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On the importance of organization of glucan chains on thermal properties of starch

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ABSTRACT

The relationship between the internal structure of amylopectin from diverse plants and thermal properties of the starch granules has been investigated. Correlations were found between structural parameters, such as number of building blocks in clusters, interblock chain length and length of external chains, and gelatinization parameters. Onset gelatinization temperature negatively correlated with number of building blocks ($r = -0.952$, $p < 0.01$) and positively correlated with inter-block chain length ($r = 0.905$, $p < 0.01$). Enthalpy of gelatinization positively correlated with external chain length ($r = 0.854$, $p < 0.01$). These data showed that the internal structure is predictive of trends in thermal properties. A model is proposed based on the backbone concept of amylopectin structure that explains how the organization of chains in the semicrystalline lamellae of starch granules relates to the thermal properties.

1. Introduction

Starch is a composite semicrystalline polymer made up of anhydroglucose units linked by α-1,4 and α-1,6 glycosidic bonds. The major components are amylose and amylopectin that differ in molecular size and degree of branching. Amylopectin with specific chain lengths are organized into supramolecular structures with specific architecture. These chains can be distinguished as external chains, which build up the crystalline lamellae, and internal chains found among the clusters of branches in the amorphous lamellae (Pérez & Bertoft, 2010). Amylopectin structure is generally characterized by the unit chain length profile that exhibits a polymodal distribution (Hanashiro, Abe, & Hizukuri, 1996; Hizukuri, 1986). However, detailed studies on the internal unit chain profile of amylopectin demonstrated that the organization of chains in the amorphous lamellae potentially plays an important role in starch granule architecture (Bertoft, 2004; Bertoft, Koch, & Åman, 2012; Bertoft, Piyachomkwan, Chatakanonda, & Sriroth, 2008). Clusters in amylopectin were defined as groups of chains separated by internal chain segments with less than nine glucosyl residues (Bertoft, 2007). These clusters consist of smaller, tightly branched units named building blocks. Several parameters were elaborated in these studies, which describe unit chain organization of amylopectin, such as the external chain length (ECL), DP of clusters, number of building blocks in clusters (NBbl), and the interblock chain length (IB-CL, defined as the length of the chain segment between adjacent building blocks). A schematic model depicting these parameters is shown in Fig. 1 and a detailed description of how they are measured is found in Bertoft et al. (2012).

Several researchers have investigated the relationship between unit chain length distribution of amylopectin and its impact on functionality, which include gelatinization (Fredriksson, Silverio, Andersson, Eliasson, & Aman, 1998; Gomand et al., 2010; Shi & Seib, 1992, 1995; Tziotis, Seetharaman, Klucinec, Keeling, & White, 2005), retrogradation (Fredriksson et al., 1998; Silverio, Fredriksson, Andersson, Eliasson, & Aman, 2000; Tziotis et al., 2005; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003), pasting (Han & Hamaker, 2001; Tziotis et al., 2005) and gel textural properties (Hansen, Blennow, Pedersen, Norgaard, & Engelsen, 2008; Ong & Blanshard, 1995; Tziotis et al., 2005). In most of these studies, amylopectin structure has been considered as average chain length (CL) or as chains grouped into different size-categories, of which the most common classification is based on Hanashiro et al. (1996).

In polymer chemistry, it has been documented that chain flexibility, stiffness, geometric configuration and branching are determinants of glass transition temperature (Stevens, 1999). Interestingly, it has also been shown that the amorphous regions in the granules influence the physicochemical properties of the starch (Donovan, 1979; Genkina, Wikman, Bertoft, & Yuryev, 2007; Slade & Levine, 1988; Waigh, Gidley, Komanshek, & Donald, 2000). This suggests that the thermal properties of starch are a function of the supramolecular architecture of the amorphous and/or crystalline structure and not likely simply related to the unit chain

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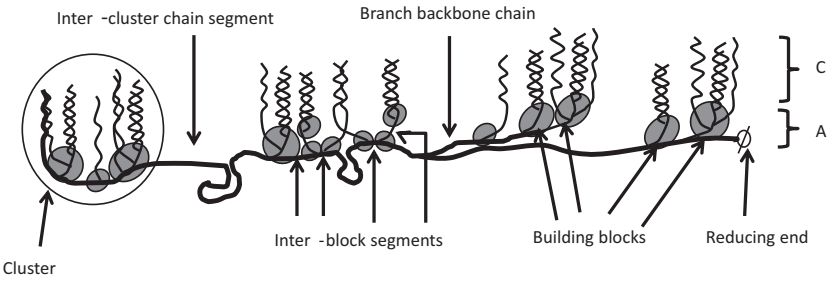

Fig. 1. Schematic model of the backbone structure of amylopectin highlighting specific internal structures. C, crystalline lamella; A, amorphous lamella.

distribution of amylopectin. Therefore, it is hypothesized that the organization of chains in the amorphous lamella has a significant impact on lamellar organization, polymer mobility and interaction. To our knowledge, only two investigations so far have related the internal structure of amylopectin to the physicochemical properties of granular starches (Kong, Bertoft, Bao, & Corke, 2008; Zhu, Corke, & Bertoft, 2011).

The objective of this study was to examine the relationship of the internal structure (organization of chains in the amorphous lamella) of amylopectin (Bertoft et al., 2008, 2012) with the thermal properties of the starches. This research demonstrates that the internal structure is predictive of trends in thermal properties, whereas correlations with individual chains or groups of chains can be misleading.

2. Experimental

2.1. Samples

Starch samples were selected from the series used in previous studies (Bertoft et al., 2008, 2012), in which their origin and structural details were described. The samples included Andean yam bean (*Pachyrhizus ahipa*, AYS), rye (*Secale cereale*, RS), oat (*Avena sativa*, OS), normal barley (*Hordeum vulgare*, NBS), waxy barley (*H. vulgare* WBS), waxy maize (*Zea mays*, WMS), medium amylose containing rice (*Oryza sativa*, MRS), waxy rice (*O. sativa*, WRS), sago (*Metroxylon sagu*, SS), kudzu (*Pueraria lobata*, KS), mung bean (*Vigna radiata*, MBS), West Indian arrowroot (*Maranta arundinacea*, AS), tapioca (*Manihot esculenta* TS), edible canna (or Queensland arrowroot, *Canna edulis*, CS), normal potato (*Solanum tuberosum*, NPS), waxy potato (*S. tuberosum*, WPS) and lesser yam starch (*Dioscorea esculenta*, YS), for a total of 17 starch samples. Selected structural data of the samples are found in Supplementary Table 1.

2.2. Differential scanning calorimetry (DSC)

Gelatinization parameters of starches were measured using a TA Instruments, Q1000 differential scanning calorimeter equipped with a thermal analysis data station and data recording software (TA Instruments, Universal Analysis 2000). Starch dispersions in water (1:3) were equilibrated for 3 h at room temperature before DSC analysis. The scanning temperature range and the heating rates were 20–120 °C and 5 °C/min, respectively. In all measurements, the thermogram was recorded with an empty aluminum pan as a reference. The transition temperatures reported are the onset (T_o), peak (T_p) and conclusion (T_c) temperatures. The enthalpy of gelatinization (ΔH) was estimated by integrating the area between the thermogram and a base line under the peak and was expressed as J/g of dry starch.

2.3. Statistical analysis

Statistical analysis was performed by SPSS statistical software (IBM SPSS STATISTICS 20). All determinations were replicated three times and mean values and standard deviations reported. A comparison of the means of gelatinization parameters was ascertained by Tukey's test, to a 5% level of significance using analysis of the variance (ANOVA). Pearson correlation analysis was conducted to study the correlation between internal chain length distribution and thermal properties.

3. Results and discussion

3.1. Gelatinization parameters of starches from the four structural groups

Based on the internal unit chain profiles obtained from φ,β-limit dextrins, Bertoft et al. (2008) classified starches into 4 groups. In this classification 17 amylopectin samples were used from different botanical sources. Group 1 possessed the lowest number of long chains and the size-distribution of the short chains was broad, which typically resulted in poor resolution of these major categories of chains. Group 4 possessed the highest number of long chains, whereas groups 2 and 3 were intermediate in chain distribution. Generally, the internal chains were divided into short B-chains (DP 3–25), and long chains, which were sub-categorized as B2 (DP ~26–50) and B3-chains (DP > 50) (the exact divisions being dependent on the individual samples).

Starches from different amylopectin groups showed different gelatinization attributes (T_o, T_p and T_c), gelatinization temperature range (T_c–T_o) and enthalpy of gelatinization (Figs. 2 and 3). It has been shown that the melting temperature of starch increases with increasing amylose content (Matveev et al., 2001). However, in this study no correlation was found between amylose content and melting temperature. Waxy starches from group 1 and group 4 exhibited higher T_o compared to their normal counterparts, whereas the waxy starch from group 2 showed lower T_o. Earlier studies showed that A-type crystallites melt at higher temperatures compared to B-type crystallites (Cooke & Gidley, 1992; Whittam, Noel, & Ring, 1990). These studies were conducted on non-granular materials such as re-crystallized debranched glycogen chains (Cooke & Gidley, 1992) and spherulites from amylose (Whittam et al., 1990). However, in this study native granular starches were used, and the gelatinization parameters appeared to be related to the structural groups of amylopectin rather than the type of crystal allomorph (Figs. 2 and 3). The lowest gelatinization temperature was observed for group 1 starches with a general trend of group 1 < group 2 < group 3 < group 4. (Fig. 2 and Supplementary Table 2). This suggests a relationship between the structural type of amylopectin and the thermal properties of starch granules. Statistical analysis showed that gelatinization temperatures (T_o, T_p and T_c) of group 1 significantly ($p < 0.05$) differed from groups 2,

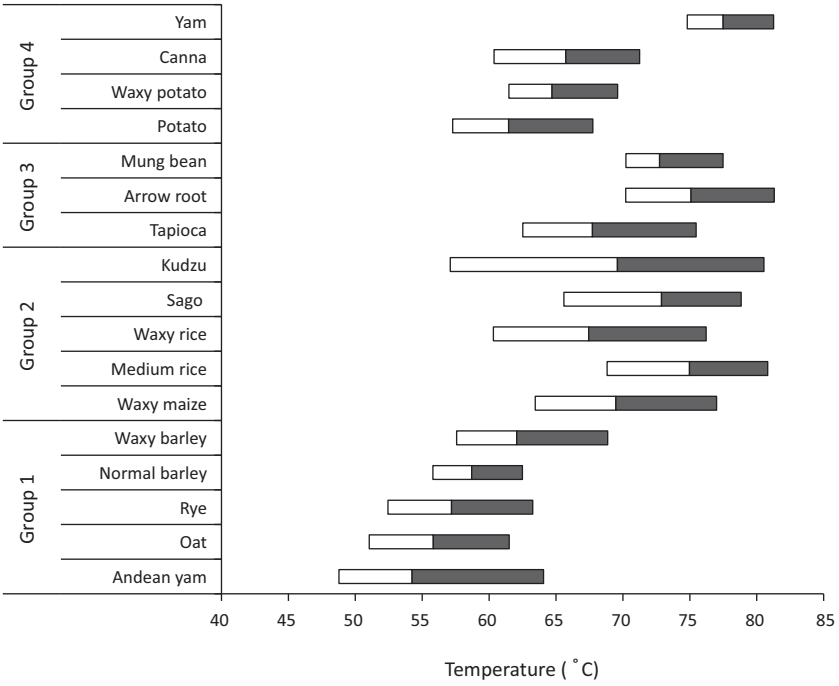

Fig. 2. Gelatinization transition temperatures of starches with four structural groups of amylopectin. Bars indicate the temperature range of gelatinization (T_o–T_c) and border verifies the position of T_p.

3, and 4. However, no significant difference was found between other groups. Gelatinization enthalpy of group 4 significantly differed from groups 1 and 2. Furthermore, potato is the most analyzed starch of the B-crystalline type and most of its structural features have been taken as typical for B-type crystalline starches. In this study all starches in group 4, that includes potato, exhibit B-type X-ray pattern (Bertoft et al., 2008). The general trend of increasing gelatinization temperature from group 1 to group 4 suggested that only yam starch behaved as a part of this systematic series, whereas potato, waxy potato and canna starch possessed divergent behavior.

In group 4, potato, waxy potato and canna showed lower gelatinization temperature and relatively broader gelatinization temperature range than lesser yam. It was also shown that the amount of phosphate monoester groups in amylopectin (Lim, Kasemuswan, & Jane, 1994; McPherson & Jane, 1999) and crystalline defects (Yuryev et al., 2004) are the important factors that contribute to the melting temperatures of starch. However, Karim et al. (2007) demonstrated that phosphate content had no influence on thermal properties of potato starches with widely varying phosphate content. A distinct difference in the amylopectin structure among samples within group 4 was a higher content of the short "fingerprint" A-chains in potato and canna compared to yam (Supplementary Table 1). "Fingerprint" A-chains (A_{fp}) is a distinct sub-group of the shortest chains of amylopectin at DP 6–8 and its profile is characteristic to the source of plant (Bertoft et al., 2008). These short external chains possibly introduce defects in the crystalline structure (Noda et al., 2009), rather than participating in double helix formation (Gidley & Bulpin, 1987). The high content of A_{fp}-chains in potato and canna therefore suggested a higher degree of structural defects compared to yam, which could explain the lower gelatinization temperature in the former starches.

In group 1, Andean yam bean starch gelatinized at relatively low temperature (Fig. 2). The amylopectin in this starch also possessed

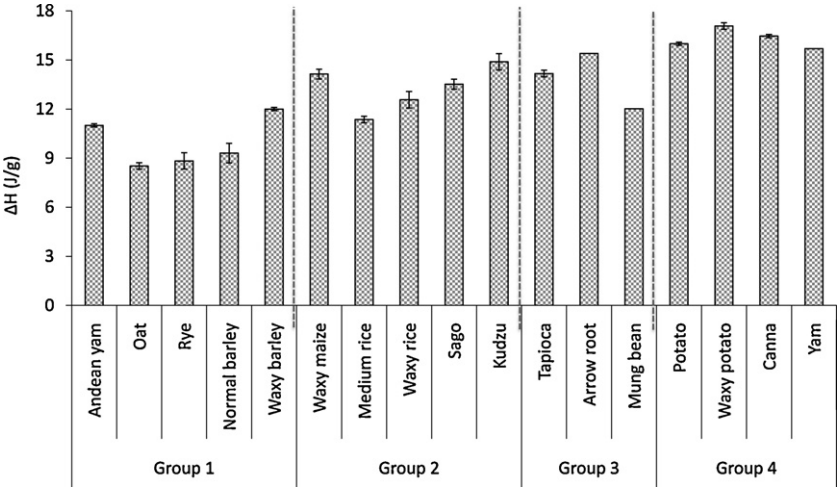

Fig. 3. Gelatinization enthalpy (ΔH) of starches with four structural groups of amylopectin.

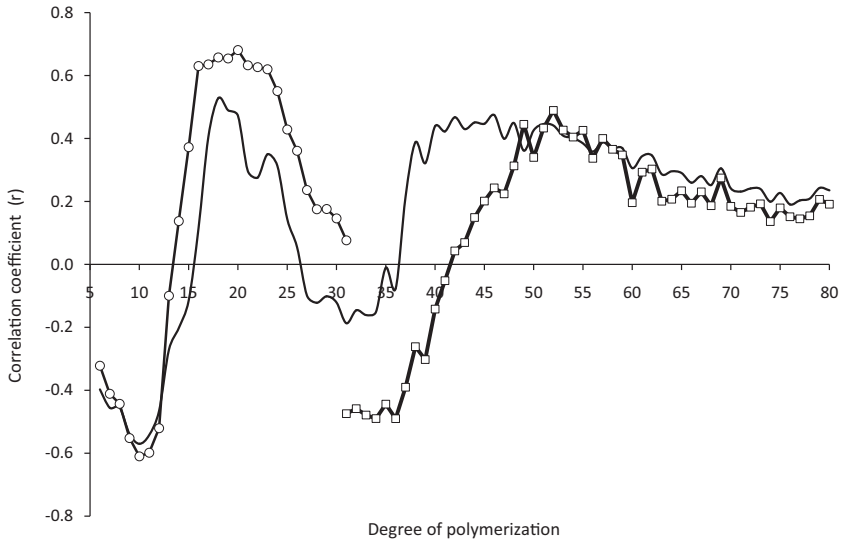

Fig. 4. Plot of correlation coefficients between the levels of chain (weight percent) DP 6–31 (○), 31–80 (□), and 6–80 (–), and the onset temperature of gelatinization (T_o) as a function of DP.

a high content of A_{fp}-chains (Bertoft et al., 2008). Interestingly, a closer inspection revealed that within each group of amylopectin structure there was a negative correlation between T_o and the amount of A_{fp}-chains (group 1, $r = -0.800$; group 2, $r = -0.678$; group 3, $r = -0.741$; group 4, $r = -0.786$), albeit the correlations were not statistically significant probably due to the small number of samples in each group. The results are in close agreement with earlier published results for amaranth starch (Kong et al., 2008). However, there was no correlation of A_{fp}-chains and T_o between the groups. As these chains are external segments, this indicates that the observed difference in gelatinization temperatures between the groups is influenced by the molecular organization of the internal segments of amylopectin.

Like with gelatinization temperature, the gelatinization enthalpy was also low for group 1 starches, whereas group 4 starches exhibited highest ΔH and groups 2 and 3 had intermediate values (Fig. 3). However, waxy starches showed higher ΔH compared to their normal counterparts. ΔH reflects the overall measure of crystalline quality and quantity (Cooke & Gidley, 1992), and the absence of amylose therefore apparently increased the relative crystallinity.

3.2. Unit chain distribution of amylopectin related to gelatinization parameters

Correlation between the relative amount (weight basis) of individual chains of amylopectin (Bertoft et al., 2008) and the onset gelatinization temperature (T_o) is shown in Fig. 4 The range of unit chains used in the calculations (and considered as 100% of the chains) was arbitrarily varied. Fig. 4 illustrates the results when only chains between DP 6–31 and 31–80 was considered, and this is compared with the result when all chains from DP 6 to 80 were included in the calculations. It is interesting to note that depending on which groups of chains were considered, the correlation values, the crossover DP, as well as positive or negative correlations, changed. Similar results, but at different correlation levels, were obtained when the relative molar concentration of chains (i.e., the relative number of chains) were used instead of mass (figure not shown). Therefore, it is highly unlikely that relative quantitative data from unit chain length distributions of amylopectin per se explain gelatinization properties of granular starches.

3.3. Organization of amylopectin chains related to gelatinization parameters

Despite considerable progress in many aspects of starch structure, there is still a gap in understanding how amylopectin molecules are organized and interact within the granule. The unit chain profile of amylopectin shows the composition of chains in the macromolecule. However, any given set of chains of different lengths can be organized in different ways (Bertoft, 2004), and thus, importantly, resulting in different functional properties during a thermal process. In the traditional cluster model of amylopectin structure (Hizukuri, 1986), the clusters of short chains are interconnected through long chains. Long chains participate in crystalline and amorphous lamellae. In the alternative backbone model (Bertoft, 2004) the direction of the clustered chains is perpendicular to the direction of an amorphous backbone consisting mainly of the long B-chains. In essence, therefore, the double helices in the crystalline lattice are interconnected and organized through the amorphous backbone. Based on the organization of amylopectin chains in a starch granule, one could potentially predict different physical behavior or functional properties, or one could propose different mechanisms to explain the changes during thermal process. Therefore, a thorough understanding of the organization of unit chains in amylopectin is essential to better understand the structure–function relationship and, without doubt, the nature of starch biosynthesis.

A detailed study on building block organization of clusters in amylopectin (Bertoft et al., 2012) showed that clusters from amylopectin samples of group 1 and group 2 had larger size, higher numbers of building blocks, and shorter interblock segments (Fig. 1) compared to those of groups 3 and 4. Furthermore, the backbone in samples from groups 1 and 2 was suggested to be more branched (Fig. 1) than in samples of groups 3 and 4. Several structural parameters were described earlier for ten selected starch samples (OS, RS, AYS, MRS, WMS, SS, AS, MBS, CS, YS) (Bertoft et al., 2012) representing the four different groups of amylopectin structure. We analyzed the correlation between gelatinization parameters and all other available structural data we have, namely amylose content, relative crystallinity, unit chain length distribution, internal chain length, total internal chain length and the abundance of different chain categories. Of these structural parameters, especially ECL, IB-CL and NBbl correlated with the gelatinization parameters obtained in

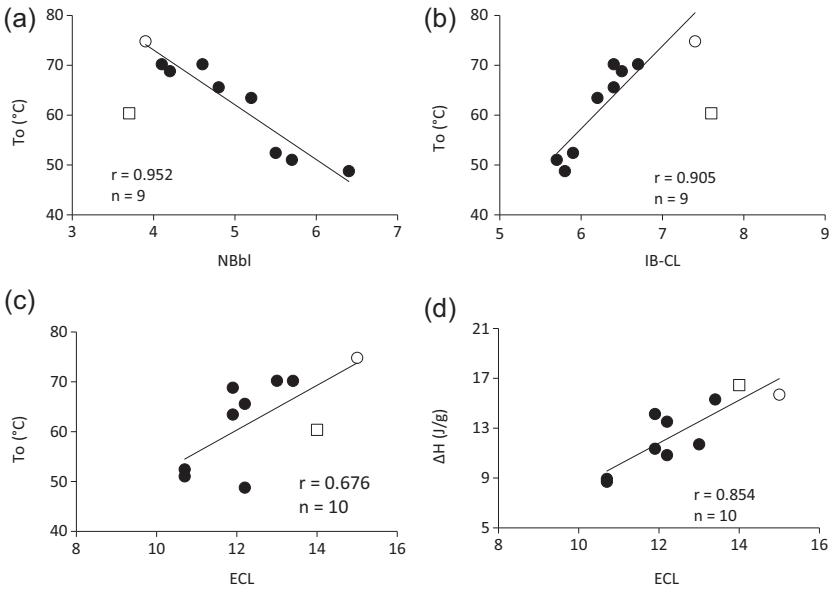

Fig. 5. Correlation coefficient (r) for the relationship between amylopectin structure and gelatinization parameters. In (a) and (b) the r-value does not include canna starch. Filled circles indicate samples from groups 1, 2 and 3. Open circle indicates yam and open square canna of group 4.

this work; T_o negatively correlated with NBbl ($r = -0.952$, $p < 0.01$) (Fig. 5a) and positively correlated with IB-CL ($r = 0.905$, $p < 0.01$) (Fig. 5b). In this correlation analysis only yam starch was included from group 4 because canna behaved differently from the rest of the data (i.e., when this single point was included, the regression coefficient decreased significantly to $r = 0.812$, $p < 0.01$ and $r = -0.647$, $p < 0.05$, respectively; data not shown). Other studies (Brunnschweiler et al., 2005; Jyothi, Moorthy, & Vimala, 2003; Peroni, Rocha, & Franco, 2006) also showed that in B-type starches, potato and canna starches are similar but different from those of lesser yam starch. The results further showed that the average external chain length (ECL) mostly affects gelatinization enthalpy (ΔH) ($r = 0.854$, $p < 0.01$, the correlation includes canna starch) (Fig. 5d) but no clear correlation was observed between ECL and T_o ($r = 0.676$, $p < 0.05$) (Fig. 5c). This seems plausible since gelatinization involves the uncoiling and melting of the external chains of amylopectin that are packed together as double helices in clusters (Cooke & Gidley, 1992).

Computer simulations of amylopectin models demonstrated that the branch points might initiate and/or stabilize the double helix (Imberty & Pérez, 1989) and only very limited combinations of certain internal chain lengths lead to parallel double helical arrangement (O'Sullivan & Perez, 1999). Any other combination of the length of the spacer arms between double helices results in non-parallel arrangement and therefore less stable crystallites. These chain lengths are in the order of the experimentally found

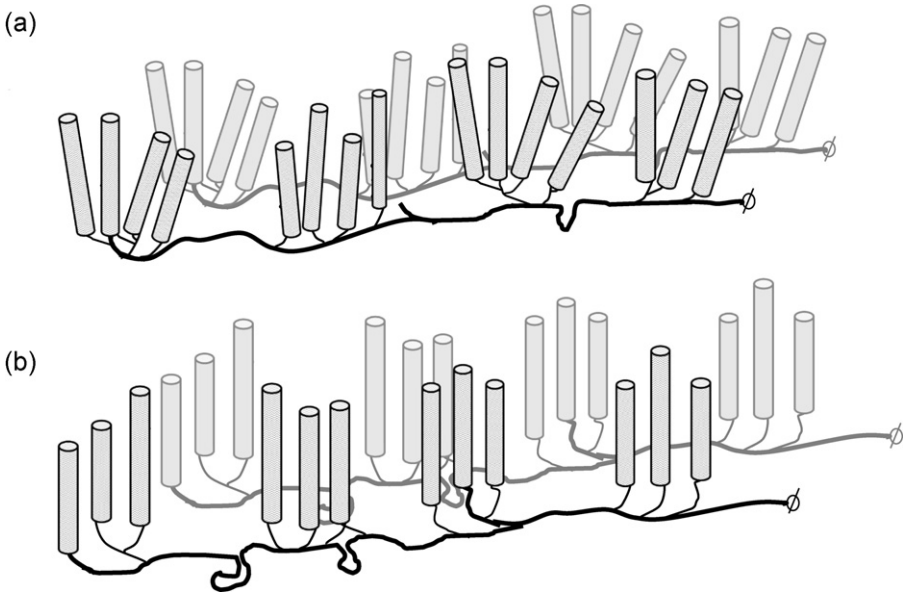

Fig. 6. Schematic diagram for organization of double helices in the crystalline lamella through internal chain segments in the backbone of amylopectin. Cylinders symbolize double helices, thick lines trace the backbone, and gray indicates another amylopectin molecule participating in the semi-crystalline arrangement in the starch granule. (a) Model for group 1 starches. Large clusters with high NBbl and short IB-CL limits the parallel packing of double helices. Large clusters have also more branches on the backbone, which contribute to a less perfect aligning of the amylopectin molecules. (b) Model for group 4 starches. Small clusters with less NBbl and long IB-CL facilitates the parallel packing of adjacent double helices. A less branched backbone also allows a more perfect aligning of the amylopectin molecules.

internal chain lengths within and between building blocks, and it suggests that the alignment of external chains and crystalline packing depends on the flexibility of the spacers between the double helices (either within or between the building blocks). A higher number of building blocks in the clusters, which simultaneously means a high number of interblock segments, and short interblock chain length was found typically in group 1 amylopectins, but also in group 2 (Bertoft et al., 2012). This possibly increases the number of non-parallel double helices due to unfavorable combinations of spacer arms and their short lengths decreases the flexibility of internal chains (Fig. 6a) within the cluster during biosynthesis. In contrast, small clusters and long interblock chain length, typical for group 3, and especially group 4 amylopectins (Bertoft et al., 2012), could facilitate the parallel alignment of external chains of amylopectin within the cluster (Fig. 6b). When double helices organize into crystallites, additional hydrogen bonds between double helices are established (Bogracheva, Wang, & Hedley, 2001) due to the close alignment of strands, which strengthen the crystal structure. This proposed alignment would resist plasticization during heating and thus elevate gelatinization temperatures.

Besides intra-molecular organization of the double helices, the dimensions of crystallites in the starch granules suggest that they are organized through inter-molecular arrangements (Pérez & Bertoft, 2010). A linear backbone, such as proposed for group 4 starches (Bertoft et al., 2012), potentially favors the alignment of the amylopectin molecules promoting a perfection of the crystals, whereas a branched backbone, such as was proposed for group 1 starches, prevents it, as schematically illustrated in Fig. 6. Overall, the results suggest that the internal organization of chains in amylopectin determines the alignment of chains within the crystalline lattice and thereby the thermal properties of the starch granules. However, other factors also contribute to and influence on the gelatinization parameters, such as the thermal history of the sample (e.g. annealing) (Alvani, Qi, & Tester, 2012). This is the subject of a forthcoming communication from our laboratory.

4. Conclusion

Whereas the length of the external chains of amylopectin have a large impact on melting enthalpy, the internal structure of amylopectin in terms of unit chain organization have a major influence on gelatinization transition temperatures of starch granules. Thus, among the many parameters that describe the structure of amylopectin, only the number of building blocks in clusters and the inter-block chain length appears to be parameters of major interest to predict the onset temperature of gelatinization. This suggests that a common granular organization of starch granules throughout the plant kingdom stems from the general principles of the building block structure.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.11.003.

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