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How does temperature govern mechanisms of starch changes during extrusion?

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ABSTRACT

Potato and pea starches were processed on a twin-screw extruder under various moisture and thermomechanical conditions, chosen to keep material temperature T_e close to starch melting temperature, T_m, whilst avoiding die expansion. Extruded rods were analysed by asymmetrical flow field flow fractionation coupled with light scattering, X-ray diffraction, DSC, and light microscopy with image analysis. Molar mass of extruded materials decreased more for potato than for pea starch, when specific mechanical energy *SME* increased, likely because of larger amylopectin sensitivity to shear. No crystallinity was detected when $\Delta T = (T_m\text{-}T_e) \leq 0$. Residual gelatinization enthalpy ΔH_g decreased with ΔT. As illustrated by larger ΔT values for $\Delta H_g = 0$, decreasing moisture favored melting, likely by increasing solid friction. The fraction of granular remnants of potato starch was inversely correlated to *SME*. These results could be explained by considering starch melting during extrusion as a suspension of solid particles embedded in a continuous amorphous matrix.

1. Introduction

The interest of starch extrusion lies on the broad field of applications ranging from non-food products, like materials for the replacement of petroleum based polymers, to various foods because of enhanced nutritional properties as a macronutrient. Indeed final starch structure governs material and functional properties. Extrusion processing can be tuned in order to obtain the relevant structure for the target application, provided the structural changes of starch during processing are well controlled. During extrusion, starch can be converted into a homogenous molten state, sometimes called "thermoplastic starch", before it is shaped by flowing through the die (Tajuddin, Xie, Nicholson, Liu, & Halley, 2011). This conversion may encompass various structural changes, such as granules disruption, crystals melting, molecular degradation (depolymerization) (see for instance Liu, Xie, Yu, Chen, & Li, 2009; Liu, Halley, & Gilbert, 2010). These changes are very important because they will provide the extruded starchy materials with the relevant properties either for various food or non-food applications (Colonna, Tayeb, & Mercier, 1989; Kristiawan, Chaunier, Della Valle, Ndiaye, & Vergnes, 2016; Li et al., 2015; Liu et al., 2009; van der Sman & Broeze, 2013; Zhang et al., 2011). They are due to both thermal and mechanical inputs from the process. In a first approach, crystal melting is mainly due to heat by increasing material temperature above calorimetric melting temperature T_m (Cooke & Gidley, 1992; Donovan, 1979), while molecular degradation is rather due to mechanical input through shear stress that favors chain splitting (Brümmer, Meuser, van Lengerich, & Niemann, 2002; Liu et al., 2010; van den Einde, Akkermans, Van der Goot, & Boom, 2004). In turn, molecular degradation induces a drop of starch melt viscosity during extrusion (Xie, Halley, & Averous, 2012). This rheological change can be taken into account in modelling twin screw extrusion of starch by coupling shear energy and viscosity (Berzin, Tara, Tighzert, & Vergnes, 2010).

These energy transfers may be assessed by the measurement of temperature (extruder barrel and material) and specific mechanical energy (*SME*). However, accurate quantification of these transfers is challenged by (1) the difficulty of accurate temperature measurement inside an extruder and (2) the accumulation in *SME* of mechanical forces acting on material along the screw(s). Moreover the possible conversion of mechanical energy into heat by friction phenomena, solid

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Table 1
Main operating conditions, extrusion variables and structural features for (a) pea and (b) potato starches. (-) means that the sample was not analysed. D_{50} and N_A were not determined for pea starch, because micrographs could not be analysed.

(a) Barrel & die T (°C)	T_m (°C)	MC (%)	V (rpm)	Q (kg/h)	SME (J g^{-1})	T_e (°C)	$\bar{M}_w$ (%)	ΔH_g (%)	*Crystallinity* (%, WAXS)	D_{50} (µm)	N_A (mm^{-2})
95	95	30	40	0.4	470	95	–	0	–	20	340
95	95	30	50	0.6	480	95	32	0	0	20	180
95	95	30	50	1	290	95	–	0	0	25	370
95	95	30	50	1.35	250	95	–	0	–	22	460
95	95	30	90	0.4	1060	96	–	0	–	16	95
95	95	30	90	1	470	98	28	0	0	17	190
95	95	30	90	1.5	375	98	–	0	–	18	365
95	95	30	120	0.45	1395	100	–	0	–	14	25
95	95	30	120	0.6	1045	100	–	0	–	27	25
90	105	25	50	0.4	654	97	–	0	–	26	265
90	105	25	50	0.8	393	97	60	0	0	25	340
90	105	25	50	1.2	305	98	–	0	–	19	350
90	105	25	90	0.8	707	105	–	0	–	19	50
90	105	25	90	1.2	510	105	19	0	0	17	245
80	30	30	50	0.75	349	86	78	0	29	19	465
80	30	30	50	1.3	242	88	–	0	29	21	415
80	30	30	90	0.8	471	93	–	0	–	17	170
80	30	30	90	1.2	393	93	38	0	14	19	195

(b) Barrel & die T (°C)	T_m (°C)	MC (%)	V (rpm)	Q (kg/h)	SME (J g^{-1})	T_e (°C)	$\bar{M}_w$ (%)	DH_g (%)	Crystallinity (%, WAXS)
95	120	30	50	0.3	873	96	–	31	15
95	120	30	50	0.55	476	98	–	20	–
95	120	30	50	0.9	378	98	–	27	15
95	120	30	50	1.2	305	98	–	33	–
95	120	30	90	0.4	825	103	40	9	10
95	120	30	90	0.85	499	103	–	11	–
95	120	30	90	1.35	384	103	–	11	–
95	120	30	120	0.4	1257	105	–	5	0
95	120	30	120	1.2	471	105	–	6	–
95	120	30	120	0.65	870	106	32	5	10
95	120	30	120	1.8	419	106	–	8	–
95	115	35	50	0.3	524	100	49	16	–
95	115	35	50	1	209	100	–	12	15
95	115	35	90	0.6	471	103	–	5	–
95	115	35	90	1.5	220	103	63	5	10
95	115	35	120	0.85	443	105	–	0	5
95	115	35	120	1.7	222	105	–	0	10

when starch is in granular powdery state and viscous dissipation, when material has begun melting, also makes difficult to separate heat and mechanical effects. Although this issue may be addressed by a convenient experimental design (Brümmer et al., 2002; Li, Hasjim, Xie, Halley, & Gilbert, 2014), the quantitative information provided is limited to the domain studied and the mechanisms still need to be ascertained.

The action of mechanical energy can be decoupled from heat dissipation by applying cryo-milling as performed by Dhital, Shrestha, Flanagan, Hasjim, and Gidley (2011), who showed that mechanical forces could disrupt crystalline structure without molecular degradation, whereas hammer milling could induce molecular degradation in the case of rice grain (Tran et al., 2011). However, the energy levels that caused granule fragmentation, still need to be quantified, in order to transpose these findings to starch melting under shear during extrusion. Using a capillary rheometer with pre-shearing to simulate extrusion, Barron, Buleon, Colonna, and Della Valle (2000) and Barron, Bouchet, Della Valle, Gallant, and Planchot (2001) have shown that shear forces could induce granule fragmentation and a partial loss of crystallinity, even for temperature lower than T_m, and for rather low *SME* levels (≥ 150 J g^{-1}). Moreover, all these works have shown that this conversion could also depend on starch botanical origin, because of distinct thermal transitions (melting temperature, glass transition) or composition (amylose/amylopectin ratio).

Based on these results, our main hypothesis is that starch melting during extrusion, i.e. under shear, is mainly governed by the temperature of crystals melting, or T_m, whatever the way this temperature is reached, either by heat from the extruder barrel or by conversion of mechanical energy through solid friction between granules or viscous dissipation in the early molten part. Such hypothesis implies that starch melting in the extruder does not depend on starch botanical origin, once T_m differences are taken into account. It also leads to consider that granule fragmentation and crystal disruption do not play a major role in the phenomenon, and that macromolecular chain splitting could be limited.

So, the objective of our work was to ascertain the mechanisms of starch melting under extrusion conditions and determine how each structural level is impacted by testing this hypothesis. In this purpose, two different starches, smooth pea and potato, different in amylose content and granular structure were chosen and the role of melting temperature T_m was monitored, especially by different moisture settings.

2. Materials and methods

2.1. Materials

Smooth pea and potato starches were supplied by Roquette Frères (Lestrem, France). Their initial moisture content (*MC*, total wet basis), respectively 12.9% and 15.6% for smooth pea and potato starch, was