof, M. A., Farhat, I. A., & Rutledge, D. N. (2006). Outer-product analysis (OPA) using PLS regression to study the retrogradation of starch. *Vibrational Spectroscopy, 40*, 10–19.

Lionetto, F., Maffezzoli, A., Ottenhof, M.-A., Farhat, I. A., & Mitchell, J. R. (2005). The retrogradation of concentrated wheat starch systems. *Starch/Staerke, 57*(1), 16–24.

Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties and enzymatic digestibility of hydroxypropylated ae, wx, and normal maize starch. *Carbohydrate Polymers, 40*(3), 175–182.

Liu, Z. Q., Yi, X.-S., & Feng, Y. (2001). Effects of glycerin and glycerol monostearate on performance of thermoplastic starch. *Journal of Materials Science, 36*(7), 1809–1815.

Ma, X., & Yu, J. (2004). The effects of plasticizers containing amide groups on the properties of thermoplastic starch. *Starch/Staerke, 56*(11), 545–551.

Mani, R., & Bhattacharya, M. (1998). Properties of injection moulded starch/synthetic polymer blends – III. Effect of amylopectin to amylose ratio in starch. *European Polymer Journal, 34*(10), 1467–1475.

Nabar, Y., Narayan, R., & Schindler, M. (2006). Twin-screw extrusion production and characterization of starch foam products for use in cushioning and insulation applications. *Polymer Engineering and Science, 46*(4), 438–451.

Onteniente, J.-P., Abbes, B., & Safa, L. H. (2000). Fully biodegradable lubricated thermoplastic wheat starch: Mechanical and rheological properties of an injection grade. *Starch/Staerke, 52*(4), 112–117.

Pal, J., Singhal, R. S., & Kulkarni, P. R. (2002). Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers, 48*(1), 49–53.

Perera, C., Hoover, R., & Martin, A. M. (1997). The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat-moisture treated potato starches. *Food Research International, 30*(3–4), 235–247.

Rosa, R. C. R. S., & Andrade, C. T. (2004). Effect of chitin addition on injection-molded thermoplastic corn starch. *Journal of Applied Polymer Science, 92*(4), 2706–2713.

Scandola, M., Finelli, L., Sarti, B., Mergaert, J., Swings, J., Ruffieux, K., et al. (1998). Biodegradation of a starch containing thermoplastic in standardized test systems. *Journal of Macromolecular Science – Pure and Applied Chemistry, A35*(4), 589–608.

Srichuwong, S., Sunarti, T. C., Mishima, T., Isono, N., & Hisamatsu, M. (2005). Starches from different botanical sources. I: Contribution of amylopectin fine structure to thermal properties and enzyme digestibility. *Carbohydrate Polymers, 60*(4), 529–538.

Stepto, R. F. T. (2003). The processing of starch as a thermoplastic. *Macromolecular Symposia, 201*, 203–212.

Thuwall, M., Boldizar, A., & Rigdahl, M. (2006a). Compression molding and tensile properties of thermoplastic potato starch materials. *Biomacromolecules, 7*(3), 981–986.

Thuwall, M., Boldizar, A., & Rigdahl, M. (2006b). Extrusion processing of high amylose potato starch materials. *Carbohydrate Polymers, 65*(4), 441–446.

Van Soest, J. J. G., & Borger, D. B. (1997). Structure and properties of compression-molded thermoplastic starch materials from normal and high-amylose maize starches. *Journal of Applied Polymer Science, 64*(4), 631–644.

Yu, L., & Christie, G. (2005). Microstructure and mechanical properties of orientated thermoplastic starches. *Journal of Materials Science, 40*(1), 111–116.

Yu, J., Gao, J., & Lin, T. (1996). Biodegradable thermoplastic starch. *Journal of Applied Polymer Science, 62*(9), 1491–1494.

Zheng, Y., Yanful, E. K., & Bassi, A. S. (2005). A review of plastic waste biodegradation. *Critical Reviews in Biotechnology, 25*(4), 243–250.