Food Chemistry 315 (2020) 126267

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Review

A review of milling damaged starch: Generation, measurement, functionality and its effect on starch-based food systems

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ARTICLE INFO

Keywords:
Milling damaged starch
Functionality
Flour
Dough
Food products

ABSTRACT

Starchy food is quiet common in human diet. Starch is often modified to be endowed with specific functionalities. Making flour by milling is almost inevitable during starch-based food processing. So milling modified starch, i.e. milling damaged starch (MDS) is discussed in this paper. Starch damage degree depends on both milling conditions and raw materials. In comparison with native starch, MDS has changed granular structure, disrupted crystalline region and molecular degradation. Hence, its functionalities are modified, including gelatinization, pasting property, digestion and water hydration properties. Furthermore, this review summarizes the effect of MDS on flour, dough and starchy food products. Controlling MDS at a moderate level is essential for the production of starch(y) foods with desirable quality. The measurement of MDS is also summarized. This paper provides a comprehensive knowledge of MDS in order to promote the flourishing of novel starch(y) foods production.

1. Introduction

Considered to be one of the most inexpensive polysaccharide on earth, starch exists as the major component in many grains, legumes, tubes as well as roots. It generally comprises two kinds of polymers: linear amylose or slightly branched that is formed by the linking of α-D-glucose unit through α-(1, 4) glucosidic bonds, and highly branched amylopectin containing both α-(1, 4) glucosidic and α-(1, 6) glucosidic bonds (Ogunsona, Ojogbo, & Mekonnen, 2018; Zhao et al., 2019). Besides the role of energy source for humans' consumption, starch has been extracted from various plants for certain purposes in food, pharmaceutical, paper and textile industry. For example, it could adjust bread making performance (Zi et al., 2019), improve the yoghurt texture (Wong, Wicklund, Bridges, Whaley, & Koh, 2019) and act as bioactive compounds carriers (Deladino et al., 2015) during food processing. It's of vital significance to utilize this versatile biopolymers owing to their renewable supply from nature.

Nonetheless, the conservative structure of native starches from natural materials limits their properties and couldn't always satisfy practical applications. Thus, they are usually modified by chemical, physical or enzymatical methods to be endowed with particular properties (Haq et al., 2019; Zhu, 2019). Compared with other methods, physical modification is less time-consuming, generates no harmful chemical residues and has been deemed a green and environmentally friendly technique (Thirumdas, Kadam, & Annapure, 2017). Specifically, numerous innovative physical modification techniques have been conducted nowadays, including ultrasound, ultrahigh pressure, microwave, electric field, etc (Monroy, Rivero, & García, 2018; Zeng, Gao, Han, Zeng, & Yu, 2016), the popularity of which cater for people's appetite for "natural and healthy" food products. Furthermore, milling, a quite common physical process (even inevitable in cereal industry), has been frequently proved to exhibit special effect on starch structure and functionality (Lee, Shim, Goh, Mok, & Puligundla, 2019; Yu et al., 2015).

Milling damaged starch (MDS), also called mechanically activated starch, is generated through milling process, during which starch granules are inflicted with various forces (e.g. shear, impingement, collision and friction), consequently making them broken up into smaller particles (Suki, Azura, & Azahari, 2016; Zhang et al., 2019). The disrupted structure of MDS renders them novel characteristics meeting specific industrial requirements, and the damage degree is crucially important. For instance, MDS has higher water absorption ability and enzymatic hydrolysis rate and could be readily fermented by yeasts. Moderate level of them could improve dough quality during bread making whereas excessive starch damage can cause sticky dough (Barrera, Tadini, León, & Ribotta, 2016; Liu et al., 2014; Wang, Yu, Xin, Wang, & Copeland, 2017). Recent years have witnessed multitudes of researches aiming at uncovering the varying structure, physiochemical

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https://doi.org/10.1016/j.foodchem.2020.126267
Received 5 October 2019; Received in revised form 6 January 2020; Accepted 17 January 2020
Available online 21 January 2020

property and functionality of DS (Shi, Cheng, Zhu, & Lin, 2015; Wang et al., 2018). Moreover, many efforts have been made on investigation of MDS in starchy foods (not only isolated starch) containing various components (e.g. protein, non-starch polysaccharide) (Hackenberg, Vogel, Scherf, Jekle, & Becker, 2019; Ooms, Vandromme, Brijs, & Delcour, 2018), which adds the complexity of experimental findings.

At present, the latest opinions about MDS, as a noteworthy modified starch, hasn't been summarized in literature. Based on the scattered researching data recently, the paper aims to review the knowledge of MDS, including its generation, measurement, structure (granular, crystalline and molecular), functionality and its effect on starch-based food systems (mainly flour, dough, bread and other food products), in order to provide theoretical basis and stimulate further study of MDS as well as broaden its applications in food industry.

2. Generation of MDS

Many treatments during food processing could induce starch damage, such as heating, ultrasound and cold plasma (Okyere, Bertoft, & Annor, 2019). The damaged starch in this paper refers to that generated through milling process. As the unit operation of flour production, milling makes starch granules inside grains or other materials subjected to shear or impact forces from the collision with hard grinding medium (e.g. stone, roller and ultracentrifugal rotor) (Doblado-Maldonado, Pike, Sweley, & Rose, 2012; Niwa, Yoshida, Hayashi, & Kondo, 2017), eventually causing their morphological, crystalline or molecular structure damage. Besides, jet milling, an emerging ultrafine milling technique, uses high speed pressurized air stream to make starchy particles collide and frictionate each other (Drakos, Malindretou, Mandala, & Evageliou, 2017), thus also leading to starch damage.

Damage degree of milling-treated starch is influenced by three major factors, namely quality of raw materials, flour coarseness and milling conditions. Table 1 displays changes in MDS content from different qualities of plant materials and flours. Generally, the level of MDS is higher in harder grains than softer ones when the same milling treatments are used (Kwak et al., 2017; Makowska, Szwengiel, Kubiak, & Tomaszewska-Gras, 2014), probably because stronger milling force is required to destroy the tightly-packed starch structure of harder grains, leading to the increase in damage severity. The starch composition of grain also affects the MDS content. For instance, significantly greater degree of MDS occurs in milled waxy wheat flour (containing no amylose) in comparison with wild wheat, although they have similar hardness (Xu, Mense, Ambrose, Graybosch, & Shi, 2018). The reason might be that the semi-crystalline structure of amylopectin is more susceptible to mechanical force than amorphous amylose. MDS level tends to increase with the decrease of flour particle size (Liu, Hou, Lee, Marquart, & Dubat, 2016; Siliveru, Ambrose, & Vadlani, 2017). Accordingly, flour from finer fraction of grains has higher MDS content than that from coarse fraction due to the reduced particle size (Bourré et al., 2019; Monnet et al., 2019). Besides, the difference in flour coarseness can be caused by reconstituting flours from different seed fractions, and flour blends consisting of smaller particles result in increased percentage of MDS (Xu, Xu, Wang, & Zhou, 2018).

Additionally, milling conditions have profound impact, as exemplified in Table 2. Damage degree of starch could be enhanced by increasing milling intensity, including reducing distance between grinding medium, elevating milling energy input (Inamdar & Prabhasankar, 2017), adjusting rotor speed (Deng & Manthey, 2017a), adding grinding times (Choi & Baik, 2013), increasing jet gas pressure (Hossen et al., 2011), and so on. The increase in milling temperature could also contribute to starch damage (Di Silvestro et al., 2014). It might be because of the increased molecular mobility that accelerates the disruption of starch structure. Compared to dry milling, wet milling could better ensure starch granular integrity, because the excessive addition of water absorbs the heat generated throughout milling, thus hindering the increase in temperature of systems and resulting in less starch damage (Ahmad & Rajab, 2018). Moreover, starch damage is associated with pretreatment for raw materials before milling (e.g. tempering) (Abo-Dief, Abo-Bakr, Youssef, & Moustafa, 2019).

3. Measurement of MDS

MDS could be identified through the interaction with Congo Red, which makes it stained with characteristic red color in regular light and

Table 1
MDS levels generated from various raw materials or flours.

Influencing factor	Source of MDS	Description of raw material or flour	MDS content (%)	Reference
characteristics of raw materials	triticale	Madilo (cultivar), hardness index of 110	12.30	(Makowska et al., 2014)
	triticale	Pizarro (cultivar), hardness index of 168	14.69	(Makowska et al., 2014)
	soft wheat	Zhongmai175 (cultivar), hardness of 13.6	1.8–6.0	(Yu et al., 2015)
	hard wheat	Beijing0045 (cultivar), hardness of 57.6	3.4–15.7	(Yu et al., 2015)
	rice	variety of Seolgaeng, hardness of 2.95 kg	about 7	(Kwak et al., 2017)
	rice	variety of Goami, hardness of 5.08 kg	about 11	(Kwak et al., 2017)
	wheat	Mattern, waxy type, hardness index of 67.9	13.6	(Xu et al., 2018)
	wheat	Everest, wild type, hardness index of 65.2	6.6	(Xu et al., 2018)
characteristics of flour	wheat flour	hard red winter (wheat variety), particle size < 45 μm	12.33	(Siliveru et al., 2017).
	wheat flour	hard red winter (wheat variety), particle size 75–106 μm	4.92	(Siliveru et al., 2017).
	reconstituted whole-wheat flour	hard red winter (wheat variety), MPS of 173.7 μm	9.69	(Liu et al., 2016)
	reconstituted whole-wheat flour	hard red winter (wheat variety), MPS of 104.2 μm	11.98	(Liu et al., 2016)
	rice flour	MR263 (variety), MPS of 54.3 μm	7.82	(Asmeda et al., 2016)
	rice flour	MR263 (variety), MPS of 35.3 μm	10.70	(Asmeda et al., 2016)
	pea flour (coarse fraction)	MPS of 182 μm	0.4	(Monnet et al., 2019)
	pea flour (fine fraction)	MPS of 23 μm	5.2	(Monnet et al., 2019)
	common buckwheat flour	MPS of 115.8 μm	2.86	(Wronkowska & Haros, 2014)
	common buckwheat flour	MPS of 67.8 μm	6.74	(Yu et al., 2018)
	whole navy bean flour	MPS of 455.2 μm	0.52	(Bourré et al., 2019)
	whole navy bean flour	MPS of 61.8 μm	1.17	(Bourré et al., 2019)
	wheat flour (bran and endosperm blends)	MPS of 364.6 μm	4.36	(Xu et al., 2018)
	wheat flour (bran and endosperm blends)	MPS of 49.0 μm	5.81	(Xu et al., 2018)

*MDS and MPS is the abbreviation of milling damaged starch and mean particle size, respectively.

Table 2
MDS levels generated from different milling conditions.

Plant origin of MDS	Description of milling condition	MDS content (%)	Reference
wheat	stone milling at 45 °C with the stone gap of 1.7 mm for 318 s, milling energy of 144 J/g	12.36	(Inamdar & Prabhasankar, 2017)
wheat	stone milling at 88 °C with the stone gap of 0.2 mm for 900 s, milling energy of 406.8 J/g	26.11	(Inamdar & Prabhasankar, 2017)
durum wheat	ultracentrifugal milling (rotor speed of 9000 rpm, screen aperture size of 250 μm, feed rate of 3.72 kg/h)	about 12	(Deng & Manthey, 2017a)
durum wheat	ultracentrifugal milling (rotor speed of 15000 rpm, screen aperture size of 250 μm, feed rate of 3.72 kg/h)	close to 9	(Deng & Manthey, 2017a)
durum wheat	ultracentrifugal milling (rotor speed of 12000 rpm, screen aperture size of 250 μm, feed rate of 2.22 kg/h)	7.7	(Deng & Manthey, 2017a)
durum wheat	ultracentrifugal milling (rotor speed of 12000 rpm, screen aperture size of 250 μm, feed rate of 4.72 kg/h)	8.5	(Deng & Manthey, 2017a)
club wheat	flour regrinding using a pin mill	6.1	(Choi & Baik, 2013)
club wheat	flour without regrinding	5.8	(Choi & Baik, 2013)
barley	commercially milling followed by jet milling with the gas pressure of 0.8 MPa at constant feed rate of 3.35 kg/h	7.05	(Drakos et al., 2017)
barley	commercially milling without further treatment	4.72	(Drakos et al., 2017)
corn	grinding at the roll speed of 26000 rpm for 3.5 min	6.32	(Shi et al., 2016)
corn	grinding at the roll speed of 26000 rpm for 14 min	15.36	(Shi et al., 2016)
wheat	ball milling at 200 rpm for 30 min	12.2	(Ma et al., 2016)
wheat	ball milling at 300 rpm for 30 min	15.7	(Ma et al., 2016)
white rice	jet milling with the gas pressure of 0.30 MPa at a feed rate of 12 kg/h	9	(Hossen et al., 2011)
white rice	jet milling with the gas pressure of 0.42 MPa at a feed rate of 12 kg/h	14	(Hossen et al., 2011)
durum wheat	flour grinding below 30 °C by watermill for over 45 min	20.8	(Di Silvestro et al., 2014)
durum wheat	flour grinding at 60–65 °C by stone mill for over 45 min	28.0	(Di Silvestro et al., 2014)
rice	semi-wet milling using a hammer mill, prior to which 50% water was added for 8 h of tempering	7.33	(Ahmad & Rajab, 2018)
rice	wet milling using a stone mill, prior to which 50% water was added for 8 h of tempering	3.80	(Ahmad & Rajab, 2018)
common buckwheat	stone milling at the speed of 18 rpm	6.74	(Yu et al., 2018)
common buckwheat	wet milling, prior to which grains were steeped at 20 °C for 24 h	5.62	(Yu et al., 2018)

*MDS is the abbreviation of milling damaged starch.

reveal extinction cross effect when exposed to cross-polarized light (Lamb & Loy, 2005). Ways to quantify MDS mainly consist of enzymatic method and iodine absorption method. The former is based on the principle that MDS has high susceptibility to α-amylase so that it could be readily hydrolyzed into reducing sugars. Thus, the proportion of MDS could be reflected by calculating the converted reducing sugars content in specific mass of starch samples. Reducing sugars level is often estimated by titrimetric method, colorimetric assay, Farrand method and so on (Karkalas, Tester, & Morrison, 1992; Struyf et al., 2017). Among them, titrimetric and colorimetric method has been authorized by standard of AACC 76-30A and AACC 76-31 (Rogers, Gelrothm, Langemeier & Ranhotra, 1994). Instead of reducing sugar determination, MDS percentage could also be obtained from the measurement of Brix value of hydrolyzate together with the conversion factor. This approach is more convenient owing to the reduced experimental steps, and has been observed to have highly positive correlations with AACC methods (Boyacı, Williams, & Köksel, 2004). Regarding iodine absorption method, the amount of absorbed iodine by starch granules is correlated with MDS levels. The iodine absorption index ratio is often analyzed in a solution using amperometric method via a SDmatic. This method has also been incorporated into AACC standard (Wronkowska & Haros, 2014).

Apart from these conventional means, MDS could also be characterized by a series of modern techniques. For instance, starch granules possess irregular shape, rougher surface and changed particle size when damaged during milling process. The morphological difference from native ones can be observed using scanning electron microscopy transmission electron microscopy and light diffraction (K. Zhang et al., 2019), etc. Besides, considerable characterization efforts have been focused on the crystalline and molecular structure. Particularly, MDS has disrupted crystalline region, the changes in semi-crystalline lamellae could be detected by small-angle X-ray scattering, and crystallinity degree could be reflected via the peak intensity in X-ray diffraction diagram (Tan et al., 2015). Given molecular structure, many studies have employed chromatographic separation (e.g. gel permeation chromatography) methods to analyze the characteristic molecular weight distribution and chain length of MDS (Liu et al., 2019b). Spectral methods (e.g. Fourier transform-Infrared spectroscopy) have also been adopted to assess its specific functional groups and molecular order (Lv et al., 2019). In terms of thermal property, differential scanning calorimetry (DSC) is also an approach for MDS identification, because MDS generally has lowered gelatinization temperature and endothermic enthalpy (ΔH), implying undermined thermal stability incurred by the reduction of ordered structure. Some investigations have confirmed the pronounced linear correlation between ΔH and MDS level (with r value of $-0.97 \sim -0.989$) (Loubes & Tolaba, 2014; Wu et al., 2018), which makes it possible for DSC to be integrated into quantitative methods if optimized operating conditions are established. Detailed quantitative and identification methods of MDS have been listed in Table 3 from recent references.

4. Structure of MDS

Normally, two categories of anhydroglucose polymers are contained in starch: amylose whose molecular weight is lower ($10^5 \sim 10^6$) and amylopectin possessing higher molecular weight ($10^7 \sim 10^9$) (Lu, Belanger, Donner, & Liu, 2018). Their sequential or random conformation and arrangement facilitates the formation of intricate starch structure. To make it simplified, six hierarchical structural levels have been mentioned. Among them, level 1 means linear branches composed of α-D-glucose units linked only by α- (1, 4) glucosidic bonds, while level 2 is the combination of linear branches in level 1 via α- (1, 6) glucosidic bonds in the branching point. Branches of amylopectin usually aggregate into double helical clusters. Side chains of the cluster form crystalline region, and branches near the branching point are responsible for the amorphous state. The alternating crystalline and amorphous state is the starch structure in level 3 (i.e. semi-crystalline structure), which could expand to growth rings and form the structure in level 4. Various growth rings are radially arranged towards granule surface, constituting an individual starch granule (namely level 5). Level 6 refers to the complex of starch with other matrixes (e.g. protein) in raw materials (Hasjim, Li, & Dhital, 2013). Schematic diagram of MDS structure is given in Fig. 1. Specific changes in granular (level 5 and 6), crystalline (level 3 and 4) and molecular (level 1 and 2)

Table 3
Characterization and quantitative methods of MDS in recent literature.

Plant source of MDS	Characterization method				Quantitative method	Reference
	Granular structure	Crystalline structure	Molecular structure	Thermal property		
wheat	SEM, LD	–	–	DSC	iodine absorption method	(Angelidis et al., 2016)
wheat	SEM	XRD, SAXS	–	–	enzymatic method	(Niu et al., 2017)
wheat	SEM	XRD	*SEC*	DSC	enzymatic method	(Wu et al., 2018)
wheat	SEM	XRD	–	DSC	enzymatic method	(Liu et al., 2017)
wheat	SEM, LD	XRD	–	DSC	enzymatic method	(Yu et al., 2015)
triticale	SEM, LD	–	*SEC*	DSC	iodine absorption method	(Makowska et al., 2014)
rice	SLS	XRD	–	DSC	–	(González et al., 2018)
rice	–	XRD	–	DSC	enzymatic method	(Loubes & Tolaba, 2014)
rice	SEM	XRD	*SEC*	DSC	–	(Fu et al., 2016)
corn	SEM, LD	XRD	–	DSC	–	(Shi et al., 2015)
corn	SEM, LD	PLM, XRD, SAXS	FT-Raman	–	–	(Tan et al., 2015)
corn	SEM, TEM, LD	XRD	FT-IR	–	–	(Liu et al., 2011)
common buckwheat	SEM, LD	–	–	DSC	iodine absorption method	(Wronkowska & Haros, 2014)
common buckwheat	SEM	–	–	DSC	iodine absorption method	(Yu et al., 2018)
mung bean	SEM, CLSM, LD	PLM, XRD	FT-IR	DSC	–	(Zhang et al., 2019)
sorghum	SEM, LD	XRD	–	DSC	enzymatic method	(Palavecino et al., 2019)
cassava	SEM	XRD	–	–	enzymatic method	(Liu et al., 2019a)
cassava	SEM	–	GPC	DSC	enzymatic method	(Liu et al., 2019b)
cassava, carrot	SEM	PLM, XRD	AEC, GPC	DSC	–	(Moraes et al., 2013)
potato	SEM	XRD	FT-IR	DSC	–	(Lv et al., 2019)

*MDS: milling damaged starch; SEM: scanning electron microscopy; LD: laser diffraction; SLS: static light scattering; TEM: transmission electron microscopy; CLSM: confocal laser scanning microscopy; XRD: X-ray diffraction; SAXS: small-angle X-ray scattering; PLM: polarized light microscopy; *SEC*: size exclusion chromatography; FT-Raman: Fourier Transform-Raman spectroscopy; FT-IR: Fourier Transform-Infrared spectroscopy; GPC: gel permeation chromatography; AEC: anion exchange chromatography; DSC: differential scanning calorimetry.
*"–" means that the data isn't given in literature.

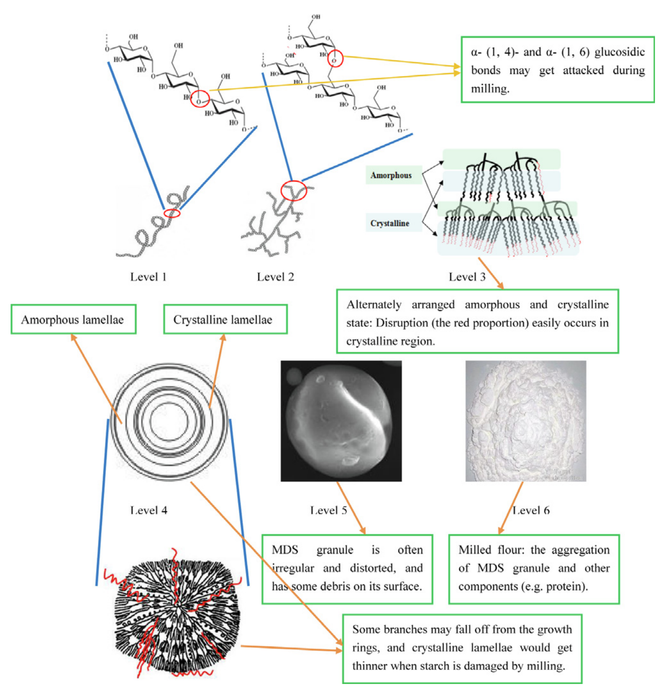

Fig. 1. Schematic diagram of MDS (milling damaged starch) hierarchical structure.

structure of MDS will be discussed in the following.

4.1. Granular structure

Different from starch damage through other treatments (e.g. heating), a most significant feature of MDS is that they have inevitably destroyed granular structure (Zavareze & Dias, 2011). Starch granules in native samples are generally slick, flat, have few concave-convex occasions, and are often packed each other or with proteins before treatment. However, the existence of MDS makes granules rough, distorted and deformed (e.g. tartary buckwheat and green gram) (Sakhare & Inamdar, 2014; Wronkowska & Haros, 2014). The greater MDS level is, the rougher and more irregular and distorted starch granule is (Barrera et al., 2013; Wu et al., 2018). Furthermore, a piece of debris could be observed falling off from granules in highly MDS (e.g. maize and cassava) (He et al., 2014; Ren, Li, Wang, Özkan, & Mao, 2010; Zhang, Ding, Ndeurumi, Wang, & Feng, 2015). Fissures, cracks, porosity and grooves have also been noted on MDS surface (e.g. maize and wheat) (Liu, Ma, Yu, Shi, & Xue, 2011; Yu et al., 2015). In comparison with MDS generated in starchy foods, these changes in that from isolated starch are more uniform among starch granules, because all parts of isolated starch suffer from similar contact frequencies with external forces (Yu et al., 2015).

Particle size distribution is markedly affected by starch damage. As acknowledged, the mean particle size of cassava and wheat starch was significantly reduced after getting damaged (El-Porai, Salama, Sharaf, Hegazy, & Gadallah, 2013; Ren et al., 2010). On the contrary, some studies indicated that damaged wheat, maize and mung bean starch had increased average particle size compared to native ones (He et al., 2014; Yu et al., 2015; Zhang et al., 2019). The discrepancy should be ascribed to the damage degree and varying internal structures of starch in different materials. Severely MDS tends to get agglomerated or adhere to other fragments, and MDS may have loosened structure, both of which contribute to the enhancement of DS particle size (Yu et al., 2015; K. Zhang et al., 2019). Moreover, starch composition could influence the particle size of MDS. Lower ratio of amylopectin to amylose results in higher particle size of MDS. As for explanation, the amorphous amylose, like a flexible mechanical plasticizer, could absorb excessive shock and cushion the destruction of crystalline amylopectin by external forces in starch granules, thus alleviating the particle size reduction (Lu, Wang, Li, & Huang, 2018).

4.2. Crystalline structure

Overall, the crystalline region (both A- and B-type) of MDS is destroyed more or less, thus leading to the decline in crystallinity degree in comparison with native starch. It has been verified on starch from many materials, including wheat, maize, rice, potato, sorghum, amaranth grain, cassava and carrot (Anzai, Hagiwara, Watanabe, Komiyama, & Suzuki, 2011; Lu, Xiao, & Huang, 2018; Moraes, Alves, & Franco, 2013; Roa, Santagapita, Buera, & Tolaba, 2014; Zhang, Zhao, & Xiong, 2017). The higher damage degree of starch is, the lower crystallinity degree is (Loubes & Tolaba, 2014; Palavecino, Penci, & Ribotta, 2019). However, the polymorphic type of starch often remains unchanged after being damaged through milling unless the crystalline state disappears completely (Li et al., 2017; Wang et al., 2018).

Reasons accounting for the crystallinity loss are various. Basically, the spatial arrangement of amolose and amylopectin is disrupted; the fragile crystalline region is more vulnerable to mechanical force than elastic amorphous one and becomes smaller and smaller as starch gets damaged (Kim & Kim, 2014). Tan et al. (2015) found a 4.8% decrease in the thickness of semi-crystalline lamellae of cornstarch when it was damaged, and a 100% decrease when it was severely damaged. Likewise, Niu, Zhang, Jia, and Zhao (2017) reported a decrease in that of whole wheat starch from 10.58 to 10.40 nm as the MDS level gradually increased. As suggested by Anzai et al. (2011), the thorough destruction of potato starch crystals should be put down to the broken hydrogen bonds that connected side chains in amylopectin clusters, eventually causing the disintegration of crystalline double helices. Indeed, the role of hydrogen bonds in maintaining MDS crystallinity can't be underestimated. For example, a unit of A-type starch crystals contains only 8 inter-helical water molecules. By contrast, a B-type crystal unit possesses up to 36 water molecules between helices, implying that much more hydrogen bonds could form in B-type crystals. The compact hydrogen-bond-network makes the crystalline lamellae more robust (Tan et al., 2015). This is the reason why B-type crystalline structure is more resistant than A-type when they are subjected to milling damage. Additionally, the decomposition of some amylose which may be also involved in the formation of crystals could give rise to crystallinity loss, although the crystalline zone of starch is mainly owed to the double helices structure of amylopectin (Liu, Hong, & Zheng, 2017). The correlation between crystallinity loss and the specific changes in MDS needs to be further clarified.

4.3. Molecular structure

As a basic element of molecular structure, molecular weight of starch can be affected when it is damaged. For example, the average molecular weight of maize starch decreased to 1.48×10^7 g/mol after getting damaged through milling, 4.7% lower than that before treatment (Shi et al., 2015). Similar decrease was also noted on cassava starch, and its average molecular weight gradually decreased with the enhancement of MDS level (Liu et al., 2019b). Undoubtedly, the reason should be the changes of molecular chain. Some studies disclosed that significant higher amylose content was detected in MDS in comparison with native starch, and higher MDS level caused greater increase of amylose at the expense of the conversion of amylopectin (Liu et al., 2019a; Shi et al., 2016). However, little marked difference was obtained in molecular weight distribution of wheat starch with varying damage degrees (1.8 ~ 28.8%), and the amylose content remained stable among all MDS levels, according to the data of Wu et al. (2018), who only found the degradation of amylopectin into smaller branched fragments. These contradictory results may be on account of the characteristic structure of starch in each botanical source and MDS generated under different conditions.

Chain length is another important factor of molecular structure. Wu et al. (2018) suggested that MDS level of 28.8% in wheat starch drastically decreased the percentage of longer chains (polymerization degree of 100 ~ 10000) whereas enhanced that of shorter ones (polymerization degree of 0 ~ 100) in contrast to MDS level of 1.8%. On the other hand, there weren't any obvious changes in the distribution of branch chain length among cassava or carrot starch possessing different MDS levels (Moraes et al., 2013). Thus, it's inferred that starch damage could induce the degradation of at most a small amount of α- (1, 4) glucosidic linkages in cassava and carrot starch. Moreover, the increase in apparent amylose content implies that α- (1, 6) glucosidic linkages might suffer more attack and be readily degraded during damage of cassava and carrot starch. But considering waxy corn starch, the reduced characteristic peak intensity associated with C_1 and C_4, as illustrated by Fourier transform Raman spectrometry diagram, suggests the possibility of disruption on α- (1, 4) glucosidic linkages in MDS (Tan et al., 2015). Besides, changes in some functional groups have also been observed as a consequence of starch damage, e.g. more hydroxyl groups were exposed in MDS chains of potato (Lv et al., 2019). When it came to mung bean starch, milling damage led to the fluctuation of chemical bonds vibration while diminishing its crystallinity (Zhang et al., 2019). Further research is essential on ascertaining changes of detailed location in MDS using more innovative methods (e.g. nuclear-magnetic resonance spectrometry).

5. Functionality of MDS

5.1. Gelatinization

Starch gelatinization is a process during which starch is heated in water, accomplishing the transition from native semicrystalline state to amorphous structure. DSC has been often used for the measurement of gelatinization property. The obtained parameters include onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and ΔH. Among them, gelatinization temperatures are indicators of crystalline heat stability. ΔH reflects the enthalpy to melt amylopectin-based crystals as well as indicates the degree of molecular disorders. The difference of T_c and T_o (namely ΔT) suggests the structural heterogeneity among starch granules within one sample (Liu, Li, Jiang, & Tian, 2018; Shi et al., 2016).

In most cases, there is a decreasing tendency in gelatinization temperature (T_o, T_p and T_c) and ΔH as the MDS level increases (Liu et al., 2019b; Liu et al., 2017; Shi et al., 2016). The tendency might be explained by the increased disorder in crystalline structure due to the degradation of amylopectin or amylose, which reduces the energy required for gelatinization. As reported previously, the ΔH of milling damaged rice starch was positively correlated with its crystallinity degree, which also demonstrated the disruption of crystalline region made it easier for MDS to gelatinize (González, Loubes, & Tolaba, 2018). Besides, there are studies concluding that T_o significantly decreased with the enhancement of MDS from wheat but little difference was noted on T_p and T_c, thus broadening the gelatinization temperature range (ΔT). The elevated ΔT implies the less uniformity of MDS granules before gelatinization, while the unchanged T_p and T_c indicates the melting of crystals during gelatinization is facilitated by starch damage and the homogeneity is improved during the process (Makowska et al., 2014; Yu et al., 2015). Moisture content has special effect on MDS gelatinization. For example, no drastic changes were observed in T_o and ΔT among varying levels of MDS from wheat at the moisture content of 43 ~ 82%. However, T_o markedly increased with the increment of MDS when moisture content declined to 35% (Barrera, León, & Ribotta, 2012). Distinct from the above results, another investigation reported an increase in T_o and T_p when maize starch got damaged. It might be attributed to the loosened and more elastic amorphous area in MDS that required more heat energy for gelatinization (Shi et al., 2015). The association of MDS gelatinization with detailed molecular structure should be established in the following studies.

5.2. Pasting property

Acting as a gelling/thickening agent is one of the important applications of starch during food processing. Starch catering for this application depends on its good pasting property (Miskelly & Suter, 2017).

Pasting property is usually evaluated by Rapid Visco Analyzer (RVA) or BrabenderMicro Viscoamylograph. Exposed to a constant stirring force, starch is heated in starch/water systems until reaching the highest temperature, and then cooled based on a programmed heating cycle. Thus, pasting profiles are recorded during the process of viscosity development (Barrera et al., 2013; Tan et al., 2015).

Compared with native starch, MDS usually has lower pasting viscosity and temperature (e.g. wheat, corn and rice) (González et al., 2018; Tan et al., 2015). Furthermore, our research group confirmed that both pasting viscosity and temperature progressively declined with the increasing degree of starch damage (Liu et al., 2017). As mentioned in the preceding section, MDS has reduced particle size and broken granular surface, which could enhance the permeability of water into granules. Besides, MDS has disrupted crystalline structure. These factors eventually cause a diminished thermal stability of starch supermolecular structure, therefore achieving a declined pasting temperature (Tan et al., 2015). Nonetheless, some reports revealed that pasting temperature rose with the increment of MDS (Barrera et al., 2013). The abnormal increase may be interpreted by the insufficiently accurate data obtained via RVA method, because pasting temperature is the temperature at which viscosity starts to develop, during which the value is changeable and difficult to measure (Wu et al., 2018). Besides, the granules aggregation in severely damaged starch through milling, which may retard the formation of dispersion system, could also account for the increase of pasting temperature.

The decrease of pasting viscosity should be ascribed to the fragile surface of broken MDS granules that is less resistant to shear force when they get swollen during heating in water (Tan et al., 2015). Based upon another researchers' opinions, the effect of enhancing MDS level is similar to that of lowering starch concentration, i.e. increasing free water content and diluting the swollen granules concentration during heating, which presumably weaken the interactions of starch molecules and thus decreases the pasting viscosity (Barrera et al., 2013; Wang et al., 2018). Also, the decrease of pasting viscosity of MDS was observed to have pronounced association with the loss of crystallinity and gelatinization degree (González et al., 2018). Additionally, the pasting profile of MDS relies on the amylose/amylopectin ratio. For instance, no characteristic pasting profile was obtained in damaged corn starch (comprising 80% amylose), since its resistant crystalline structure couldn't be melted at the highest testing temperature (Tan et al., 2015). The next researching focus should be on the specific pasting mechanism, such as the effect of molecular chain length on viscosity of MDS.

5.3. Water hydration property

When in cold water, native starch granules are insoluble and can only capture minor amounts of water, because hydroxyl groups in crystalline region interplay with each other via hydrogen bonding, which are less available for the interaction with external water molecules. Once the internal hydrogen bonding is broken down (e.g. during heating), starch granules uptake water more easily and expand to larger size along with soluble components leached into continuous phase (Amagliani, O'Regan, Kelly, & O'Mahony, 2016; Zavareze & Dias, 2011). In detail, water hydration properties consist of solubility, water absorption index (WAI) and swelling power (SP). Solubility is often expressed as the ratio of dried weight of leached soluble components to dried sample weight. WAI is the percentage of wet sedimented starch weight to dried sample weight. SP could be calculated as the ratio of wet sedimented starch weight or volume in dried sample weight (removing solubilized fractions).

MDS often has increased solubility when compared with native starch. The higher the milling severity is, the greater the MDS solubility is (e.g. wheat, maize, rice, cassava carrot and potato starch) (Dhital, Shrestha, & Gidley, 2010; Moraes et al., 2013). Meanwhile, the solubility has been found to be positively correlated with MDS content (Liu et al., 2017). As mentioned above, molecular degradation may occur in MDS, providing an opportunity for the generation of smaller soluble molecules and causing the solubility enhancement. In view of crystalline structure, a negatively exponential correlation was observed between solubility and crystallinity degree of rice starch with r^2 value above 0.9 (González et al., 2018). This implies that the structural disorder (or expansion in amorphous region) caused by crystalline destruction also contributes to the increase in solubility. Moreover, solubility of MDS is drastically elevated in hot water in contrast with that in cold environment (Wu et al., 2018). The reason might be that molecules move faster at higher temperature, expediting the dispersion of amorphous amylose and other soluble factions into water.

Starch damage during milling could result in enhanced WAI and SP. The increment in milling damage degree generally gives rise to the increased value of the two indices (Wang et al., 2018; Wu et al., 2018). However, the SP is weakened when MDS is generated under extremely severe conditions (Moraes et al., 2013). Since milling may cause the damage to hydrogen bonding, more hydroxyls inside double helices would become exposed to interact with the surrounding water molecules (Stefanie Hackenberg, Verheyen, Jekle, & Becker, 2016), thus improving water retaining ability (i.e. increasing SP). Furthermore, MDS usually has cracked surface and more holes or channels inside granules, providing freer access for water absorption. But excessively great milling damage, on the contrary, probably makes the semi-crystalline lamellae collapsed, and contributes to the decline in SP. For another, there weren't any changes in SP of wheat starch isolated from varying flour millstreams, despite the significant discrepancy in their MDS levels (Yu et al., 2015). Undeniably, starch SP is chiefly dominated by the intactness of amylopectin (Wang & Copeland, 2012). Presumably milling only poses damage to the amylose whereas has little impact on the amylopectin proportion, which could interpret the unchanged SP among varying MDS. Related molecular evaluation is needed for confirmation.

5.4. In vitro enzymatic digestibility

Digestibility is an important reflection of the nutritional value of starch. On the basis of digesting rate, starch could be classified into resistant starch (RS), slowly digestible starch (SDS) along with rapidly digestible starch (RDS) (Situ, Song, Luo, & Yang, 2019). RS couldn't be digested by enzymes present in human gastrointestinal. SDS could be hydrolyzed into glucose in small intestine for approximately 2 h. By contrast, RDS could be degraded in no more than 20 min (Šárka & Dvořáček, 2017). Moderately enhancing the digestible starch level is essential for the daily energy supplement to humans, particularly those suffering from maltrition caused by energy lacking.

MDS has augmented rate of enzymatic digestion *in vitro* in contrast to native starch, which has been exemplified on the starch of wheat, potato, maize and rice (Dhital et al., 2010; Fu, Luo, Liu, Liu, & Zhan, 2016; Yu et al., 2015). Higher damage degree could result in greater digestibility percentage. Specifically, previous studies indicated that starch damage enhanced RDS and SDS content while decreased RS content in jet milled rice starch (Fu et al., 2016). Also, noticeable positive correlation was found between RDS content and starch damage degree of isolated wheat starch (Yu et al., 2015). These changes are closely concerned with structural variation caused by starch damage. MDS has reduced granular size and enhanced surface area, more surface hollows or channels insides granules, offering greater opportunities for the interaction between enzyme and starch. Besides, the unique granular structure of MDS may contribute to easier water diffusion and enzyme penetration that is indispensable for enzymatic reactions (Almeida et al., 2019). The destroyed crystalline structure of MDS may promote the formation of flexible amorphous state, which makes it more accessible for enzymes to combine with starch (Lv et al., 2019). In addition, the molecular composition of MDS shouldn't be overlooked. As documented, starch possessing more amylose and single helices requires longer time to be digested by amylolytic enzymes (Li et al., 2019;

Xu, Chen, Guo, Liang, & Xie, 2020). More evidences are necessary for the exact relationship of MDS enzymatic digestibility and its crystalline/molecular orders.

6. Effect of MDS on starch-based food systems

6.1. Effect on flour quality

6.1.1. Gelatinization

Similar to the changes about isolated starch, the decrease in gelatinization temperature and ΔH has also been observed for starchy flour due to starch damage (Asmeda, Noorlaila, & Norziah, 2016). However, the gelatinization temperature of flour is 4–15 °C greater than that of the corresponding isolated starch, even when they get damaged during milling (Hasjim et al., 2013). The likely cause is that flour is the mixture comprising not only starch but components (e.g. ash, lipid, protein and dietary fibre), which may strengthen the physical barrier against heat transfer. Therefore, it requires more energy for flour to gelatinize. It's reported that T_o, T_p and T_c had negative correlation with MDS level of rice flours (Asmeda et al., 2016). ΔH was also inversely correlated with MDS level (Loubes, Gonzalez, & Tolaba, 2018). A positive relationship was found between gelatinization peak width and MDS content in sorghum flour (Palavecino et al., 2019). All these facts demonstrate that starch damage induced by milling facilitate the gelatinization of flour. On the other hand, some research claimed that highly MDS in wheat flour resulted in increased gelatinization temperature and ΔH (Angelidis, Protonotariou, Mandala, & Rosell, 2016). It could be explained by the aggregation of starch granules when they are severely damaged, which may hinder the swelling of granules for gelatinization and enhance the requirements for heat absorption. Table 4 illustrates gelatinization parameters of flour containing MDS from various food materials. Evidently, higher damage degree of starch doesn't necessarily lead to promoted gelatinization process, although they originate from the same material. For example, rice flour with MDS level of 10.70% had the ΔH of only 0.58 J/g, whereas higher gelatinization enthalpy (1.87 J/g) was required when MDS level rose to 54.41% (Asmeda et al., 2016; Wu et al., 2019). Besides the effect of granules aggregation, reasons for the increased ΔH of flour with highly MDS may not exclude the different bound water content in MDS among literatures and the structural variation in amorphous and crystalline region caused by different milling approaches. The unambiguous mechanism remains to be deeply investigated on starchy flours.

6.1.2. Pasting property

Table 5 displays the changes in pasting profile of flour possessing varying MDS levels from different botanical sources. Specifically, peak temperature (PT) is the temperature at which viscosity begins to develop during heating. Peak viscosity (PV) is the highest viscosity reached before cooling, final viscosity (FV) is the zenith viscosity after cooling, and trough viscosity (TV) is the minimum viscosity formed between PV and FV. Breakdown (BD) is obtained by the value of PV minus TV, and setback (SB) is the value of FV minus TV. Lower BD and SB means higher paste stability and more resistant to retrogradation (Yu et al., 2018). Our previous study reported that PT, PV, BD and SB of wheat flour gradually decreased with the increase of MDS content (Liu et al., 2014). Another former research of our group indicated that PT of wheat flour progressively increased with the elevation of MDS level, while all five viscosity values firstly increased and then declined as the starch damage degree was enhanced (Ma et al., 2016). Other investigations also pointed out that starch damage by milling didn't only cause the reduction of flour viscosity indexes but delay peak time of viscosity (Wang, Xie, & Zhang, 2013). Admittedly, adequate viscosity may be associated with the better gelatinization and gel-forming ability of flour during food cooking (Wang et al., 2018), while lowering BD or SB value is significant for restraining retrogradation and maintaining food quality (e.g. porridge). Therefore, it's crucial to control starch damage during flour milling to achieve an optimal pasting profile. However, some studies claimed that there wasn't any correlation between viscosity profile and MDS content in flour (Deng & Manthey, 2017b), and some observed that PV and FV was positively correlated with damage degree (Ross & Kongraksawech, 2018). Apparently in Table 5, a slight fluctuation in MDS (MDS level of 16.24% in wheat flour versus that of 17.9% in sorghum flour) could induce a 3–4 fold change in viscosity value. These discrepancies may be generated from the interference of non-starch constituents including lipids, protein and minerals, whose contributions to pasting property of flour should also be taken into account.

6.1.3. Water hydration properties

Besides a small amount of soluble proteins, the solubility of starchy flour is mainly related to the short-chain sugars and amylose level, whose solubility is higher than amylopectin (Loubes & Tolaba, 2014). Similar to the case of isolated starch, starch damage has also been reported to enhance the solubility of flours. There exists strongly positive correlation between MDS level and flour solubility in both cold and hot water (Hasjim, Li, & Dhital, 2012). For instance, the solubility of rice

Table 4
Gelatinization parameters of flour containing varying levels of MDS.

Flour source	MDS content (%)	Generation approach of MDS	Gelatinization parameters				Reference
			T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	
rice	7.37	wet grinding	74.32	75.31	76.84	3.55	(Asmeda et al., 2016)
rice	10.70	hammer milling	59.42	59.86	60.39	0.58	(Asmeda et al., 2016)
rice	2.80	wet milling	53.55	61.70	68.82	9.99	(Wu et al., 2019)
rice	54.41	ultrafine grinding	45.79	55.85	63.25	1.87	(Wu et al., 2019)
rice	2.70	butt milling	–	67.1	–	6.82	(Loubes et al., 2018)
rice	16.46	planetary ball milling	–	–	–	0.71	(Loubes et al., 2018)
wheat	5.32	commercially coarse milling	59.67	65.33	–	7.75	(Lazaridou, Vouris, Zoumpoulakis, & Biliaderis, 2018)
wheat	11.54	jet milling	59.57	65.46	–	5.05	(Lazaridou et al., 2018)
wheat	4.61	jet milling	56.79	61.21	67.24	2.77	(Angelidis et al., 2016)
wheat	6.51	jet milling	60.36	64.63	69.20	2.43	(Angelidis et al., 2016)
common buckwheat	5.62	wet milling	57.16	66.37	75.77	8.40	(Yu et al., 2018)
common buckwheat	6.22	high-speed roll milling	56.02	67.25	77.37	7.73	(Yu et al., 2018)
sorghum	6.2	planetary ball milling	–	–	–	4.54	(Palavecino et al., 2019)
sorghum	17.9	planetary ball milling	–	–	–	2.98	(Palavecino et al., 2019)
amaranth	–	planetary ball milling	67.52	74.51	80.32	7.04	(Roa, Baeza, & Tolaba, 2015)
amaranth	–	planetary ball milling	49.27	57.07	79.10	0.34	(Roa et al., 2015)

*MDS is the abbreviation of milling damaged starch. To, Tp, Tc and ΔH represent onset, peak and conclusion temperature and gelatinization enthalpy, respectively.
*"–" means that the data isn't given in literature.

Table 5
Pasting profile of flour containing varying levels of MDS.

Flour source	MDS content (%)	Generation approach of MDS	Pasting parameters						Reference
			PT (°C)	PV (cP)	FV (cP)	TV (cP)	BD (cP)	SB (cP)	
wheat	7.08	–	84.6	2105	2330	1362	743	968	(Wang et al., 2013)
wheat	16.24	–	87.05	582	803	195	387	608	(Wang et al., 2013)
wheat	7.30	ultrafine milling	86.95	3090	3536	2163	927	1373	(Liu et al., 2014)
wheat	12.06	ultrafine milling	67.45	2232	2761	1542	690	1219	(Liu et al., 2014)
wheat	9.3	–	83.4	1549	1931	967	582	961	(Ma et al., 2016)
wheat	30	–	87.2	1462	1834	912	551	921	(Ma et al., 2016)
wheat	2.3	ultra-centrifugal milling	–	168	246	112	56	134	(Deng & Manthey, 2017)
wheat	7.6	ultra-centrifugal milling	–	190	249	110	80	139	(Deng & Manthey, 2017)
rice	12.0	cryogenic milling	90.1	1139	1891	939	200	952	(Hasjim et al., 2013)
rice	26.1	hammer milling	90.3	921	1637	822	99	815	(Hasjim et al., 2013)
common buckwheat	5.62	wet milling	81.53	3598.5	5316	3138.5	460	2177.5	(Yu et al., 2018)
common buckwheat	6.22	high-speed roll milling	72.35	3265	4951.3	2912	353	2039.3	(Yu et al., 2018)
sorghum	6.2	planetary ball milling	–	2114	4057	1572	542	2485	(Palavecino et al., 2019)
sorghum	17.9	planetary ball milling	–	2212	3535	1639	573	1896	(Palavecino et al., 2019)
corn	20.5	air flow pulverizing	74.0	124.5	196.2	81.5	43.0	114.7	–
corn	33.6	air flow pulverizing	72.7	140.5	139.0	74.0	66.5	65.0	–

*MDS is the abbreviation of milling damaged starch. PT, PV, FV, TV, BD and SB represent pasting temperature, peak viscosity, final viscosity, trough viscosity, breakdown and setback, respectively.
*"–" means that the data isn't given in literature.

flour at 30 °C increased from 2.6% to 41.8% as MDS level was enhanced from 8.8% to 73.7% (Hossen, Sotome, Nanayama, Sasaki, & Okadome, 2016). The increase could be due to the fragmentation of starch into water-soluble short chains or more leached amorphous amylose when damaged by milling. However, Hasjim et al. (2012) suggested that no marked relationship existed between MDS solubility and changes in molecular structure. Whererupon, the improved solubility may be originated from the liberation of the inherent small molecules in native starch after getting damaged. The specific crystalline structure of MDS also has contributions, such as more exposure of hydrophillic hydroxyls. Excessive increase in flour solubility means more soluble solids loss during food cooking (e.g. noodles). Hence, the increase in MDS level should be limited to reduce solubility.

WAI and SP are indicators of the ability of flour to hold water molecules. Compared with intact starch granules, MDS could take in more water and promote the increase of flour WAI, which has been proved on the flour of rice, barley, rye and sorghum (Drakos et al., 2017; Palavecino et al., 2019). Meanwhile, starch damage also elevated the SP of flour (Kim, Oh, Jeong, & Lee, 2019). It's acknowledged that MDS granule and its corresponding flour has expanded surface area, favoring the smooth binding with water. Along with the generation of free hydroxyls from hydrogen bonding breakage, external forces triggering starch damage may make the amorphous region more loosened (Protonotariou, Drakos, Evageliou, Ritzoulis, & Mandala, 2014). All of these changes in structure would be favorable for the enhancement of WAI and SP. Interestingly, although increased percentage of MDS leads to enhanced WAI and SP of flour in cold water, both two indices declined with the increase of MDS level in water at 100 °C (e.g. rice flour) (Heo, Lee, Shim, Yoo, & Lee, 2013). It could be explained by the fact that starch granules swell to the fullest during gelatinization in hot water, and increasing starch damage degree would make more soluble components leached out, thus diminishing the sedimented starch weight and causing decline in WAI and SP. Heating starch suspension containing higher MDS content at 100 °C might facilitate the formation of amylose network that inhibits the granules swelling (María & Tolaba, 2014), which is also the likely cause. Furthermore, the interactions between MDS and other components (e.g. lipids and non-starch polysaccharides) shouldn't be ignored.

6.1.4. In vitro enzymatic digestibility

Consistent with the overall changes of isolated starch, the digestibility of starchy flour has been noted to increase with the enhancement of starch damage degree, including the elevation of digestible starch level and less generation of RS (Hossen et al., 2016; Protonotariou, Mandala, & Rosell, 2015). As revealed in Table 1, higher percentage of MDS is associated with the reduced flour particle size. Decreased flour coarseness means more cell disintegrity and larger contact area for enzymatic catalysis, thus accelerating the enzymatic digestion. Also, greater level of MDS is possibly accompanied with more detachments of macromolecules (e.g. proteins) from granules that may form surface membrane hindering starch hydrolysis (Angelidis et al., 2016). Some studies demonstrated that native starch containing short chain-length glucans had higher digestion rate (Ramadoss et al., 2019). Likewise, as for MDS in flour, perhaps molecular degradation is responsible for digestion improvement as well. For instance, the highest maltose content was detected in rice flour with the highest MDS level and greatest digestibility (Hossen et al., 2016). Nevertheless, the digestible starch content changes don't fully parallel with that of the MDS level in tef injera and brown rice sprout flour (Assefa, Emire, Villanueva, Abebe, & Ronda, 2018; Lee et al., 2019). It might be caused by the influence from other components. For example, lipid-amylose complex could restrict the combination of starch with enzymes (Sharma & Gujral, 2019). Phenolics may conjugate with MDS via glucosidic or ester bonds, forming compounds limiting enzymatic hydrolysis (Chusak et al., 2020). Unfortunately, the above changes in digestibility haven't been extensively elucidated on gelatinized MDS that could be consumed in human diet.

6.2. Effect on dough quality

6.2.1. Fermentation behavior

Dough leavening is the process involved in the conversion of fermentable sugars into ethanol and carbon dioxide by yeasts. Besides lower amounts of mono- and oligosaccharides naturally existing in grains, MDS has been proved to be an another source for yeast fermentation (Struyf et al., 2017). During development of non-yeasted dough, higher maltose and glucose content could be detected when MDS is at a greater level (Struyf, Verspreet, & Courtin, 2016), because MDS has increased surface area, more pores or channels insides granules and is easier to be hydrolyzed by enzymes inherently present in flour. According to previous reports, the maltose increase percentage after 60 min of non-yeasted dough proofing rose from 32.5% to 52.5% as the MDS level changed from 4.78% to 7.46%. However, the improved maltose concentration didn't result in increased utilization by yeasts (Hackenberg, Leitner, Jekle, & Becker, 2018). It might be due to the limited activity of hydrolytic enzymes or the insufficient fermentation time. Some researches revealed that higher MDS content (6.56%) in dough delayed the termination time of gas production by yeasts and elevated total gas volume in contrast to that of lower MDS content (4.78%) (Hackenberg et al., 2016), because higher MDS level means abundant substrate concentration for enzymatic hydrolysis. With regard to another study, the greater MDS level in superfine-ground flour gave rise to a decrease in total gas production during dough fermentation (Xu et al., 2018). As for the explanation, the generation of severely MDS may be accompanied with amylase inactivation, thus hindering the formation of fermentable sugars and reducing the capacity of yeasts to produce gas.

6.2.2. Textural property

Textural characteristic of dough has profound impact on the acceptability of final food products. Enhanced level of MDS has been confirmed to increase the hardness of both gluten and gluten-free dough (Kang, Sohn, Yoon, Lee, & Ko, 2015; Ooms et al., 2018). Undoubtedly, MDS could possess higher bound water holding capacity, thus increasing dough strength.

However, the stickness, extensibility and elasticity of dough has been all found to diminish with the increment on starch damage degree in gluten systems (Feizollahi et al., 2018; Stone, Hucl, Scanlon, & Nickerson, 2017). As well-known, the viscoelastic property of dough is largely dependent on the gluten network. Extension of dough is based on the deformation and flattening of this network, in which hydrogen bonding between groups inside protein and water molecules plays an important role (Ooms et al., 2018). Starch damage leads to increased amount of water molecules hydrated by starch, and compete with gluten network for water. Higher MDS level intensifies the competition and impairs the interfacial interactions. Furthermore, increased starch damage may enlarge the voids distributed over the network due to the greater size of hydrated MDS granules (Hackenberg et al., 2019; Khalid, Manthey, & Simsek, 2017), consequently resulting in weakened gluten network, making dough more resistant to extension and causing decline in extensibility and elasticity. The decrease of stickness could be attributed to the reduced accessibility of mobile water to dough surface caused by higher water holding capacity of MDS (Stone et al., 2017). Nevertheless, there are studies concluding that dough stickness is increased owing to the existence of MDS (Barrera, Leon, & Ribotta, 2016). The disagreement might be induced by the diminished water holding ability of severely damaged starch caused by milling, which allows more free water to reach dough surface.

On the other hand, given gluten-free system, it's worth-noting that all parameters relevant to viscoelastic property (e.g. adhesiveness and springiness) of cassava starch dough were found to rise as the MDS content increased from 11.51% to 18.65% (Liu et al., 2019a). Based on these authors' perspective, starch damage accelerates the conversion of rigid crystalline region to amorphous state, promoting the interaction of amorphous proportion and other components in granules with water molecules, facilitating the coherence of each fragment among starch granules and causing these parameters enhancement, just as the gluten network acts. It's necessitated in the next step to investigate the effect of MDS on the texture property of gluten-free starch dough from various food sources.

6.3. Effect on final product quality

Among sensorial characteristics of starchy food products, texture is a frequently-discussed element that could be affected by starch damage. For instance, the increase in MDS level of cassava starch caused a decline in hardness, chewiness and gumminess while generally elevated the cohesiveness of bread containing gluten (Liu et al., 2019b). These textural changes are closely related to the enhanced water absorption ability of MDS as well as its interaction with gluten network, as described in the section of "Effect on dough quality". Besides, the reduced specific volume is a typical feature of bread produced from flours containing high level of MDS (Hackenberg et al., 2016). Reasons for the phenomenon are various. Increased water holding capacity of MDS reduces the amount of free water, which doesn't only limit the diffusion of substrates and enzymes but hinder starch gelatinization, retarding the enzymatic hydrolysis and decreasing fermentable sugar formation and eventually diminishing the generated gas amount through fermentation (Hackenberg et al., 2016). Moreover, the disruption of gluten network caused by MDS may lead to poor ability of dough to holding gas (Liu et al., 2019b). Thus, it reduces bread volume.

Milling-induced starch damage also has influence on color of baked food products, which determines the visual appeal for consumers. Previous study suggested that the lightness of wheat bread decreased while redness increased when flour with higher MDS level was used (Vouris, Lazaridou, Mandala, & Biliaderis, 2018). Similarly, chapattis made from flour possessing higher MDS content was observed to have more dark brown spots on their surface (Inamdar & Prabhasankar, 2017). The undesirable changes in color should be explained by the fact that starch damage during milling process enhances the degradation of starch into reducing sugars, which is favorable for Maillard reaction during baking and promotes surface browning. Additionally, there existed a inverse correlation between cookies spread ratio and MDS level in wheat flour, and higher MDS content tended to causing lower diameter of cookies. The change is relied on the greater dough stiffness caused by higher water holding capacity of MDS. Besides, more water captured by MDS leads to increased concentration of sugars in cookies, enhancing the dough viscosity and obstructing cookies spreading (Barak, Mudgil, & Khatkar, 2014; Mancebo, Picón, & Gómez, 2015). In terms of dumplings and noodles, the elevation of MDS level in flour increased their cooking loss due to its higher solubility (Ahmad & Rajab, 2018; Tong et al., 2016). Gluten-free crackers produced from damaged cassava starch had improved fracturability and appearance in contrast with that from commonly used wheat flours, but its interior porous structure couldn't rival that maintained by gluten network (Liu et al., 2019a). Perhaps MDS from more edible materials could be utilized to produce novel foods to take advantage of natural sources.

Last but most significantly, controlling harmful compound formation is critical to ensure food safety during food processing. Acrylamide, which has neurotoxic and carcinogenic potential (El-Zakhem Naous, Merhi, Abboud, Mroueh, & Taleb, 2018), could be generated from the transformation of asparagine through deamination and decarboxylation in the presence of aspartic acid under thermal conditions. Aspartic acid formation is connected with Maillard reaction, during which reducing sugar plays an outstanding role (Wang et al., 2017). Starch damage could increase reducing sugar level, hence giving rise to increased acrylamide level in baked foods. For instance, the acrylamide content in chapatti rose from 45.8 to 58.6 μg/kg as MDS level in flour increased from 27% to 30% (Mulla, Bharadwaj, Annapure, & Singhal, 2010). Similar increase has also been validated in bread (Wang et al., 2017). In addition, a growing number of free radical, which is relevant to aging, has been noticed as a consequence of increased damage degree of milling-treated potato starch (Dyrek, Szymońska, Wenda, Bidzińska, & Walczak, 2013). Thereupon, MDS at an appropriate level should be considered while pursuing the beneficial properties to starchy food processing.

7. Conclusions and prospects

MDS, generated from milling, has considerable effects on the functionality of flour and the quality of dough as well as final starchy products, owing to its characteristic structure. Milling-induced starch damage causes reduced particle size, increased surface area and more channels or pores inside granules. Concomitantly, MDS often has disrupted crystalline region and molecular degradation. These structural changes give rise to variation from native starch in gelatinization, pasting property, digestibility and water hydration capacity. In most occasions, MDS consumes lower gelatinization energy, has enhanced nutritional value due to the improved digestibility, has higher WAI and SP, and could be more easily utilized during yeasts fermentation. Nevertheless, MDS should be controlled at a suitable level during flour milling, considering the adverse effect of higher starch damage degree on processing properties (e.g. cooking loss caused by higher solubility and lower viscosity) as well as the harmful compounds formation. Although many published papers have implied the relationships among MDS structure at different levels and their functionality in starch-based food systems, more quantitative correlations remain to be established. Starchy food is a mixture containing a variety of components besides starch. It would give a better understanding on the role of MDS to uncover the interaction with other components (e.g. protein and lipids) and perform more comparative investigation between food mixture and isolated starch on its functionality. With the increasing interest in gluten-free food recently, it's essential to conduct researches on the production of starch food using MDS from various food materials. The major focus should on whether the application of MDS could reach equivalent or even better textural quality as the gluten network acts. Furthermore, the molecular mechanism and the crystalline structural changes should be elucidated about its influence on products texture. More extensive and deeper study on MDS would take advantage of natural edible sources, promote innovative foods catering for people's appetite and contribute to the flourishing of food industry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was funded by National Natural Science Foundation of China (No. 31671892 and No. 31671810) and Henan Wheat Technology System Foundation (S2020-01-G06).

References

Abo-Dief, M., Abo-Bakr, T., Youssef, M., & Moustafa, A. (2019). Quality of wheat flour and pan bread as influenced by the tempering time and milling system. *Cereal Chemistry, 96*(3), 429–438. https://doi.org/10.1002/cche.10142.

Ahmad, N., & Rajab, A. (2018). Textural and cooking qualities of dry Laksa noodle made from semi-wet and wet MR253 flours. *Cereal Chemistry, 95*(6), 872–880. https://doi.org/10.1002/cche.10105.

Almeida, R. L. J., Dos Santos Pereira, T., de Andrade Freire, V., Santiago, A. M., Oliveira, H. M. L., de Sousa Conrado, L., & de Gusmao, R. P. (2019). Influence of enzymatic hydrolysis on the properties of red rice starch. *International Journal of Biological Macromolecules, 141*, 1210–1219. https://doi.org/10.1016/j.ijbiomac.2019.09.072.

Amagliani, L., O'Regan, J., Kelly, A. L., & O'Mahony, J. A. (2016). Chemistry, structure, functionality and applications of rice starch. *Journal of Cereal Science, 70*, 291–300. https://doi.org/10.1016/j.jcs.2016.06.014.

Angelidis, G., Protonotariou, S., Mandala, I., & Rosell, C. M. (2016). Jet milling effect on wheat flour characteristics and starch hydrolysis. *Journal of Food Science and Technology, 53*(1), 784–791. https://doi.org/10.1007/s13197-015-1990-1.

Anzai, M., Hagiwara, T., Watanabe, M., Komiyama, J., & Suzuki, T. (2011). Relationship between enthalpy relaxation and water sorption of ball-milled potato starch. *Journal of Food Engineering, 104*(1), 43–48. https://doi.org/10.1016/j.jfoodeng.2010.11.025.

Asmeda, R., Noorlaila, A., & Norziah, M. H. (2016). Relationships of damaged starch granules and particle size distribution with pasting and thermal profiles of milled MR263 rice flour. *Food Chemistry, 191*, 45–51. https://doi.org/10.1016/j.foodchem.2015.05.095.

Assefa, Y., Emire, S., Villanueva, M., Abebe, W., & Ronda, F. (2018). Influence of milling type on tef injera quality. *Food Chemistry, 266*, 155–160. https://doi.org/10.1016/j.foodchem.2018.05.126.

Barak, S., Mudgil, D., & Khatkar, B. S. (2014). Effect of flour particle size and damaged starch on the quality of cookies. *Journal of Food Science and Technology, 51*(7), 1342–1348. https://doi.org/10.1007/s13197-012-0627-x.

Barrera, G. N., Bustos, M. C., Iturriaga, L., Flores, S. K., León, A. E., & Ribotta, P. D. (2013). Effect of damaged starch on the rheological properties of wheat starch suspensions. *Journal of Food Engineering, 116*(1), 233–239. https://doi.org/10.1016/j.jfoodeng.2012.11.020.

Barrera, G. N., Calderon-Dominguez, G., Chanona-Perez, J., Gutierrez-Lopez, G. F., Leon, A. E., & Ribotta, P. D. (2013). Evaluation of the mechanical damage on wheat starch granules by SEM, ESEM, AFM and texture image analysis. *Carbohydrate Polymer, 98*(2), 1449–1457. https://doi.org/10.1016/j.carbpol.2013.07.056.

Barrera, G. N., León, A. E., & Ribotta, P. D. (2012). Effect of damaged starch on wheat starch thermal behavior. *Starch – Stärke, 64*(10), 786–793. https://doi.org/10.1002/star.201200022.

Barrera, G. N., Leon, A. E., & Ribotta, P. D. (2016). Use of enzymes to minimize the rheological dough problems caused by high levels of damaged starch in starch-gluten systems. *Journal of the Science of Food and Agriculture, 96*(7), 2539–2546. https://doi.org/10.1002/jsfa.7374.

Barrera, G. N., Tadini, C. C., León, A. E., & Ribotta, P. D. (2016). Use of alpha-amylase and amyloglucosidase combinations to minimize the bread quality problems caused by high levels of damaged starch. *Journal of Food Science and Technology, 53*(10), 3675–3684. https://doi.org/10.1007/s13197-016-2337-2.

Bourré, L., Frohlich, P., Young, G., Borsuk, Y., Sopiwnyk, E., Sarkar, A., ... Malcolmson, L. (2019). Influence of particle size on flour and baking properties of yellow pea, navy bean, and red lentil flours. *Cereal Chemistry, 96*(4), 655–667. https://doi.org/10.1002/cche.10161.

Boyacı, İ. H., Williams, P. C., & Köksel, H. (2004). A rapid method for the estimation of damaged starch in wheat flours. *Journal of Cereal Science, 39*(1), 139–145. https://doi.org/10.1016/j.jcs.2003.09.002.

Choi, H.-W., & Baik, B.-K. (2013). Significance of wheat flour particle size on sponge cake baking quality. *Cereal Chemistry Journal, 90*(2), 150–156. https://doi.org/10.1094/cchem-07-12-0088-r.

Chusak, C., Chanbunyawat, P., Chumnumduang, P., Chantarasinlapin, P., Suantawee, T., & Adisakwattana, S. (2020). Effect of gac fruit (Momordica cochinchinensis) powder on in vitro starch digestibility, nutritional quality, textural and sensory characteristics of pasta. *LWT – Food Science and Technology, 118*, 108856. https://doi.org/10.1016/j.lwt.2019.108856.

Deladino, L., Teixeira, A. S., Navarro, A. S., Alvarez, I., Molina-García, A. D., & Martino, M. (2015). Corn starch systems as carriers for yerba mate (Ilex paraguariensis) antioxidants. *Food and Bioproducts Processing, 94*, 463–472. https://doi.org/10.1016/j.fbp.2014.07.001.

Deng, L., & Manthey, F. A. (2017a). Laboratory-scale milling of whole-durum flour quality: Effect of mill configuration and seed conditioning. *Journal of the Science of Food and Agriculture, 97*(10), 3141–3150. https://doi.org/10.1002/jsfa.8156.

Deng, L., & Manthey, F. A. (2017b). Effect of single-pass and multipass milling systems on whole wheat durum flour and whole wheat pasta quality. *Cereal Chemistry, 94*(6), 963–969. https://doi.org/10.1094/cchem-05-17-0087-r.

Dhital, S., Shrestha, A. K., & Gidley, M. J. (2010). Effect of cryo-milling on starches: Functionality and digestibility. *Food Hydrocolloids, 24*(2–3), 152–163. https://doi.org/10.1016/j.foodhyd.2009.08.013.

Di Silvestro, R., Di Loreto, A., Marotti, I., Bosi, S., Bregola, V., Gianotti, A., ... Dinelli, G. (2014). Effects of flour storage and heat generated during milling on starch, dietary fibre and polyphenols in stoneground flours from two durum-type wheats. *International Journal of Food Science & Technology, 49*(10), 2230–2236. https://doi.org/10.1111/ijfs.12536.

Doblado-Maldonado, A. F., Pike, O. A., Sweley, J. C., & Rose, D. J. (2012). Key issues and challenges in whole wheat flour milling and storage. *Journal of Cereal Science, 56*(2), 119–126. https://doi.org/10.1016/j.jcs.2012.02.015.

Drakos, A., Kyriakakis, G., Evageliou, V., Protonotariou, S., Mandala, I., & Ritzoulis, C. (2017). Influence of jet milling and particle size on the composition, physicochemical and mechanical properties of barley and rye flours. *Food Chemistry, 215*, 326–332. https://doi.org/10.1016/j.foodchem.2016.07.169.

Drakos, A., Malindretou, K., Mandala, I., & Evageliou, V. (2017). Protein isolation from jet milled rye flours differing in particle size. *Food and Bioproducts Processing, 104*, 13–18. https://doi.org/10.1016/j.fbp.2017.04.004.

Dyrek, K., Szymońska, J., Wenda, E., Bidzińska, E., & Walczak, M. (2013). Characterization of free radicals mechanically and thermally induced in potato starch. *Starch – Stärke, 65*(7–8), 653–659. https://doi.org/10.1002/star.201200160.

El-Porai, E. S., Salama, A. E., Sharaf, A. M., Hegazy, A. I., & Gadallah, M. G. E. (2013). Effect of different milling processes on Egyptian wheat flour properties and pan bread quality. *Annals of Agricultural Sciences, 58*(1), 51–59. https://doi.org/10.1016/j.aoas.2013.01.008.

El-Zakhem Naous, G., Merhi, A., Abboud, M. I., Mroueh, M., & Taleb, R. I. (2018). Carcinogenic and neurotoxic risks of acrylamide consumed through caffeinated beverages among the lebanese population. *Chemosphere, 208*, 352–357. https://doi.org/10.1016/j.chemosphere.2018.05.185.

Feizollahi, E., Mirmoghtadaie, L., Mohammadifar, M. A., Jazaeri, S., Hadaegh, H., Nazari, B., & Lalegani, S. (2018). Sensory, digestion, and texture quality of commercial gluten-free bread: Impact of broken rice flour type. *Journal of Texture Studies, 49*(4), 395–403. https://doi.org/10.1111/jtxs.12326.

Fu, Z., Luo, S.-J., Liu, W., Liu, C.-M., & Zhan, L.-J. (2016). Structural changes induced by high speed jet onin vitrodigestibility and hydroxypropylation of rice starch. *International Journal of Food Science & Technology, 51*(4), 1034–1040. https://doi.org/10.1111/ijfs.13046.

González, L. C., Loubes, M. A., & Tolaba, M. P. (2018). Incidence of milling energy on dry-milling attributes of rice starch modified by planetary ball milling. *Food Hydrocolloids, 82*, 155–163. https://doi.org/10.1016/j.foodhyd.2018.03.051.

Hackenberg, S., Leitner, T., Jekle, M., & Becker, T. (2018). Maltose formation in wheat dough depending on mechanical starch modification and dough hydration. *Carbohydrate Polymer, 185*, 153–158. https://doi.org/10.1016/j.carbpol.2017.12.064.

Hackenberg, S., Verheyen, C., Jekle, M., & Becker, T. (2016). Effect of mechanically modified wheat flour on dough fermentation properties and bread quality. *European*

Food Research and Technology, 243(2), 287–296. https://doi.org/10.1007/s00217-016-2743-8.

Hackenberg, S., Vogel, C., Scherf, K. A., Jekle, M., & Becker, T. (2019). Impact of altered starch functionality on wheat dough microstructure and its elongation behaviour. *Food Chemistry, 290*, 64–71. https://doi.org/10.1016/j.foodchem.2019.03.016.

Haq, F., Yu, H., Wang, L., Teng, L., Haroon, M., Khan, R. U., ... Nazir, A. (2019). Advances in chemical modifications of starches and their applications. *Carbohydrate Research, 476*, 12–35. https://doi.org/10.1016/j.carres.2019.02.007.

Hasjim, J., Li, E., & Dhital, S. (2012). Milling of rice grains: The roles of starch structures in the solubility and swelling properties of rice flour. *Starch – Stärke, 64*(8), 631–645. https://doi.org/10.1002/star.201100204.

Hasjim, J., Li, E., & Dhital, S. (2013). Milling of rice grains: Effects of starch/flour structures on gelatinization and pasting properties. *Carbohydrate Polymer, 92*(1), 682–690. https://doi.org/10.1016/j.carbpol.2012.09.023.

He, S., Qin, Y., Walid, E., Li, L., Cui, J., & Ma, Y. (2014). Effect of ball-milling on the physicochemical properties of maize starch. *Biotechnology Reports (Amst), 3*, 54–59. https://doi.org/10.1016/j.btre.2014.06.004.

Heo, S., Lee, S. M., Shim, J.-H., Yoo, S.-H., & Lee, S. (2013). Effect of dry- and wet-milled rice flours on the quality attributes of gluten-free dough and noodles. *Journal of Food Engineering, 116*(1), 213–217. https://doi.org/10.1016/j.jfoodeng.2012.11.017.

Hossen, M. S., Sotome, I., Nanayama, K., Sasaki, T., & Okadome, H. (2016). Functional properties of submicron-scale rice flour produced by wet media grinding. *Cereal Chemistry, 93*(1), 53–57. https://doi.org/10.1094/cchem-03-15-0045-r.

Hossen, M. S., Sotome, I., Takenaka, M., Isobe, S., Nakajima, M., & Okadome, H. (2011). Starch damage and pasting properties of rice flours produced by dry jet grinding. *Cereal Chemistry, 88*(1), 6–11. https://doi.org/10.1094/cchem-04-10-0061.

Inamdar, A. A., & Prabhasankar, P. (2017). Influence of stone chakki settings on the characteristics of whole wheat flour (atta) and its chapati making quality. *Journal of Food Processing and Preservation, 41*(3), e12966. https://doi.org/10.1111/jfpp.12966.

Kang, T.-Y., Sohn, K. H., Yoon, M.-R., Lee, J.-S., & Ko, S. (2015). Effect of the shape of rice starch granules on flour characteristics and gluten-free bread quality. *International Journal of Food Science & Technology, 50*(8), 1743–1749. https://doi.org/10.1111/ijfs.12835.

Karkalas, J., Tester, R. F., & Morrison, W. R. (1992). Properties of damaged starch granules. I. Comparison of a micromethod for the enzymic determination of damaged starch with the standard AACC and Farrand methods. *Journal of Cereal Science, 16*(3), 237–251. https://doi.org/10.1016/S0733-5210(09)80087-8.

Khalid, K. H., Manthey, F., & Simsek, S. (2017). Whole grain wheat flour production using an ultracentrifugal mill. *Cereal Chemistry, 94*(6), 1001–1007. https://doi.org/10.1094/cchem-05-17-0117-r.

Kim, S. K., & Kim, H. Y. (2014). Pasting properties of colored rice starch by ball-mill treatment. *Journal of Crop Science and Biotechnology, 17*(3), 161–166. https://doi.org/10.1007/s12892-014-0046-9.

Kim, M., Oh, I., Jeong, S., & Lee, S. (2019). Particle size effect of rice flour in a rice-zein noodle system for gluten-free noodles slit from sheeted doughs. *Journal of Cereal Science, 86*, 48–53. https://doi.org/10.1016/j.jcs.2019.01.006.

Kwak, J., Yoon, M. R., Lee, J. S., Lee, J. H., Ko, S., Tai, T. H., & Won, Y. J. (2017). Morphological and starch characteristics of the Japonica rice mutant variety Seolgaeng for dry-milled flour. *Food Science and Biotechnology, 26*(1), 43–48. https://doi.org/10.1007/s10068-017-0006-5.

Lamb, J., & Loy, T. (2005). Seeing red: The use of Congo Red dye to identify cooked and damaged starch grains in archaeological residues. *Journal of Archaeological Science, 32*(10), 1433–1440. https://doi.org/10.1016/j.jas.2005.03.020.

Lazaridou, A., Vouris, D. G., Zoumpoulakis, P., & Biliaderis, C. G. (2018). Physicochemical properties of jet milled wheat flours and doughs. *Food Hydrocolloids, 80*, 111–121. https://doi.org/10.1016/j.foodhyd.2018.01.044.

Lee, Y. T., Shim, M. J., Goh, H. K., Mok, C., & Puligundla, P. (2019). Effect of jet milling on the physicochemical properties, pasting properties, and in vitro starch digestibility of germinated brown rice flour. *Food Chemistry, 282*, 164–168. https://doi.org/10.1016/j.foodchem.2018.07.179.

Li, N., Guo, Y., Zhao, S., Kong, J., Qiao, D., Lin, L., Lin, Q., & Zhang, B. (2019). Amylose content and molecular-order stability synergistically affect the digestion rate of indica rice starches. *International Journal of Biological Macromolecules, 144*, 373–379. https://doi.org/10.1016/j.ijbiomac.2019.12.095.

Li, N., Niu, M., Zhang, B., Zhao, S., Xiong, S., & Xie, F. (2017). Effects of concurrent ball milling and octenyl succinylation on structure and physicochemical properties of starch. *Carbohydrate Polymer, 155*, 109–116. https://doi.org/10.1016/j.carbpol.2016.08.063.

Liu, X., Li, E., Jiang, Y., & Tian, Y. (2018). Milling Process of Starch. 155-174. doi: 10.1007/978-981-13-0725-6_9.

Liu, C., Hong, J., & Zheng, X. (2017). Effect of heat-moisture treatment on morphological, structural and functional characteristics of ball-milled wheat starches. *Starch – Stärke, 69*(5–6), 1500141. https://doi.org/10.1002/star.201500141.

Liu, T., Hou, G. G., Lee, B., Marquart, L., & Dubat, A. (2016). Effects of particle size on the quality attributes of reconstituted whole-wheat flour and tortillas made from it. *Journal of Cereal Science, 71*, 145–152. https://doi.org/10.1016/j.jcs.2016.08.013.

Liu, C., Li, L., Hong, J., Zheng, X., Bian, K., Sun, Y., & Zhang, J. (2014). Effect of mechanically damaged starch on wheat flour, noodle and steamed bread making quality. *International Journal of Food Science & Technology, 49*(1), 253–260. https://doi.org/10.1111/ijfs.12306.

Liu, T. Y., Ma, Y., Yu, S. F., Shi, J., & Xue, S. (2011). The effect of ball milling treatment on structure and porosity of maize starch granule. *Innovative Food Science & Emerging Technologies, 12*(4), 586–593. https://doi.org/10.1016/j.ifset.2011.06.009.

Liu, R., Sun, W., Zhang, Y., Huang, Z., Hu, H., & Zhao, M. (2019). Preparation of starch dough using damaged cassava starch induced by mechanical activation to develop staple foods: Application in crackers. *Food Chemistry, 271*, 284–290. https://doi.org/10.1016/j.foodchem.2018.07.202.

Liu, R., Sun, W., Zhang, Y., Huang, Z., Hu, H., Zhao, M., & Li, W. (2019). Development of a novel model dough based on mechanically activated cassava starch and gluten protein: Application in bread. *Food Chemistry, 300*, 125196. https://doi.org/10.1016/j.foodchem.2019.125196.

Loubes, M. A., Gonzalez, L. C., & Tolaba, M. P. (2018). Pasting behaviour of high impact ball milled rice flours and its correlation with the starch structure. *Journal of Food Science andi Technology, 55*(8), 2985–2993. https://doi.org/10.1007/s13197-018-3216-9.

Loubes, M. A., & Tolaba, M. P. (2014). Thermo-mechanical rice flour modification by planetary ball milling. *LWT – Food Science and Technology, 57*(1), 320–328. https://doi.org/10.1016/j.lwt.2013.12.048.

Lu, Z. H., Belanger, N., Donner, E., & Liu, Q. (2018). Debranching of pea starch using pullulanase and ultrasonication synergistically to enhance slowly digestible and resistant starch. *Food Chemistry, 268*, 533–541. https://doi.org/10.1016/j.foodchem.2018.06.115.

Lu, X., Wang, Y., Li, Y., & Huang, Q. (2018). Assembly of Pickering emulsions using milled starch particles with different amylose/amylopectin ratios. *Food Hydrocolloids, 84*, 47–57. https://doi.org/10.1016/j.foodhyd.2018.05.045.

Lu, X., Xiao, J., & Huang, Q. (2018). Pickering emulsions stabilized by media-milled starch particles. *Food Research International, 105*, 140–149. https://doi.org/10.1016/j.foodres.2017.11.006.

Lv, Y., Zhang, L., Li, M., He, X., Hao, L., & Dai, Y. (2019). Physicochemical properties and digestibility of potato starch treated by ball milling with tea polyphenols. *International Journal of Biological Macromolecules, 129*, 207–213. https://doi.org/10.1016/j.ijbiomac.2019.02.028.

Ma, S., Li, L., Wang, X. X., Zheng, X. L., Bian, K., & Bao, Q. D. (2016). Effect of mechanically damaged starch from wheat flour on the quality of frozen dough and steamed bread. *Food Chemistry, 202*, 120–124. https://doi.org/10.1016/j.foodchem.2016.01.075.

Makowska, A., Szwengiel, A., Kubiak, P., & Tomaszewska-Gras, J. (2014). Characteristics and structure of starch isolated from triticale. *Starch – Stärke, 66*(9–10), 895–902. https://doi.org/10.1002/star.201300264.

Mancebo, C. M., Picón, J., & Gómez, M. (2015). Effect of flour properties on the quality characteristics of gluten free sugar-snap cookies. *LWT – Food Science and Technology, 64*(1), 264–269. https://doi.org/10.1016/j.lwt.2015.05.057.

Miskelly, D., & Suter, D. (2017). Assessing and managing wheat-flour quality before, during and after milling. 607-634. doi: 10.1016/b978-0-08-100719-8.00022-x.

Monnet, A. F., Eurieult, A., Berland, S., Almeida, G., Jeuffroy, M. H., & Michon, C. (2019). Damaged starch in pea versus wheat flours: Fragmentation behavior and contribution of fine and coarse fractions. *Cereal Chemistry, 96*(3), 465–477. https://doi.org/10.1002/cche.10146.

Monroy, Y., Rivero, S., & García, M. A. (2018). Microstructural and techno-functional properties of cassava starch modified by ultrasound. *Ultrasonics Sonochemistry, 42*, 795–804. https://doi.org/10.1016/j.ultsonch.2017.12.048.

Moraes, J., Alves, F. S., & Franco, C. M. L. (2013). Effect of ball milling on structural and physicochemical characteristics of cassava and Peruvian carrot starches. *Starch – Stärke, 65*(3–4), 200–209. https://doi.org/10.1002/star.201200059.

Mulla, M. Z., Bharadwaj, V. R., Annapure, U. S., & Singhal, R. S. (2010). Effect of damaged starch on acrylamide formation in whole wheat flour based Indian traditional staples, chapattis and pooris. *Food Chemistry, 120*(3), 805–809. https://doi.org/10.1016/j.foodchem.2009.11.016.

Niu, M., Zhang, B., Jia, C., & Zhao, S. (2017). Multi-scale structures and pasting characteristics of starch in whole-wheat flour treated by superfine grinding. *International Journal of Biological Macromolcules, 104*(Pt A), 837–845. https://doi.org/10.1016/j.ijbiomac.2017.06.125.

Niwa, T., Yoshida, M., Hayashi, N., & Kondo, K. (2017). One step preparation of spherical drug particles by contamination-free dry milling technique with corn starch beads. *International Journal of Pharmaceutics, 528*(1–2), 624–636. https://doi.org/10.1016/j.ijpharm.2017.06.062.

Ogunsona, E., Ojogbo, E., & Mekonnen, T. (2018). Advanced material applications of starch and its derivatives. *European Polymer Journal, 108*, 570–581. https://doi.org/10.1016/j.eurpolymj.2018.09.039.

Okyere, A. Y., Bertoft, E., & Annor, G. A. (2019). Modification of cereal and tuber waxy starches with radio frequency cold plasma and its effects on waxy starch properties. *Carbohydrate Polymers, 223*, 115075. https://doi.org/10.1016/j.carbpol.2019.115075.

Ooms, N., Vandromme, E., Brijs, K., & Delcour, J. A. (2018). Intact and damaged wheat starch and amylase functionality during multilayered fermented pastry making. *Journal of Food Science, 83*(10), 2489–2499. https://doi.org/10.1111/1750-3841.14329.

Palavecino, P. M., Penci, M. C., & Ribotta, P. D. (2019). Effect of planetary ball milling on physicochemical and morphological properties of sorghum flour. *Journal of Food Engineering, 262*, 22–28. https://doi.org/10.1016/j.jfoodeng.2019.05.007.

Protonotariou, S., Drakos, A., Evageliou, V., Ritzoulis, C., & Mandala, I. (2014). Sieving fractionation and jet mill micronization affect the functional properties of wheat flour. *Journal of Food Engineering, 134*, 24–29. https://doi.org/10.1016/j.jfoodeng.2014.02.008.

Protonotariou, S., Mandala, I., & Rosell, C. M. (2015). Jet milling effect on functionality, quality and in vitro digestibility of whole wheat flour and bread. *Food and Bioprocess Technology, 8*(6), 1319–1329. https://doi.org/10.1007/s11947-015-1494-z.

Ramadoss, B. R., Gangola, M. P., Agasimani, S., Jaiswal, S., Venkatesan, T., Sundaram, G. R., & Chibbar, R. N. (2019). Starch granule size and amylopectin chain length influence starch in vitro enzymatic digestibility in selected rice mutants with similar amylose concentration. *Journal of Food Science and Technology, 56*(1), 391–400.

Ren, G.-Y., Li, D., Wang, L.-J., Özkan, N., & Mao, Z.-H. (2010). Morphological properties

and thermoanalysis of micronized cassava starch. *Carbohydrate Polymers, 79*(1), 101–105. https://doi.org/10.1016/j.carbpol.2009.07.031.
Roa, D. F., Baeza, R. I., & Tolaba, M. P. (2015). Effect of ball milling energy on rheological and thermal properties of amaranth flour. *Journal of Food Science and Technology, 52*(12), 8389–8394. https://doi.org/10.1007/s13197-015-1976-z.
Roa, D. F., Santagapita, P. R., Buera, M. P., & Tolaba, M. P. (2014). Ball milling of amaranth starch-enriched fraction. Changes on particle size, starch crystallinity, and functionality as a function of milling energy. *Food and Bioprocess Technology, 7*(9), 2723–2731. https://doi.org/10.1007/s11947-014-1283-0.
Rogers, D. E., Gelroth, J. A., Langemeier, J. M., & Ranhotra, G. S. (1994). Evaluation of starch damage values determined enzymatically or amperometrically. Cereal Chemistry, 71(6), 578–581.
Ross, A. S., & Kongraksawech, T. (2018). Characterizing whole-wheat flours produced using a commercial stone mill, laboratory mills, and household single-stream flour mills. *Cereal Chemistry, 95*(2), 239–252. https://doi.org/10.1002/cche.10029.
Sakhare, S. D., Inamdar, A. A., Gaikwad, S. B., D, I., & G, V. R. (2014). Roller milling fractionation of green gram (Vigna radiata): optimization of milling conditions and chemical characterization of millstreams. Journal of Food Science and Technology, 51(12), 3854-3861. doi: 10.1007/s13197-012-0903-9.
Šárka, E., & Dvořáček, V. (2017). New processing and applications of waxy starch (a review). *Journal of Food Engineering, 206*, 77–87. https://doi.org/10.1016/j.jfoodeng.2017.03.006.
Sharma, B., & Gujral, H. S. (2019). Influence of nutritional and antinutritional components on dough rheology and in vitro protein & starch digestibility of minor millets. *Food Chemistry, 299*, 125115. https://doi.org/10.1016/j.foodchem.2019.125115.
Shi, L., Cheng, F., Zhu, P. X., & Lin, Y. (2015). Physicochemical changes of maize starch treated by ball milling with limited water content. *Starch – Stärke, 67*(9–10), 772–779. https://doi.org/10.1002/star.201500026.
Shi, L., Li, W., Sun, J., Qiu, Y., Wei, X., Luan, G., ... Tatsumi, E. (2016). Grinding of maize: The effects of fine grinding on compositional, functional and physicochemical properties of maize flour. *Journal of Cereal Science, 68*, 25–30. https://doi.org/10.1016/j.jcs.2015.11.004.
Siliveru, K., Ambrose, R. K., & Vadlani, P. V. (2017). Significance of composition and particle size on the shear flow properties of wheat flour. *Journal of the Science of Food and Agriculture, 97*(8), 2300–2306.
Situ, W., Song, X., Luo, S., & Yang, J. (2019). Digestibility and structures of vinasse starches with different types of raw rice and fermented leaven. *Food Chemistry, 294*, 96–103. https://doi.org/10.1016/j.foodchem.2019.05.036.
Stone, A. K., Hucl, P. J., Scanlon, M. G., & Nickerson, M. T. (2017). Effect of damaged starch and NaCl level on the dough handling properties of a Canadian western red spring wheat. *Cereal Chemistry, 94*(6), 970–977. https://doi.org/10.1094/cchem-05-17-0096-r.
Struyf, N., Laurent, J., Lefevere, B., Verspreet, J., Verstrepen, K. J., & Courtin, C. M. (2017). Establishing the relative importance of damaged starch and fructan as sources of fermentable sugars in wheat flour and whole meal bread dough fermentations. *Food Chemistry, 218*, 89–98. https://doi.org/10.1016/j.foodchem.2016.09.004.
Struyf, N., Verspreet, J., & Courtin, C. M. (2016). The effect of amylolytic activity and substrate availability on sugar release in non-yeasted dough. *Journal of Cereal Science, 69*, 111–118. https://doi.org/10.1016/j.jcs.2016.02.016.
Suki, F. M. M., Azura, A. R., & Azahari, B. (2016). Effect of ball milled and ultrasonic sago starch dispersion on sago starch filled natural rubber latex (SSNRL) films. *Procedia Chemistry, 19*, 782–787. https://doi.org/10.1016/j.proche.2016.03.085.
Tan, X., Zhang, B., Chen, L., Li, X., Li, L., & Xie, F. (2015). Effect of planetary ball-milling on multi-scale structures and pasting properties of waxy and high-amylose cornstarches. *Innovative Food Science & Emerging Technologies, 30*, 198–207. https://doi.org/10.1016/j.ifset.2015.03.013.
Thirumdas, R., Kadam, D., & Annapure, U. S. (2017). Cold plasma: An alternative technology for the starch modification. *Food Biophysics, 12*(1), 129–139. https://doi.org/10.1007/s11483-017-9468-5.
Tong, L.-T., Gao, X., Zhou, X., Zhong, K., Liu, L., Wang, L., & Zhou, S. (2016). Milling of glutinous rice by semidry method to produce sweet dumplings. *Journal of Food Process Engineering, 39*(4), 330–334. https://doi.org/10.1111/jfpe.12223.
Vouris, D. G., Lazaridou, A., Mandala, I. G., & Biliaderis, C. G. (2018). Wheat bread quality attributes using jet milling flour fractions. *LWT – Food Science and Technology, 92*, 540–547. https://doi.org/10.1016/j.lwt.2018.02.065.
Wang, S., & Copeland, L. (2012). Nature of thermal transitions of native and acid-hydrolysed pea starch: Does gelatinization really happen? *Carbohydrate Polymers, 87*(2), 1507–1514. https://doi.org/10.1016/j.carbpol.2011.09.047.
Wang, L., Wang, P., Saleh, A. S. M., Yang, Q., Ge, Y., Wang, N., ... Xiao, Z. (2018). Influence of fluidized bed jet milling on structural and functional properties of normal maize starch. *Starch – Stärke, 70*(11–12), 1700290. https://doi.org/10.1002/star.201700290.
Wang, J., Xie, A., & Zhang, C. (2013). Feature of air classification product in wheat milling: Physicochemical, rheological properties of filter flour. *Journal of Cereal Science, 57*(3), 537–542. https://doi.org/10.1016/j.jcs.2013.03.001.
Wang, S., Yu, J., Xin, Q., Wang, S., & Copeland, L. (2017). Effects of starch damage and yeast fermentation on acrylamide formation in bread. *Food Control, 73*, 230–236. https://doi.org/10.1016/j.foodcont.2016.08.002.
Wong, S.-S., Wicklund, R., Bridges, J., Whaley, J., & Koh, Y. B. (2019). Starch swelling behavior and texture development in stirred yogurt. *Food Hydrocolloids, 98*, 105274. https://doi.org/10.1016/j.foodhyd.2019.105274.
Wronkowska, M., & Haros, M. (2014). Wet-milling of buckwheat with hull and dehulled – The properties of the obtained starch fraction. *Journal of Cereal Science, 60*(3), 477–483. https://doi.org/10.1016/j.jcs.2014.09.004.
Wu, F., Li, J., Yang, N., Chen, Y., Jin, Y., & Xu, X. (2018). The roles of starch structures in the pasting properties of wheat starch with different degrees of damage. *Starch – Stärke, 70*(5–6), 1700190. https://doi.org/10.1002/star.201700190.
Wu, T., Wang, L., Li, Y., Qian, H., Liu, L., Tong, L., ... Zhou, S. (2019). Effect of milling methods on the properties of rice flour and gluten-free rice bread. *LWT – Food Science and Technology, 108*, 137–144. https://doi.org/10.1016/j.lwt.2019.03.050.
Xu, J., Chen, L., Guo, X., Liang, Y., & Xie, F. (2020). Understanding the multi-scale structure and digestibility of different waxy maize starches. *International Journal of Biological Macromolecules, 144*, 252–258. https://doi.org/10.1016/j.ijbiomac.2019.12.110.
Xu, B., Mense, A., Ambrose, K., Graybosch, R., & Shi, Y.-C. (2018). Milling performance of waxy wheat and wild-type wheat using two laboratory milling methods. *Cereal Chemistry, 95*(5), 708–719. https://doi.org/10.1002/cche.10086.
Xu, X., Xu, Y., Wang, N., & Zhou, Y. (2018). Effects of superfine grinding of bran on the properties of dough and qualities of steamed bread. *Journal of Cereal Science, 81*, 76–82. https://doi.org/10.1016/j.jcs.2018.04.002.
Yu, D., Chen, J., Ma, J., Sun, H., Yuan, Y., Ju, Q., ... Luan, G. (2018). Effects of different milling methods on physicochemical properties of common buckwheat flour. *LWT – Food Science and Technology, 92*, 220–226. https://doi.org/10.1016/j.lwt.2018.02.033.
Yu, J., Wang, S., Wang, J., Li, C., Xin, Q., Huang, W., ... Wang, S. (2015). Effect of laboratory milling on properties of starches isolated from different flour millstreams of hard and soft wheat. *Food Chemistry, 172*, 504–514. https://doi.org/10.1016/j.foodchem.2014.09.070.
Zavareze, E. d. R., & Dias, A. R. G. (2011). Impact of heat-moisture treatment and annealing in starches: A review. Carbohydrate Polymers, 83(2), 317–328. doi: 10.1016/j.carbpol.2010.08.064.
Zeng, F., Gao, Q.-Y., Han, Z., Zeng, X.-A., & Yu, S.-J. (2016). Structural properties and digestibility of pulsed electric field treated waxy rice starch. *Food Chemistry, 194*, 1313–1319. https://doi.org/10.1016/j.foodchem.2015.08.104.
Zhang, K., Dai, Y., Hou, H., Li, X., Dong, H., Wang, W., & Zhang, H. (2019). Influences of grinding on structures and properties of mung bean starch and quality of acetylated starch. *Food Chemistry, 294*, 285–292. https://doi.org/10.1016/j.foodchem.2019.05.055.
Zhang, W., Ding, W., Ndeurumi, K. H., Wang, Z., & Feng, Y. (2015). Effect of wet ball milling on physicochemical properties and crosslinking reaction performance of corn starch. *Starch – Stärke, 67*(11–12), 958–963. https://doi.org/10.1002/star.201400251.
Zhang, Y., Zhao, M., Wang, H., Hu, H., Liu, R., Huang, Z., ... Feng, Z. (2019). Damaged starch derived carbon foam-supported heteropolyacid for catalytic conversion of cellulose: Improved catalytic performance and efficient reusability. *Bioresource Technology, 288*, 121532. https://doi.org/10.1016/j.biortech.2019.121532.
Zhang, Z., Zhao, S., & Xiong, S. (2017). Physicochemical properties of Indica rice starch modified by mechanical activation and octenyl succinic anhydride. *Starch – Stärke, 69*(9–10), 1600008. https://doi.org/10.1002/star.201600008.
Zhao, T., Li, X., Zhu, R., Ma, Z., Liu, L., Wang, X., & Hu, X. (2019). Effect of natural fermentation on the structure and physicochemical properties of wheat starch. *Carbohydrate Polymers, 218*, 163–169. https://doi.org/10.1016/j.carbpol.2019.04.061.
Zhu, F. (2019). Recent advances in modifications and applications of sago starch. *Food Hydrocolloids, 96*, 412–423. https://doi.org/10.1016/j.foodhyd.2019.05.035.
Zi, Y., Shen, H., Dai, S., Ma, X., Ju, W., Wang, C., ... Song, J. (2019). Comparison of starch physicochemical properties of wheat cultivars differing in bread- and noodle-making quality. *Food Hydrocolloids, 93*, 78–86. https://doi.org/10.1016/j.foodhyd.2019.02.014.