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Original article

Effect of amylose/amylopectin ratio and extent of processing on the physical properties of expanded maize starches

Daniel Beech,[1] John Beech,[2] Joanne Gould[1*] & Sandra Hill[3]

1 Division of Food, Nutrition and Dietetics, University of Nottingham, Leicestershire, UK
2 Real World Business Solutions Ltd, Leicestershire, UK
3 Biopolymer Solutions Ltd, Leicestershire, UK

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Summary Low-density expanded starchy products are often desirable, particularly in the snack food industry. Levels of shear and amylose are often deemed crucial factors for expansion. In this study, maize starches containing low (waxy), normal and high levels of amylose were compared after processing. Low shear processing used a popping head (similar to a rice-cake machine), while high shear (~450 kJ kg^{-1}) samples (pellets and directly expanded) were created using twin-screw thermomechanical extrusion. Native starches and ground extruded materials (<106 μm) were popped using the same conditions (230 °C, 4 s, water content 12% wwb). All samples tested created fused aerated cakes, which had little or no remaining crystallinity, except for the directly popped waxy sample, which retained ~17% of its original crystallinity. Water absorbances and solubilities were influenced greatly by the starch source and marginally by the amount of processing. On processing, waxy samples showed increased solubility while those with normal amylose content had greater absorption. The densities of all the popped samples were similar despite marked differences in shear regime history and the major variations in the amylose and amylopectin ratios. These results challenge the expected relationships between shear and different starches' potential to expand.

Keywords Amylose/amylopectin ratio, bubble growth, expansion, high temperature RVA, popping, starch conversion, thermomechanical extrusion.

Introduction

Solid foams often form the structural component of food products; breads, cakes and expanded snacks being examples. For many aerated solid foods, the essential ingredient forming the bubble wall is starch and it is necessary for the processing to cause changes to the native granules that allow the starchy material sufficient flexibility and integrity to support the bubble wall. The creation of an expanded product can be complex and requires bubble nucleation and growth; there may also be bubble coalescence and shrinkage (Kristiawan *et al*., 2020). At the point when the expansion forces (typically water transitioning to steam) stop, the viscosity of this wall needs to be such that the expanded network does not collapse (Fan *et al*., 1994; Purlis *et al*., 2021). To predict starch expansions, an understanding of the status of the starch over a wide range of length scales and knowledge of several different phase transitions would be necessary (Purlis *et al*., 2021). Although there are substantial bodies of work investigating starch expansion, as it is important for human, animal and fish feeds (Drew *et al*., 2007; Corsato Alvarenga *et al*., 2021), as well as in packaging (González-Seligra *et al*., 2017; Lauer & Smith, 2020), ingredient preparation (Vedove *et al*., 2021) and waste utilisation, generic understanding of the critical factors for expansion is limited (Drew *et al*., 2007; González-Seligra *et al*., 2017; Lauer & Smith, 2020; Corsato Alvarenga *et al*., 2021; Vedove *et al*., 2021).

Mechanisms of hydration and changes to the microstructures of the starch (including loss of granule integrity, loss of helical and crystalline order, reduction in molecular weight, phase separation and alignment of the components) occur in thermomechanical extrusions (Montilla-Buitrago *et al*., 2021). Realignment and creation of new ordered forms may occur on holding plasticised amorphous materials post the original heating and shearing stages (Montilla-Buitrago *et al*., 2021). Thus, the microstructures of the starchy matrix of pellets (non-expanded extrudates) may vary significantly from directly expanded extrudates, which

*Correspondent: E-mails: joanne.gould@nottingham.ac.uk

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would undergo a rapid transition from a rubbery to glass status on exiting the extruder die and would therefore have little time for realignment and association (Morris, 1990).

The breakdown of the starch, often called degree of starch gelatinisation (Singh *et al.*, 2007; Xie *et al.*, 2007) or starch conversion (Mitchell *et al.*, 1997), is often related to the starches' performance as film formers, barriers and in stabilising the bubble wall (Domene-López *et al.*, 2019). For thermomechanical extrusion, using one ingredient or simple blends of ingredients, the most important processing variable is considered to be the shear forces applied to the melt (Kantrong *et al.*, 2018; Kristiawan *et al.*, 2020; Espinosa-Ramírez *et al.*, 2021; Purlis *et al.*, 2021). The specific mechanical energy, which combines the amount of material processed, the torque and the speed of the screws, will often correlate well with expansion (Ilo *et al.*, 1996; Filli *et al.*, 2012). The general idea is that the shear forces on the amorphous melted starch breaks and blends the different starch macromolecules, and may depolymerise the amylopectin, and thus gives rise to lower viscosity and homogenous material at the bubble wall surface, which allows for greater expansion (Moraru & Kokini, 2003; Hellemans *et al.*, 2020).

What seems far less clear is the relationship between the different types of starchy ingredients, the level of shear applied and reassociation of the molecules, and how these correlate with the expansion of the sample. Many factors or combinations of factors could be influential for bubble wall quality, but the most often quoted variable is the amylose to amylopectin ratio (Chinnaswamy & Hanna, 1988; Della Valle *et al.*, 1997; Thuwall *et al.*, 2006; Hellemans *et al.*, 2020; Corsato Alvarenga *et al.*, 2021). Although there is often a statistical correlation between the amylose/amylopectin ratio and expansion, it is not a simple dependency and the mechanism by which the ratio of macromolecules influences the expansion is not clear. Some findings may be confounded by using different starch species to provide the range of amylose and amylopectin ratios; in other studies, non-purified starches are used and therefore other materials may be having a major influence. As the influence of the ingredients, their processing and interactions between these factors can be hard to control, for the current work radical differences in amylose/amylopectin ratios and shear were studied, while limiting other possible variables.

Maize starches, with very different levels of amylose, were subjected to two very different levels of shear. Although it could not be fully controlled, temperature regimes were meticulously followed and matched when possible. The shear was imparted by use of twin-screw thermomechanical extrusion and/or use of a traditional rice type popping head. Thus, unified fused samples, which were sufficiently robust to be handled, were created so that their expansion could be measured. The extruded samples, in the form of directly expanded materials and pellets, were then comminuted so that the powders could be fed into a popping head and their expansion could be directly compared to samples that had not undergone the high shear forces within the extruder. These samples made it possible to compare the influence of amylose/amylopectin ratios on expansion and to establish if this can be understood in relationship to the applied shear forces, storage of samples in their rubbery state and the associated starch conversion.

Materials and Methods

Materials

Three maize starches that represent different amylose: amylopectin levels were used for the work. The samples were used without further processing (native), as extrudates (Ex) and after being popped (pop). Coding for the samples is given in Table 1.

Native maize starches of waxy (Amioca, Ingredion UK Ltd, Manchester, UK) , normal (Meritena, Tereos UK & Ireland Ltd, Normanton, UK) and high amylose (Hylon VII, Ingredion UK Ltd, Manchester, UK) varieties were purchased from Univar UK Ltd (Bradford, UK).

Extrusion

All extrusion work was carried out using a Thermo Prism TSE MC co-rotating twin-screw extruder (Fisher Scientific UK Ltd, Loughborough, UK) with a barrel length of 960 mm and screw diameter of 24 mm, fitted with a 4.1-mm diameter pinhole die. Starch powders were fed into the extruder at a constant rate of 8 kg h^{-1} via gravimetric feeder and RO water was pumped in at a rate of 1.536 kg h^{-1}, resulting in a total feed water content of 26% (wet basis), which included water associated with the native starch powders. Screw configuration and temperature profiles are shown in Figure 1. Two temperature profiles were used, one with die temperature set at 60 °C to produce unexpanded starch pellets and one with die temperature of 120 °C to produce directly expanded starch extrudates.

Screw speed was kept constant at 300 rpm and the *torque* required to maintain this speed was recorded. Specific mechanical energy (*SME*) was calculated using the following formula:

$$SME\left(\frac{kJ}{kg}\right) = \frac{Torque\,(Nm) * Screw\,speed\left(\frac{rad}{s}\right)}{Mass\,flow\,rate\left(\frac{kg}{s}\right) * 1000} \quad (1)$$

Following extrusion, samples were dried at 105 °C for 2 h and left out on trays to equilibrate overnight prior to long-term storage in plastic containers.

Table 1 Characterisation of raw materials and functional properties of samples ± standard deviation where appropriate. Samples within the same column labelled with different letters are statistically different to one another to a significance level of $P < 0.05$

Identifier	Starch type	Nominal AM/AP ratio[1]	Particle size (μm)[2]	State before popping	Popping	WAI (g g^{-1})[3]	WSI (%)[3]	Density (kg m^{-3})[4]
W	Waxy	0/100	16.99 ± 11.91	Native	Not popped	2.570 ± 0.046^{cd}	0.78 ± 0.69^{a}	
N	Normal	25/75	19.41 ± 12.86			2.310 ± 0.093 ^{cd}	0.44 ± 0.51^{a}	
A	High amylose	70/30	46.10 ± 53.11			2.693 ± 0.048^{de}	0.89 ± 0.69^{a}	
W-Ex	Waxy			Extruded, direct expansion	Not popped	1.182 ± 0.177^{ab}	93.33 ± 1.73^{hi}	486.0 ± 53.6^{ef}
N-Ex	Normal					11.319 ± 0.284^{j}	36.11 ± 0.69^{e}	393.9 ± 36.9^{de}
A-Ex	High amylose					3.901 ± 0.190^{f}	7.11 ± 1.39^{bc}	348.2 ± 20.5 cd
W-P	Waxy			Extruded, intermediate pellets	Not popped	2.888 ± 0.876^{de}	70.00 ± 5.24^{g}	1070.1 ± 72.9^{h}
N-P	Normal					8.914 ± 0.054^{hi}	34.67 ± 0.33^{e}	647.6 ± 83.6^{g}
A-P	High amylose					3.448 ± 0.063^{ef}	3.22 ± 0.51^{ab}	752.7 ± 84.1^{g}
W-pop	Waxy			Native	Popped	3.682 ± 0.286^{f}	52.89 ± 3.53^{f}	302.6 ± 98.8^{bcd}
N-pop	Normal					4.698 ± 0.158^{g}	17.78 ± 0.19^{d}	148.0 ± 23.2^{a}
A-pop	High amylose					3.919 ± 0.095^{f}	8.78 ± 0.77^{c}	227.0 ± 75.4^{abc}
W-Ex-pop	Waxy			Extruded, direct expansion	Popped	1.114 ± 0.148^{a}	95.00 ± 0.67^{i}	129.1 ± 25.5^{a}
N-Ex-pop	Normal					9.596 ± 0.101^{i}	38.78 ± 0.38^{e}	134.0 ± 18.4^{a}
A-Ex-pop	High amylose					4.090 ± 0.040^{fg}	11.44 ± 0.38^{c}	224.2 ± 57.4^{ab}
W-P-pop	Waxy			Extruded, intermediate pellets	Popped	1.910 ± 0.104^{bc}	88.89 ± 1.35^{h}	107.9 ± 6.7^{a}
N-P-pop	Normal					8.570 ± 0.091^{h}	38.22 ± 0.69^{e}	134.8 ± 35.2^{a}
A-P-pop	High amylose					4.199 ± 0.087^{fg}	8.78 ± 0.84^{c}	107.4 ± 7.3^{a}

[1]Nominal AM/AP ratios based on values stated in manufacturer specifications and existing literature (Valachová & Horváthová, 2007; Juhász & Salgó, 2008; Kibar *et al.*, 2010; Šárka & Dvořáček, 2017).
[2]Mean particle diameters obtained from two replicates.
[3]WAI and WSI values average of three replicates.
[4]Density values average of three replicates for un-popped extrudate samples and five samples for all popped samples.

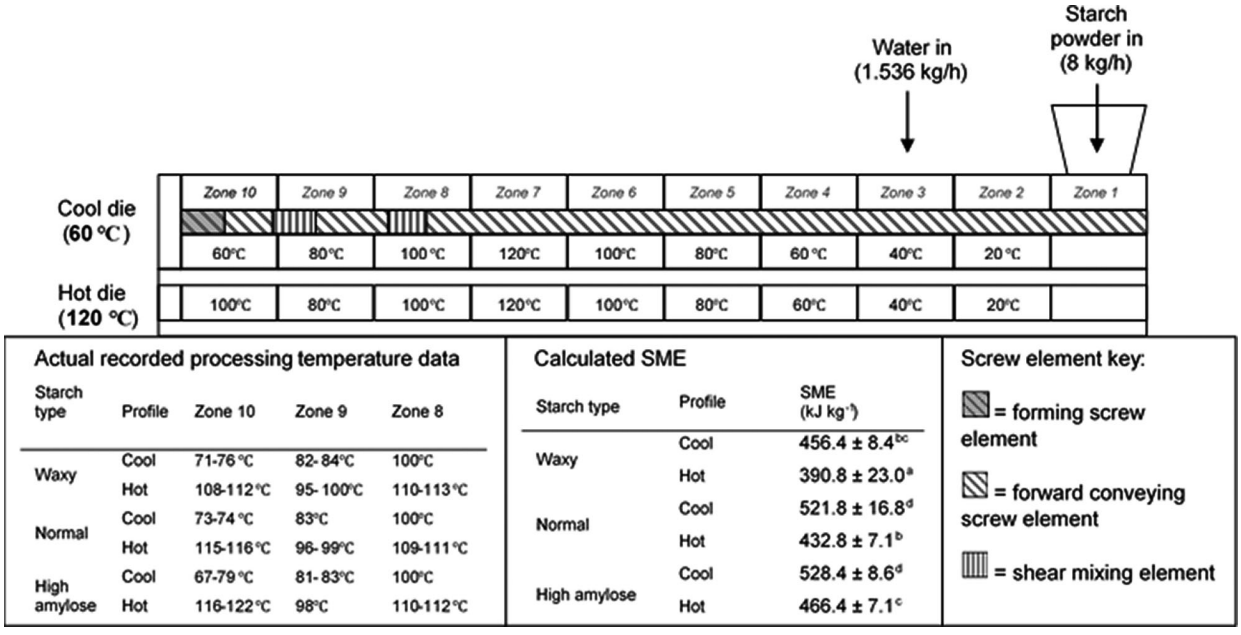


Figure 1 Screw configurations and set temperature profiles used to create unexpanded starch pellets (P) and directly expanded starch extrudates (Ex). Actual temperatures recorded in zones 10, 9 and 8 are given as well as the calculated SME obtained from at least two replicates ± standard deviation. Subscripts denote samples significantly different one from another at the 5% level.

The samples obtained at this stage were pellet (P) and expanded (Ex) extrudates.

Water content adjustment

Uncooked starch powders, pellet and expanded extrudates were milled using a coffee grinder (De'Longhi Appliances Srl, Treviso, Italy) if necessary and passed through a 106-μm sieve. All samples were then dried at 105 °C until constant weight. These dried samples were then suspended over water in foil trays within a closed container kept at 50 °C until they had rehydrated to 12% water wwb.

Popping

The sieved, hydrated powder samples were finally expanded or 'popped' using a heat press (custom build, University of Nottingham) to create final products similar to miniature rice cakes. Samples (1.8 g) were weighed into an aluminium pie tray which had been moulded to fit the dimensions of the heat press base platen recess (diameter 45 mm, depth 10 mm). The heat press head and base platens were both set to 230 °C and all samples were pressed at this temperature for 4 s under at a gauge pressure of 4 bar.

Analyses

RVA of raw materials
Pasting properties of the raw materials were assessed using a high temperature rapid visco analyser (Perten RVA 4800, Calibre Control International Ltd, Warrington, UK). Sample (4.5g) was first mixed with 2 g of ethanol and then 21.5 g RO water, resulting in a 14% starch solution (wwb). Stirring speed was 960 rpm for the first 10 s, and then reduced to 160 rpm. The temperature profile is presented in Fig. .

Particle size determination of raw materials
Particle size (diameter) distribution of the raw materials was determined via laser diffraction using an LS 13 320 Particle Size Analyser fitted with a Tornado dry powder module (Beckman Coulter UK Ltd, High Wycombe, UK).

Product density
Product density was calculated using rapeseed displacement (AACC, 2000).

Water absorption and solubility indices
Popped samples were ground, sieved (106 μm) and dried at 105 °C. Powdered sample (0.3 g) was mixed with 10 ml of RO water and left to hydrate and sediment overnight. The resulting suspension was centrifuged at 2045 g for 10 min and the supernatant was evaporated at 105 °C. Water absorption index (WAI) was calculated as the weight of the pellet per gram of sample and water solubility index (WSI) was calculated as the weight of the dry solids in the supernatant as a percentage of the initial sample weight. This method is a modified version of that described by Anderson *et al*. (1970).

Differential Scanning Calorimetry (DSC)
Approximately 8 mg samples were mixed with RO water in a ratio of 1:3 sample to water and hermetically sealed in stainless steel DSC pans. Samples were scanned from 0-150 °C at a rate of 10 °C/min using a DSC 3+ (Mettler-Toledo Ltd, Leicester, UK).

Statistical analysis

Statistical analyses were carried out using Genstat 19th Edition software. One-, two- and three-way ANOVA, as appropriate, followed by Tukey test were used to identify significant effects of factors, interactions between factors and relationships between data groups.

Results and discussion

Sample creation

Figure. 3 shows images of the samples created from the different processing regimes. Extrusion was carried out at a water content of 26% and popping at 12% (wwb). Despite the short-term heating, approximately 30 s for extrusion and 4 s for the popping, and relatively low temperatures, max 122 °C for extrusion (see Fig. 1) and a set temperature of 230 °C for the popping platens (with pressures set at 4 bar, the water temperature should have not exceeded 152 °C) all three starch types with their varying level of amylose (Table 1) had their native structures sufficiently disrupted to allow the initial powders to create solid fused masses that had sufficient integrity to be handled (Fig. 3). All samples showed densities that are indicative of solid foam (Table 1).

Starch characterisation

A feature of the three maize starches chosen for this work, in association with the different levels of amylose and amylopectin in the starch granules, is the variation in the temperature dependence on the loss of crystallinity and the starch granules' swelling behaviour in excess water. Table 1 shows typical amylose/amylopectin values quoted for the starches and Fig 2 demonstrates the swelling behaviour of the native starches when pasted in excess water (14% starch). High temperature RVA of the native starches showed

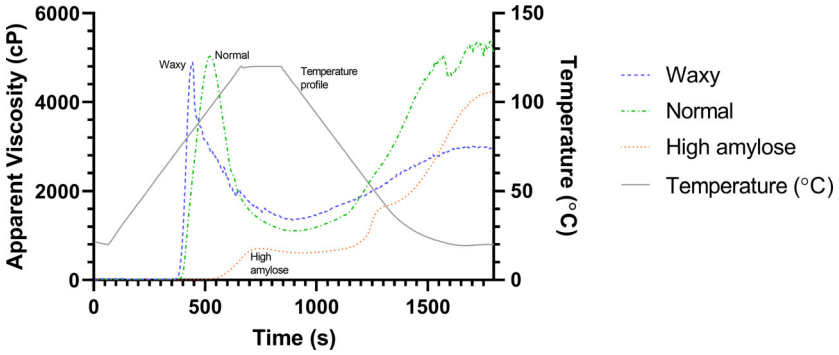
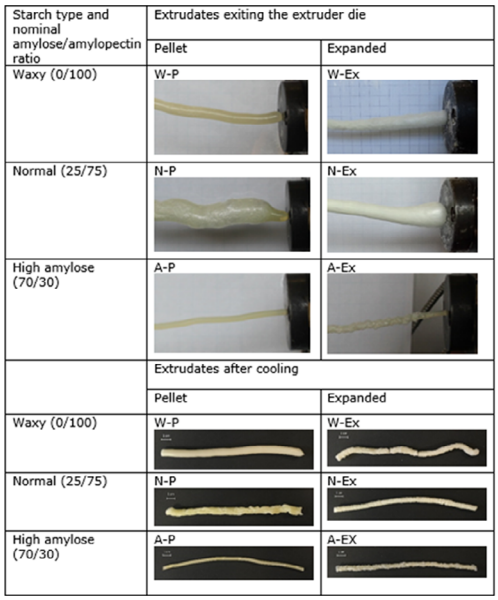


Figure 2 RVA profiles for raw materials (waxy, normal and high amylose maize starch powders) measured in excess water over a temperature range of 20-120°C



Starch type and nominal amylose/ amylopectin ratio	Uncooked starches	Extrudates (milled, sieved and rehydrated to 12% water wwb)		Popped		
		Pellet	Expanded	Uncooked	Pellet	Expanded
Waxy (0/100)	W	W-P	W-Ex	W-pop	W-P-pop	W-Ex-pop
Normal (25/75)	N	N-P	N-Ex	N-pop	N-P-pop	N-Ex-pop
High amylose (70/30)	A	A-P	A-Ex	A-pop	A-P-pop	A-Ex-pop

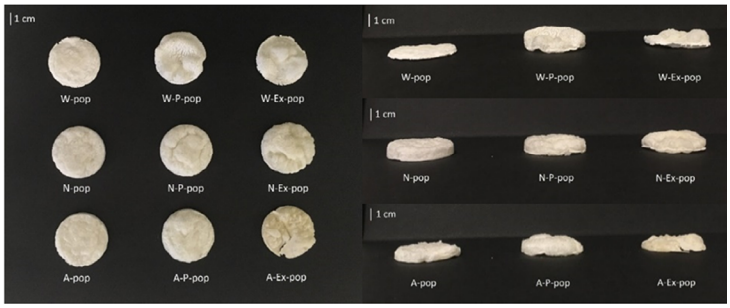


Figure 3 Example images of extrudates and popped samples along with their labelling key according to starch type and level of processing.

that the waxy (W) and normal (N) maize starches had very similar pasting temperatures (around 75 °C), peak viscosities and holding strengths. The RVA curve indicates that for high amylose maize starch, there was a much higher pasting temperature (>100 °C) and much lower peak viscosity than the other maize starch samples. It has been suggested that the high amylose content inhibits granule swelling, thereby delaying or changing the process of gelatinisation (Tester & Morrison, 1990; Jane *et al*., 1999; Ratnayake & Jackson, 2006; Vamadevan & Bertoft, 2020). Figure. 4 shows the DSC traces for the native samples; again the water level was in excess of that used in the processing conditions. The maximum loss of order occurs for the waxy and normal maize at approximately 70 °C, while some order is lost for the high amylose samples across a broad range of temperatures and the endotherm is still apparent at >100 °C. These data are compatible with most authors and suggest that the three maize samples used for the work are typical examples of waxy, normal amylose and high amylose maize.

Liu *et al*. (2006) studied the enthalpic changes occurring for maize starches at different water contents as they were heated at 5 °C per minute. Their endotherm peaks were in the region of 175–190 °C for the waxy and high amylose starch, with normal maize being at 140°C for 26% water (extrusion conditions for this study), whilst for 12% water (popping conditions in this study), values of 180–190 °C were recorded for normal and waxy starch, with the high amylose starch not having a clearly definable endotherm peak. Flory–Huggins free volume theory would again suggest that the temperatures used in this study are unlikely to disrupt all of the crystalline structures of the amylopectin

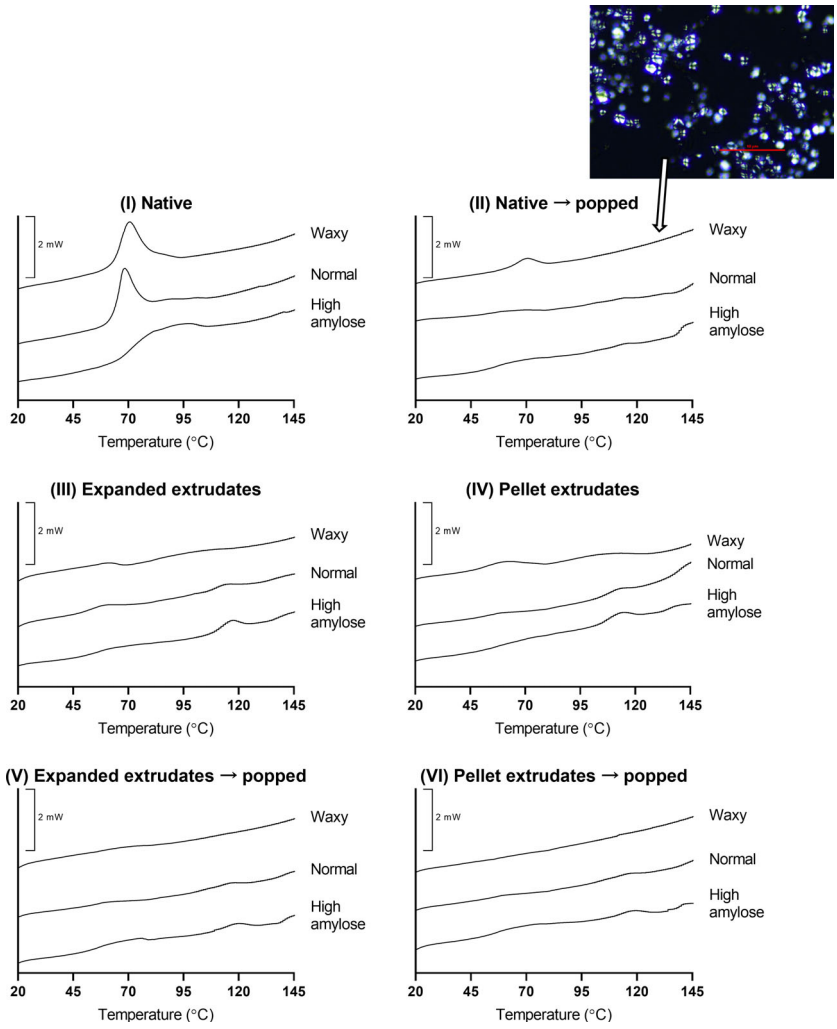


Figure 4 DSC endotherms (heated at 10 °C per minute from 20 to 145 °C at starch to water levels of 1:3) for samples from three different maize starch types, having been processed at different levels of shear prior to analyses. Processing levels prior to assessment are ranked from lowest to highest as demarked by I to VI. Micrograph shows waxy maize popped sample (W-pop) under polarised light prior to DSC (scale bar 10 μm)

within the native starch granules (Van der Sman & Meinders, 2011; Li *et al.*, 2020).

Based on temperature alone, our processing conditions should have been insufficient to simply melt out the order associated with the amylopectin and allow movement of polymer from the granules to act as adhesive between the starch granule remnants and polymers. However, it is evident that sufficient disruption of the starch structures occurred to allow for these associations. In the dry heat treatment of maize starch at <10% water and using temperatures equivalent or higher to those used in the popping head, but with the duration of heating being for two hours compared to the 4 seconds used for popping, Lei *et al.* (2020) still detected x-ray order within the starches. This may highlight the importance of the precise plasticiser level as the samples are heated. However, as demonstrated in Fig. 3, the creation of the samples via extrusion and popping must indicate that changes to the structures, at a level that allows a continuous network of polymers to be created, have occurred.

Processing and order loss

The processing methods were chosen to have different shear regimes. It could be expected that the popping head would allowing heating, but then the only shear forces would be during the expansion of the materials. This would contrast with the extrusion where flow of the materials between the screw and the barrel gives rise to measurable specific mechanical energies. The native maize starches do have different shapes and sizes of granules (Chen *et al.*, 2006, 2012), and this may impact on their packing within the extruder barrel and the shear to which the samples are subjected (Wang & Zheng, 1995), but it is generally considered that the mechanical energy to which the melt is subjected is most relevant to the extrudates behaviour

(Wang & Zheng, 1995; Chen *et al*., 2006, 2012; Kantrong *et al*., 2018; Li *et al*., 2020; Vamadevan & Bertoft, 2020; Espinosa-Ramírez *et al*., 2021). The values for the SME during extrusion, as calculated according to Equation 1 and shown in Fig. 1, show a narrow range from 391 to 528 kJ kg^{-1}; values that correspond approximately to those associated with the manufacture of directly expanded products such as breakfast cereals and crispy flatbreads (Bouvier & Campanella, 2014). Despite the first eight out of nine barrel temperature zones, where the melt should be occurring, being set to the same values, the temperatures at the end zones seem to be affecting the overall SME, with the higher temperature profile producing lower SME values ($P < 0.001$) presumably due to the viscosity–temperature relationship (Remsen & Clark, 1978; Vergnes & Villemaire, 1987; Chang *et al*., 1999; Leonard *et al*., 2020).

Regardless of the temperature profile, the waxy maize samples, which contain close to 100% amylopectin and no amylose, had lower SME ($P < 0.001$) when compared with the amylose-containing samples. Despite the different quantities of amylose between the normal and high amylose samples, there was not a significant difference in the measured SME in the cool die temperature profile ($P > 0.05$). For the hot die profile, SME was greater for high amylose than the normal sample ($P < 0.05$). No significant interaction was found between temperature profile and starch type ($P = 0.134$).

It has been suggested that the bulky branched structure of amylopectin makes it more susceptible to shear degradation than amorphous amylose, which is comparatively flexible (Chaudhary *et al*., 2008; Li *et al*., 2014). Additionally, it is believed that the linear amylose chains form polymer–polymer associations and entanglements in the form of double helices between amylose and the outer chains of amylopectin, thereby increasing the overall viscosity of the starch matrix (Van Soest & Borger, 1997; Thunwall *et al*., 2006). The lack of amylose in the waxy starch means that possibly both the reduction in molecular size by shear degradation and the lack of polymer–polymer interactions contribute to a lower viscosity of the polymer melt, and hence lower SME compared to the amylose-containing starches.

DSC was used to determine if order had been lost due to processing of the samples. The DSC endotherms of the processed samples, which were ground and added to excess water, are shown in Fig. 4 and demonstrate that all processes decrease the measured order in the samples. The process time–temperature regimes, although seemingly near to the minimum to achieve loss of order, appear adequate to remove the order. The only sample that seemed to retain some order (17% of the total energy) was the popped waxy sample. Micrographs of the expanded and then ground popped waxy sample showed Maltese Cross images, indicating that original semi-crystalline structure of many of the native granules had been retained (Fig. 4). The waxy sample, which could be expected to have the lowest gelatinisation temperature, seemed to be the most robust under the popping processing conditions used.

The environment within the popping head could be equated with what occurs in the pans used in DSC, but the time frames for heating in the popping head are much shorter (4 seconds). As water content decreases, endotherms obtained by DSC become more complex and are thought to demonstrate separation of the events of melting of amylopectin crystals, annealing of crystals, formation and melting of amylose–lipid complexes and melting of amylose–amylose associations (Russell, 1987; Liu *et al*., 2006). At the water contents used in extrusion, and with sufficiently high temperatures, mobility of the backbone and spacers at the branching points in the macromolecules structure can occur and there would be cooperative uncoiling of the helices. However, at water contents of <20%, the crystallites would need to melt directly from their helical state to coils and thus require higher thermal activation (Waigh *et al*., 2000). At moderate water contents, the waxy samples gelatinise at relatively low temperatures, despite much of the polymeric material being in the helical form, but the lack of plasticisation at low water levels (12% wwb) would seem to prevent the transitions necessary for direct melting of the amylopectin crystallites.

Creation of the non-expanded pellet allowed the relevance of regained starch order to be studied. Non-expanded hot melt from the extruder, which was then left to cool, could be expected to form a range of ordered structures that would include some amylopectin retrogradation. Time scales and levels of reorganisation of the starch polymers are dependent on their structures and the lengths of the smaller chains (Han *et al*., 2017; Zhu & Liu, 2020), and therefore it has been reported that even samples of very similar amylose to amylopectin ratios have very different retrogradation properties (Liu *et al*., 2009).

Some reordering did occur in the pellets, as the waxy sample from the cool die exhibited DSC endotherm peaks at a temperature lower than 70 °C (~3.5 J g^{-1} starch). It was harder to detect amylose reassociation or low levels of amylose lipid complexation. Although the high moistures used in the RVA may not be the best model for consideration of the starch polymer melt (Balet *et al*., 2019), the pasting profiles shown in Fig. 2 denote a marked increase in viscosity of the high amylose starch as the temperature decreased from 120 °C. Both normal and high amylose had higher final viscosities than waxy maize starch

when the temperatures declined to below 60 °C. This observation is consistent with the findings of Liu *et al.* (2019) and is believed to be the result of amylose reassociating. Rapid entanglement of the amylose (amylose retrogradation) could play an important role in rheology of the bubble wall as it undergoes biaxial extension. Amylose association, occurring during alignment at the die or on holding at lower temperatures, but above the glass transition temperature, may provide linear agglomerates that could form strong extensible structures suitable for allowing bubble growth. Amylose reassociation would be difficult to see in the DSC traces, but for the normal and high amylose starches, there may well be evidence of amylose–lipid complexation. If these complexes are formed during the creation of the sample rather than during the DSC process, their formation may well contribute to the viscosity and integrity of bubble wall during an expansion phase.

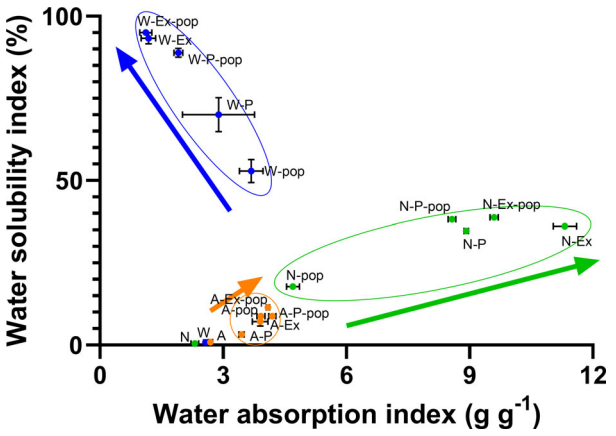


Figure 5 Comparison of the water absorbance and water solubility of the processed and non-processed starches. Sample coding as given in Table 1. Samples encircled indicate different starch types and arrows indicate approximate increase in shear.

Starch Conversion

Often starches are considered to form homogeneous melts during thermomechanical extrusion. In these melts, not only are the semicrystalline regions within the starch granules lost, but the starch macromolecules are totally disassociated from the original granule structure and mixed in a consistent format. There could be alignment of the macromolecules at the die and, in the high shear regimes created within the melt as it passes down the barrel of the extruder, molecules are likely to be broken and there will be a loss in molecular weight, particularly of the branched amylopectin (Chaudhary *et al.*, 2008; Li *et al.*, 2014).

The term 'starch conversion' is expected to convey the idea that melting of crystallites, blending of starch polymers and their depolymerisation is a continuum of events that can occur in starch processing (Wang *et al.*, 1992; Mitchell *et al.*, 1997). 'Degree of starch gelatinisation' is also used to convey changes at multiple length scales that occur within the starch structure (Xie *et al.*, 2007; Ye *et al.*, 2018). DSC can indicate the amounts of order left in the starch structure post processing. For all the samples created in this study, the DSC indicated that most crystalline order within the granules had been lost. Measures of water uptake by the samples and the comparison of their solubilities in water give an indication of the severity of starch disruption (Ye *et al.*, 2018). Table 1 and Fig. 5 show that the native starches have low water absorbance and low solubility. All processing increased the solubility, with the water absorbance increasing for the high amylose and normal samples. After an initial increase in the water absorbance when popping the native waxy starch, the extruded and popped-extruded samples had lower water absorbance values.

It would seem that the high amylose samples retained sufficient structure for the ground powdered samples not to imbibe water and swell, nor for the polymers to become soluble in the ambient temperature water. The amount of polymer becoming soluble is less than the expected level of amylopectin in the system, so it would appear that the high level of amylose holds the branched polymer in place as well as the linear material. Whether the amylose would have been less robust as a melt is not known.

Comparison of densities

The three starch samples showed different behaviours as they directly expand at the die. Each extrudate, on exiting the die, had a moisture content of 26% wwb. For the hot die, waxy starch expanded in a stable way, while the maize starch with normal amylose levels showed expansion and then shrinkage and the high amylose starch had an unstable expansion, with high expansion followed by waves of collapse. On drying, the extrudates had densities in the region of 400 kg m^{-3} and therefore show considerable amounts of gas incorporation into the structures.

The cool die temperature was set at 60 °C, but temperatures rose as high as 79 °C and there was appreciable swelling of the extrudate from the cool dies. The normal sample showed the greatest swelling (Fig. 3) and the waxy sample had the highest density (Table 1).

As could be expected, samples from the cool die were denser than from the hot die, but the cool die extrudates, which were termed pellets, still all contained gas, which had been entrapped during the melting phase. Significantly greater densities than those

observed for the pellets (in the range 630–1 000 kg m^{-3}) could be expected for native starches (1 500 kg m^{-3}), and it has been reported that there is little difference in density between high amylose and waxy native starches (Marousis & Saravacos, 1990).

In this work, there was no attempt to optimise the expansion of the extrudates, except to create dense pellets and directly expanded products. However, the SMEs, temperatures (except for the cool die settings) and screw configurations used were typical for the creation of expanded starchy materials (Guy & Horne, 1988). Della Valle *et al.* (1997) reported that at SMEs just above those used for this work (400–500 kJ kg^{-1}), the amount of torque did not distinguish between the high amylose or waxy starches, but if the *SME* rose to >500 kJ kg^{-1}, then the amylopectin would be reduced in molecular weight to sufficiently reduce the expansion of the extrudate. Although other processing parameters need to be considered, it could be assumed that the native samples were significantly disrupted by the shear forces applied in the extruder for this current work. Starch conversion was observed as changes in the samples' water solubility and water absorbance (Table 1). Figure 6 demonstrates that the water solubilities achieved for the different starches are closely aligned with the starch type, but there was no correlation between the densities of the products and the solubility of the starch.

The shear forces applied in the popping head must be very small compared to those during thermomechanical extrusion; however, expansion for the directly popped native samples is great, with densities of 300 kg m^{-3} and below being achieved. These values are comparable with the bulk densities achieved for commercial products (Maskus & Arntfield, 2015). Comparisons between the directly expanded samples from the extruder and native starch popping may not be justified as the format of the samples and the water content for expansion were different. The grinding of the extrudates and then popping the resultant powders at specific water content should allow direct comparison between highly sheared starches and those that had not undergone shear. The particle sizes for the ground extrudates were <106 μm while the native starches averaged in the range 17–46 μm. As shown in Table 1, the densities of the popped cakes produced from extruded samples, whatever the source of starch, showed no significant differences. Even more surprisingly, there was little difference in the densities between the popped native samples and those that had undergone a previous high shear regime. Only the popped native waxy sample could be distinguished ($P < 0.05$) from the other popped examples (having a higher density than most) and in this sample, it had been established that there was still crystalline order left in the popped starch (Figure. 4).

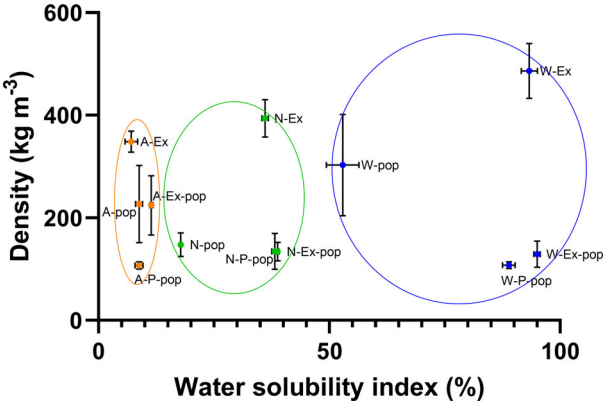


Figure 6 Comparison of the water solubility of the processed expanded starches and their densities. Sample coding as given in Table 1. Samples encircled indicate different starch types.

Conclusions

Both materials and processing conditions are known to affect the quality of expanded products. The interactions between the operating parameters and the ingredients also make an understanding of the key factors to achieve nucleation and expansion difficult. The starches chosen for the current study demonstrated the differences in starch melting behaviour and viscosities reported for maize starches with varying amylose levels when investigated in high levels of water. The processing methodologies used were extremes of shear in processing. In the popping regime, the native starches had only 12% water present and therefore it could be predicted that melting of the associated starch assemblies would only just be occurring. With the shear being limited, mixing of the polymers would seem to be restricted and the rapid loss of moisture would not allow reassociation of any melted molecular structures. This contrasts with the extruded samples. There was 26% water in the extruder and the shear forces present were of sufficient magnitude to cause not only disruption of the native starch granules but also macromolecular structures and possibly depolymerisation of the amylopectin (Orford *et al.*, 1993; Berzin *et al.*, 2010). For the directly expanded sample, the macromolecules would not be expected to reassociate, but for the cool die pellet, there would be amylopectin and amylose retrogradation.

By comminution of the pre-expanded and pelletised extrudates, samples post extrusion could be directly matched with native starch samples for their expansion characteristics. This should allow direct comparison of high and low sheared samples with differing amylose to amylopectin ratios. Expansion for all these key

samples has been assessed by a simple density measurement of the final cakes. It is recognised that this may be a crude estimate of the starch's performance to support bubble structure as it does distinguish neither initial expansion and shrinkage, nor bubble size and distribution. However, it is considered that with the major variations in the shear regimes and starch types, this measure would have provided directional indicators of the key factors for the relationship between starch macromolecular structures and performance.

For the popped native samples, it was apparent that disruption of the starch structures in the three maize starches tested was sufficient to allow the polymers to melt and interact to form a matrix. This matrix could be expanded by the superheated steam generated by the 12% water (wwb) incorporated into the samples. Not only will the water act as the blowing agent, but it also aids in the plasticising of the different molecular structures of the starches' organised assemblies. As the three maize starches have varying molecular organisations, it is possible that the critical water level for the different starches is not the same.

The same maize starch sources, after being extruded, dried and ground, also could form fused aerated masses on popping. The waxy, normal and high amylose starches showed the expected marked differences in the amount of breakdown and possible reassociation in their structures, as measured by water absorbance and water solubility. While changes to the high amylose starches were small, the starch with the normal amylose levels showed marked changes in the water absorbance. For the waxy sample, the solubility increased to near 100% on processing, but loss of crystalline order at the mildest treatment (popping native sample) was not fully achieved. Comparison of the densities of the samples after popping showed that, even though their starch polymeric structures were very different, their overall expansion performances were similar. This leads to the conclusions that, under the conditions used, the critical features of the polymer forming the bubble wall have not been defined. It does not seem to be dependent on the total amount of branched or linear glucan, nor on the intimate mixing of the polymers, nor on the breakdown of the aggregated starch structures, as long as the majority of the amylopectin crystalline structures have been disrupted.

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Author Contribution

Daniel Beech: Data curation (lead); Investigation (lead); Methodology (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **John Beech:** Conceptualization (equal); Methodology (equal); Supervision (equal). **Joanne Gould:** Funding acquisition (equal); Project administration (lead); Resources (lead); Supervision (equal). **Sandra Hill:** Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Supervision (equal); Visualization (equal); Writing – review & editing (equal).

Author statements

All data supporting this study are openly available from the University of Nottingham data repository at https://doi.org/10.17639/nott.7160.

Ethics approval was not required for this research.

The Authors declare no conflict of interest.

Data citation

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Peer review

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Data Availability Statement

All data supporting this study are openly available from the University of Nottingham data repository.

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