称号及び氏名	博士（学術）PHAM　VAN　HUNG
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論　　文　　名	「PHYSICOCHEMICAL CHARACTERISTICS OF CEREAL STARCHES AND THEIR DERIVATIVES, AND APPLICATION FOR STARCH-BASED FOODS」（穀類デンプン及びそれら誘導体の物理化学的特性とデンプン性食品への応用）
論文審査委員	主査　森田　尚文 副査　宮武　和孝 副査　北村　進一

論文要旨

Wheat endosperm has a bimodal granule-size distribution with significant differences in chemical compositions and functional properties such as amylose and lipid contents and gelatinization characteristics between two granule types. These differences are believed to affect starch modification such as chemical reactivity and subpopulation, distinguished by substitution level. In the first study, large (A-type) and small (B-type) wheat starch granules were characterized and used for modification. The physicochemical properties of cross-linked, and/or hydroxypropylated, and/or acetylated starches from the large and small wheat starch granules are also investigated. The large granules had higher amylose content and transition enthalpy and lower gelatinization temperature than the small granules. Although no difference in pasting temperature between the large and small granules, the viscosity of paste from the large granules was higher than that of the small granules. Both large and small granules had the characteristics of A-type crystal as shown by X-ray diffraction patterns. However, the large

granules contained lower amount of amylose-lipid complex than did the small granules. The large granules showed less reactivity with cross-linking reagents than did the small granules. In contrast, the large granules more reacted with reagents of acetylation or hydroxypropylation as compared to the small granules. The cross-linked starches from the large granules had lower gelatinization temperature and higher enthalpy, reduced rapidly paste viscosities and swelling factors as compared with those from the small granules. However, the pastes of cross-linked starches from the small granules exhibited more stable than those from the large granules during freeze-thaw treatment. The acetylated starches (AS), and acetylated and cross-linked starches (ACS) from the large granules showed lower gelatinization temperature, and higher enthalpy and paste viscosities than those from the small granules. The pastes of AS and ACS from the large and small granules had similar resistance to freeze-thaw treatment. While the hydroxypropylated starches (HS), and hydroxypropylated and cross-linked starches (HCS) from the large granules showed higher swelling power and paste consistency, and more clarity than those from the small granules. The starches modified by hydroxypropylation and cross-linking had lower gelatinization temperature and more tolerance to freeze-thaw, higher swelling power and paste consistency than the native starches. SEM also showed less damaged granules of the small granules after modification than the large granules.

Wheat starch, the predominant component of wheat grain, is responsible for the unique character in many wheat-based food products and is consequently an important parameter in the quality assessment of wheat flour. Along with the increase in consumption of products made from wheat flours, people are also being suffered the life-related diseases such as coronary heart disease, cancer and type II diabetes mainly derived from westernized foods. Therefore, recent interest in the nondigestible carbohydrates has created because of their healthy benefits. Resistant starch (RS),

which escapes digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine, also has beneficially physiological effects similar to dietary fiber such as laxation and/or blood cholesterol attenuation, and/or blood glucose attenuation. Highly cross-linked starch is also resistant to α-amylase and classified as the fourth categories of RS (RS_4). However, cross-linked starch exhibited low swelling and solubility, and rigid granules resulting in a change in the texture of products. In the second study, the cross-linked cornstarches (CLCS) with different levels of swelling and amylose contents were substituted for wheat flour to evaluate dough properties and bread qualities. The doughs made from the substituted flours were stronger and more stable than that from the control during mixing and proofing. The substitution with cross-linked waxy cornstarch made the dough softer and more extensible than that with cross-linked non-waxy cornstarch. Specific volume of bread baked from the substituted flours was higher than that of the control and the specific volume of bread baked with high-swelling-degree CLCS was the biggest. Breadcrumbs baked from the flours substituted with 5% or 10% of the cross-linked non-waxy cornstarch were softer than that from the control, while firmness of breadcrumbs baked from the flours substituted with the cross-linked waxy cornstarch was lower than that of the control and decreased with increasing in the amount of substitutions. These results show that highly cross-linked starches (RS_4) prepared from waxy starch might be used for breadmaking.

Furthermore, RS can be produced with baking and food processing relating to retrograded starch polymers and classifying as RS_3. During cooling, the retrogradation of amylose is major cause for formation of RS. Therefore, starch with high amylose content is believed to produce high amount of RS in bread. However, the high-amylose wheat flour was reported to have inferior quality for breadmaking. In the third study, the high-amylose wheat flour was used to substitute for normal wheat in breadmaking

and formation of RS in bread during storage was determined. The substitution with high-amylose wheat flour decreased peak and final viscosities, breakdown and setback. The doughs made from the substituted flours were weaker than that from the control with lower development and stability time during mixing. Compression stress, modulus of elasticity and viscosity coefficient of dough made from the substituted flours decreased with increase in the amounts of substitutions. This means the doughs with high-amylose wheat flour substitutions were softer and had weaker elasticity than that with the normal wheat flour because the high-amylose wheat flour had weaker gluten and higher dietary fiber than the normal wheat flour. At time zero after baking, RS contents in breads with 10, 30 and 50% of high-amylose wheat flour substitutions were 1.6, 2.6 and 3.0% (db), respectively, higher than that of the control (0.9%, db). The amounts of RS increased gradually during storage for 1, 3 and 5 days. With substitutions of 30 and 50% of high-amylose wheat flour, the total levels of dietary fiber and resistant starch in bread after 5 days of storage were 15.5 and 16.8% (db), respectively, as compared to 13.0% (db) in bread from the normal wheat flour. The increase in amount of RS in bread during storage illustrated that the retrogradation of amylose after gelatinization is major cause of formation of RS. The loaf volume and appearance of breadcrumbs made from 10 and 30% of high-amylose wheat flour substitutions were not significantly different from those of the control, whereas the substitution with 50% of high-amylose wheat flour made lower loaf volume and inferior appearance of breadcrumbs. After baking, the firmness of breadcrumb increased along with increase in amounts of high-amylose wheat flour substitutions. However, breadcrumbs with 30 and 50% of high-amylose wheat flour substitutions were less firm than the control and 10% of high-amylose wheat flour substitution during storage. This result was due to higher moisture content remaining in bread with high-amylose wheat flour substitutions than the control. As a result, high-amylose wheat flour might be

substituted for up to 50% of the normal wheat flour to make bread with acceptable bread quality and higher amount of RS.

審査結果の要旨

小麦粉の特性を決めるのは一般的には蛋白質と考えられているが、構成成分の 70%を占めるのは澱粉で小麦粉由来の加工食品への特徴的な性質を与えていることより、小麦粉の品質評価の重要なパラメーターとなっている。小麦澱粉は小麦の胚乳に大小２種類の粒子として存在するがアミロース含量、脂質含量、糊化特性のような化学組成、機能特性等の諸性質が異なる。そこで本研究ではこれらの澱粉の持つ特性を明らかにするとともに、それぞれの澱粉の化学修飾をおこない、それらの化学的、機能特性等を明らかにするとともに、食品加工への利用について検討した。

その内容は以下のように要約される。

第１章では小麦大（L 型）澱粉、小（S 型）澱粉粒子の特性を検討すると共に、L 型、S 型の澱粉粒子の　架橋化、ヒドロキシプロピル化、或いはアセチル化による修飾をおこない、それらの物理化学的性質について検討した。L 型粒子は S 型粒子に比べアミロース含量及び転移エンタルピーは高いが、糊化温度は低かった。L 型、S 型澱粉粒子間ではペースト温度には差が認められなかったが、L 型粒子のペーストの粘度は S 型粒子に比べ高粘性であった。L 型及び S 型の粒子とも X 線回折図形では A 型の結晶の特徴を示し、L 型澱粉粒子は S 型に比べ澱粉―脂質複合体の含量が少なく、且つ架橋化剤との反応性が低かった。一方、L 型澱粉粒子はアセチル化またはヒドロキシプロピル化における試薬との反応性が高いことを明らかにした。L 型澱粉粒子から得られる架橋化澱粉は低糊化温度と高エンタルピーを示し、ペースト粘度及び膨潤係数を急激に低下させた。S 型澱粉粒子から得られる架橋澱粉のペーストは L 型粒子のそれに比べ凍結―融解処理において、良好な安定性を示した。

L 型澱粉のアセチル化（AS）、アセチル化および架橋化（ACS）澱粉粒子は、低糊化温度、高粘度を示した。また、AS 化、ACS 化の澱粉ペーストは、いずれの粒子とも凍結―融解に同様な抵抗性を示した。一方、L 型澱粉粒子からのヒドロキシプロピル（HS）化、HS 化及び架橋化(HCS）澱粉は S 型澱粉に比べそれぞれ高い膨潤化能、ペースト粘度、透明性を示した。HCS 化澱粉は未修飾の生澱粉に比べ低い糊化温度、凍結―融解反応に高い耐性を示し、高い膨潤力、ペースト粘度を示した。SEM 観察からは、これらの修飾により S 型澱粉粒の方が L 型澱粉粒に比べ損傷の程度が少ないことを明らかにした。

近年の健康志向から難消化性多糖類に焦点が当てられてきたが、高度に 架橋化 された澱粉はα-アミラーゼでは分解されにくいことよりレジスタント澱粉（RS）であり、特にカ

テゴリー4のRS４に分類されている。第２章では種々の膨潤度と アミロース含量を持つ架橋コーンスターチを小麦粉に代替しドウの物性と製パン製を検討した。これら混捏、ホイロ後のドウは強くなり、安定性に優れ、架橋結合をしたウルチ性コーンスターチに比べ軟らかく、伸展性に富んでいた。代替粉パンの比容積は対照に比べて大きく、その値は高膨潤度の架橋結合コーンスターチで焼成したものが最も大きかった。5%と 10%の架橋結合ウルチ性コーンスターチの代替で焼成したパンクラムは軟らかくなった。また、モチ性の架橋結合コーンスターチで焼成したパンクラムの硬さは対照と比べ低下した。これらのことよりモチ性澱粉から調製したRS4を含む高度架橋澱粉は製パンに使用できることを明らかにした。

第 3 章では高アミロース含量の小麦粉を通常小麦粉に代替して製パンを行い保存中のパンに含まれるRSの生成を調べたところ、高アミロース粉の小麦粉の代替ではピーク、ブレークダウン、セットバック粘度等を減少させた。また、このドウは対照に比べドウ生地の形成時間、安定性を低下させ、軟らかいドウで、且つ弱い弾性を示すが、このことは高アミロース小麦粉の持つ弱いグルテン特性、高い食物繊維含量を反映したといえる。高アミロース粉 10%、30%、50%を代替し焼成直後に含まれる RS 含量は、対照(0.9%)に比べ 1.6、2.6、3.0%と高い値を示した。更に、そのRS含量は保存1、3、5日の間に徐々に増加した。30%、50%の代替により焼成したパン中の 5 日後の食物繊維とRSの含量は対照の 13%に対し15.5%、16.8%と増加した。このパンの貯蔵中のRSの増加は糊化後のアミロースの老化がRSの形成の主要な理由である。10%、30%の高アミロースの代替による比容積とパンクラムの外観は対照のものと顕著な差はなかったが、50%の代替では低い比容積と好ましからざる外観を示した。製パン後のパンクラムの硬さは高アミロース粉の代替量の増大につれて増加した。30%、50%の高アミロース粉の代替により焼成したパンクラムは、対照及び10%代替粉に比べ保存中の硬さの進行が抑えられた。これは高アミロース粉代替パン中に残存する水分含量が対照よりも高いことに起因することを明らかにした。このように高アミロース小麦粉は 50%までの添加により良好な製パン特性を持ち、多量のRSを持ったパンを焼成できることを明らかにした。

以上の成果は、食品化学、食品製造学、食品物理学、食品化工学の分野に大きく貢献するものであり、本論文の審査並びに、最終試験の結果と併せて、博士（学術）の学位を授与することを適当と認める。