



Introduction to Fibersym® RW, a RS4-Type Resistant Wheat Starch

MGP Ingredients, Inc.
Atchison, Kansas

Creating Better Solutions...Naturally

Outline

- Historical Account of Starch Indigestibility
- RS4–Type Resistant Wheat Starch
(Phosphated Distarch Phosphate)
- Mechanism of Resistance to Amylase Digestion as Viewed by SEM



Consumer Attitudes to Fiber

- 70% of parents believe fiber is an important part of a child's diet
- 60% of parents said fiber is useful to help maintain or control children's health
- 35% of parents believe consuming products with fiber helps children with digestion
- 36% of consumers are most interested in foods with an "excellent source of fiber" claim
- 80% of consumers believe "promotes healthy digestion" on yogurt is appealing
- 70% of consumers find "helps manage your weight" claims appealing

Source: Tate & Lyle, BakingBusiness.com, October 14, 2008



Dietary Fiber Consumption

Then

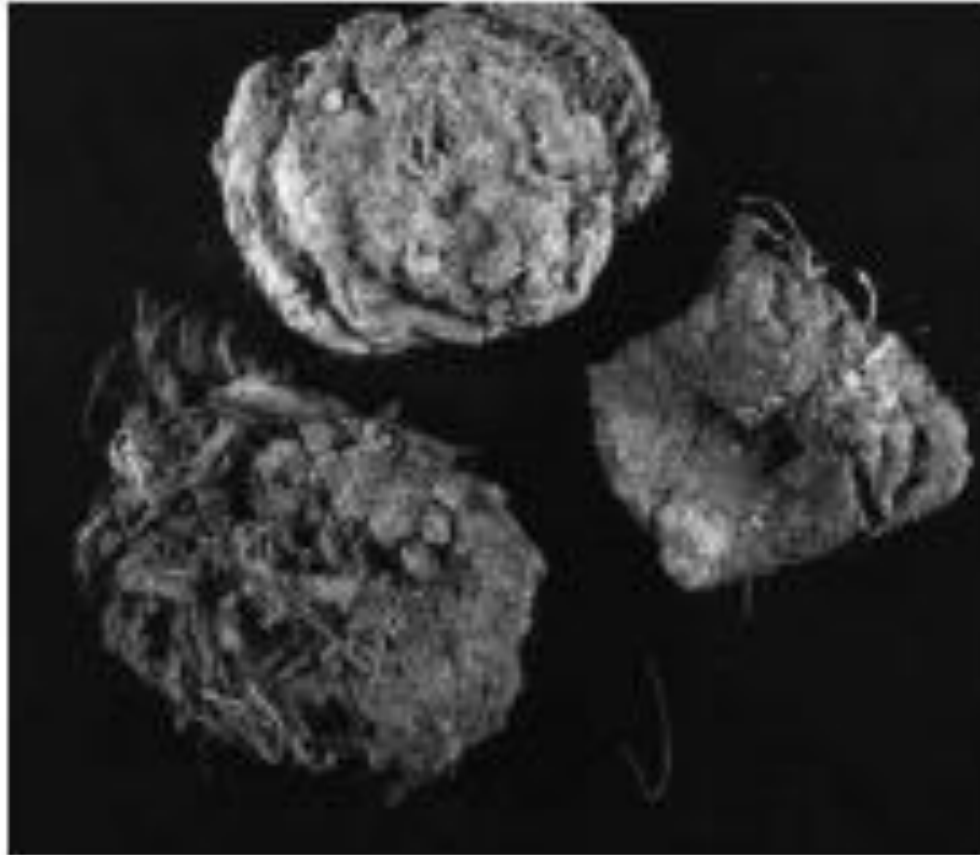
- Australian aborigines: 80 – 130 grams/day
- North American Indians (west Texas): 150 - 250 grams/day

Now

- United States: 15 grams/day
- Great Britain: 12-24 grams/day
- Australia: 18-25 grams/day

Source: Brand-Miller and Holt 1998; Sobolik 1994
American Dietary Association; British Nutrition Foundation
www.healthyeatingclub.com

Coprolites of North American Indians



Fossilized human feces (5500 years old) recovered in west Texas caves with undigested fiber visible

Source: Leach, 2007

Ohalo II Excavation

- Excavation site on the shores of the Sea of Galilee, Israel; explored in 1989-1991 and 1999-2001
- Materials dated 23,000 years ago
- Staple foods: more than 90,000 plant remains, of which nearly 19,000 were grass grains
- 16,000 short-grained grasses, 2,503 barley grains and 102 emmer wheat grains
- Found concentrated around a grinding stone

Source: Weiss et al 2004



Daily Intake of Resistant Starch

| Country | Range |
|-----------|---------------------|
| U.S.A. | 2.8 – 7.9 grams/day |
| Australia | 3.4 – 9.4 grams/day |
| Europe | 3.2 – 5.7 grams/day |

Source: Murphy et al 2008

Definition of Resistant Starch

- The sum of starch and products of starch degradation not absorbed in the small intestines of healthy individuals (Asp 1992)

Included in the Definitions of Dietary Fiber

- American Association of Cereal Chemists International (2001)
- Codex Alimentarius (2007)
- European Food Safety Authority (2007)

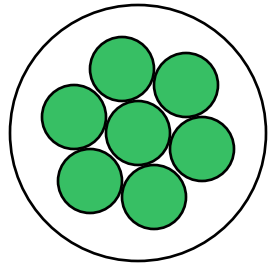
Discovery of “Resistant Starch”

Englyst et al 1982

Starch “resistant” to:

- Hog pancreatic alpha-amylase + pullulanase
 - 100 – 200 mg sample in 10 ml 0.1M NaOAc buffer, pH 5.2
 - 1 hour in boiling water bath
 - 0.1 ml enzyme solution (5,000 units of alpha-amylase and 5 units of pullulanase per milliliter of NaOAc buffer, pH 5.2), 42^o C, 16 hours
- Determination of “resistant starch”
 - Solubilization in 2 M KOH
 - Glucoamylase hydrolysis at pH 4.5 and 65^o C for 1 hour
 - GLC determination of released glucose

Four Types of RS in the Diet



Types of RS

RS1 - Physically inaccessible starch

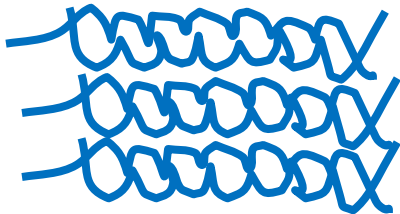
Occurrence

Partially milled grains, seeds and legumes



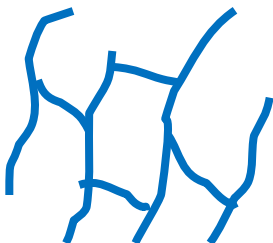
RS2 - Granular starch

Native, uncooked banana starch and potato starch



RS3 - Nongranular, retrograded amylose

Cooked and cooled potato

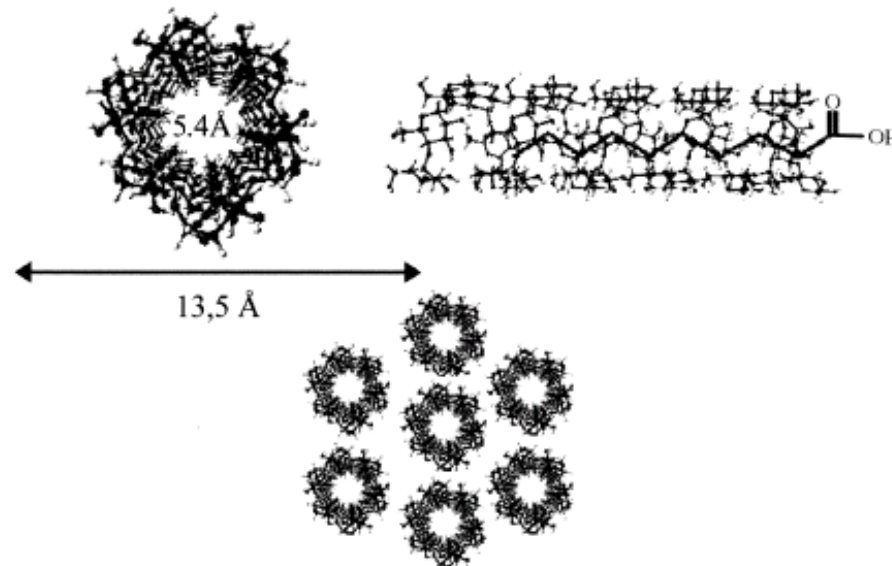


RS4 - Chemically modified starch

Cross-linked or hydroxypropylated

RS5 – Type Resistant Starch

- Proposed by Brown et al 2006
- Exists as amylose-lipid complex
- Exhibits resistance to amylolysis



Source: J. Jpn. Assoc. Diet. Fiber Res. 10: 1-9, 2006; Eliasson 2004

Langworthy and Deuel 1920

Thorpe 1913 – Starch in a raw state is to man an almost indigestible substance, but when previously subjected to the operation of cooking it is digested with great facility

Fofanow 1911 – He found in human subjects that raw wheat, oat, and rice starches were practically assimilated, while raw potato starch was from 2 ½ to 4 times less well digested

Source: J. Biol. Chem. 42: 27-40, 1920



Daniels and Strickler 1917

| Product | Indigestible Starch, % |
|------------------------|------------------------|
| Pastry | 31.8 |
| Angel Cake | 11.2 |
| Crackers | 18.5 |
| Bread | 2.2 |
| Baking Powder Biscuits | 3.3 |
| Pan Cake | 15.1 |
| Butter Cake | 1.7 |
| Omelet | 5.8 |

Source: J. Home Econ. 9:109-114,1917

Human Study

- Raw corn and wheat starches were found to be completely assimilated and no trace of them could be found in the feces
- Raw potato starch has an average digestibility of 78.2%

Source: J. Biol. Chem. 42: 27-40, 1920



Chemically Modified Starch/RS4-Type

Digestibility studies prior to 1982:

Janzen 1969

Filer 1971

Conway and Hood 1976

Hood and Arneson 1976

Wooton and Chaudhry 1979

Wooton and Chaudhry 1981

Biliaderis 1982

Pancreatin Digestion

Digestibility relative to gelatinized, unmodified starch

Distarch phosphate of wheat = 97.5%

Hydroxypropyl (M.S.=0.06) distarch phosphate of wheat = 74.8%

Acetylated (D.S. = 0.07) distarch phosphate of wheat = 89.2%

Source: Janzen 1969



Hog Pancreatic Alpha-Amylase Digestibility

Relative to unmodified starch

Hydroxypropyl distarch phosphate (M.S.=0.09) of
Waxy Maize = 87%

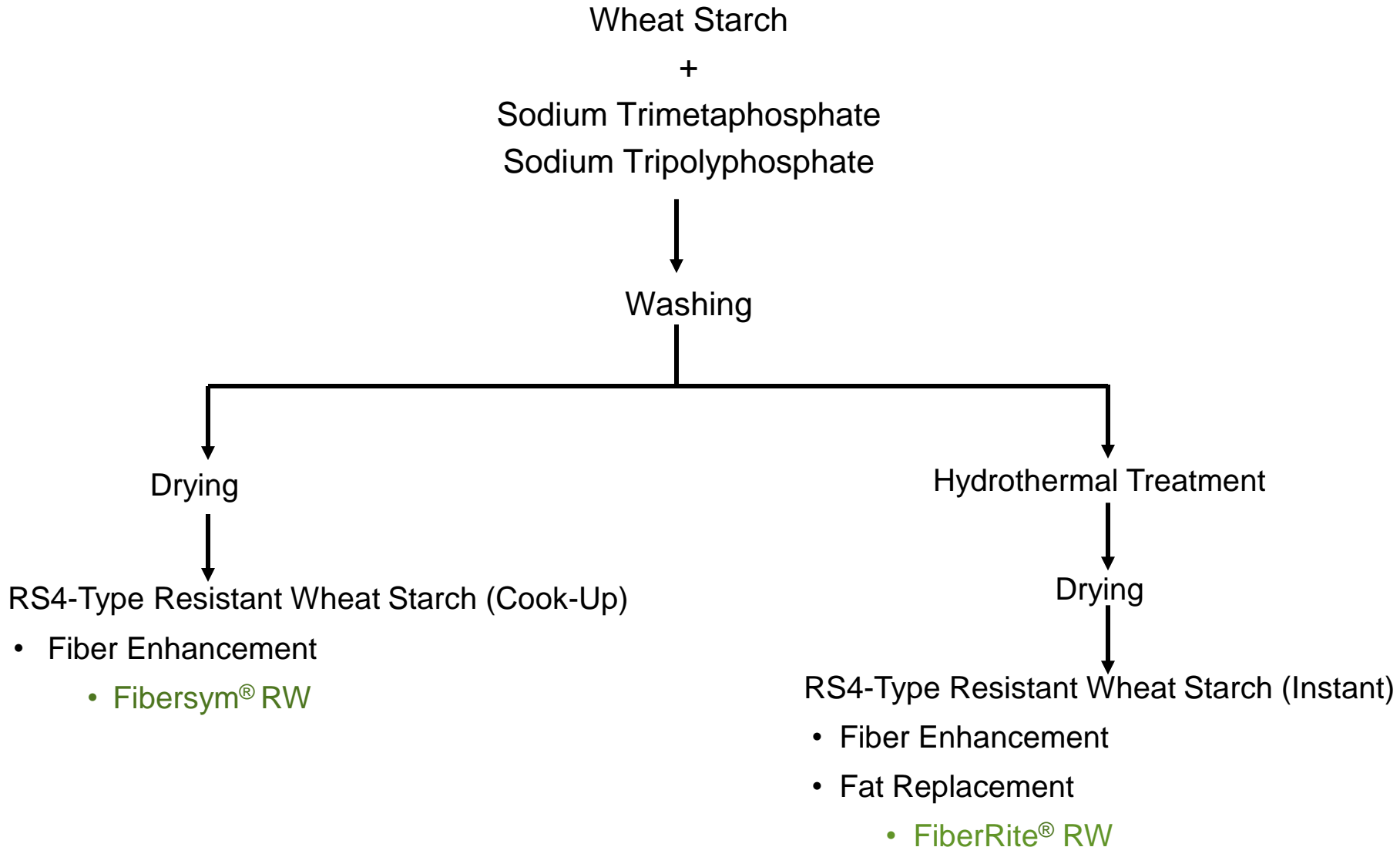
Acetylated (D.S. = 0.06) smooth pea starch = 94%

Acetylated (D.S. = 0.06) distarch phosphate of
smooth pea starch = 91%

Source: Biliaderis 1982



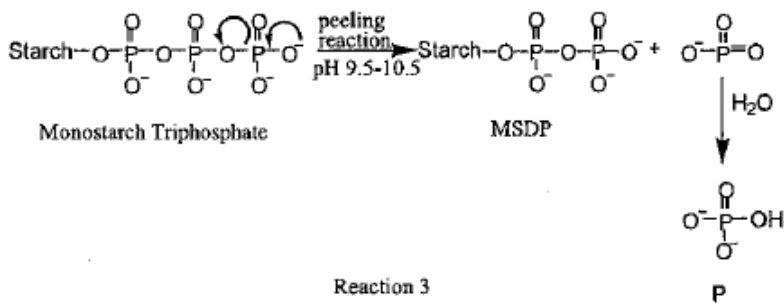
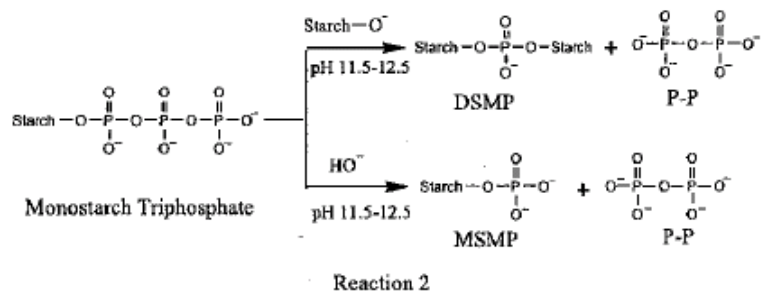
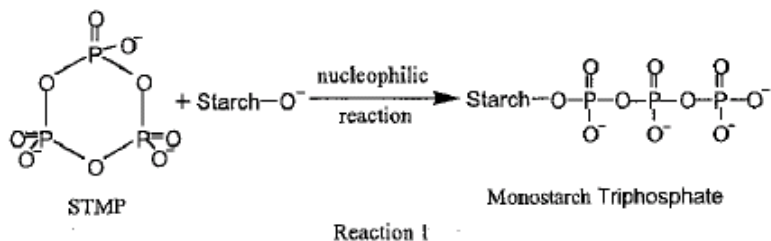
Simplified Manufacturing Process for RS4



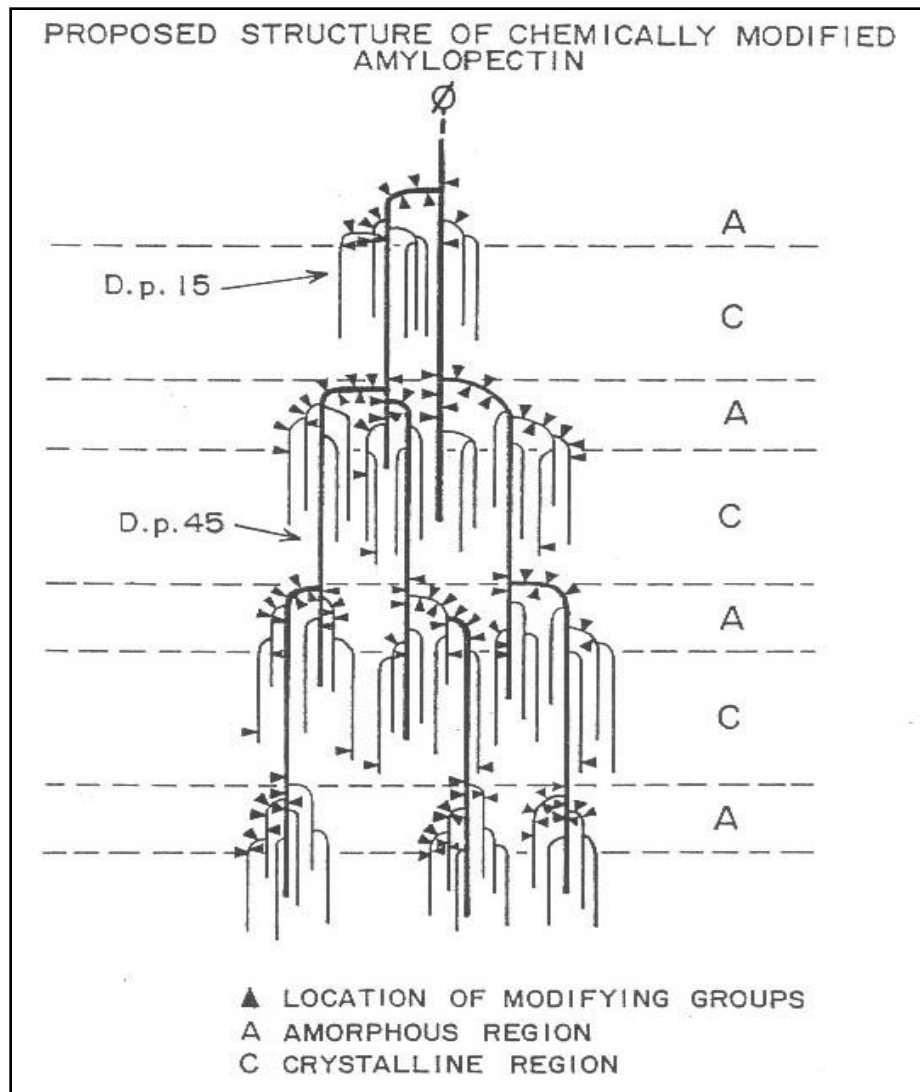
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Chemical Reactions for RS4

Y. Sang et al. / Carbohydrate Polymers 67 (2007) 201-212



Proposed Structure of Chemically Modified Amylopectin



Probable locations of phosphate cross-links?

Source: Biliaderis 1982



Content of Total Dietary Fiber

Fibersym[®] RW = 85% (minimum, d.b.)

FiberRite[®] RW = 75% (minimum, d.b.)



Chemical Name

Fibersym[®] RW and FiberRite[®] RW
are both
Phosphated Distarch Phosphate



Ingredient Statement

Both Fibersym[®] RW and FiberRite[®] RW
are labeled

Modified Wheat Starch

on the ingredient deck of consumer food
packages

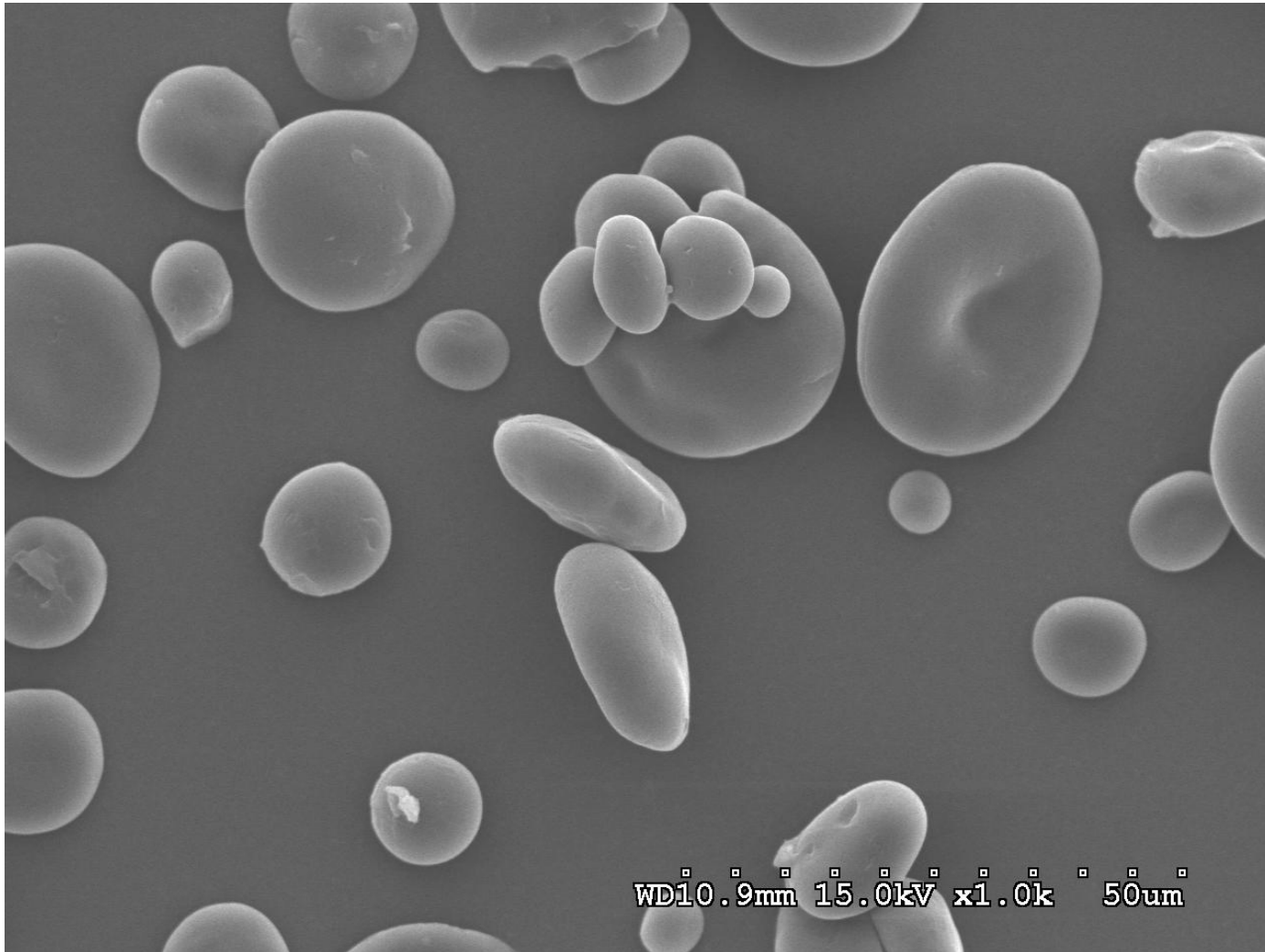


Commercial Applications of Fibersym[®] RW and FiberRite[®] RW

- Bread
- Flour Tortilla
- Cookies
- Muffin Bars
- Muffins
- Bagels
- Puff Pastries
- Toaster Pastries
- Pizza Crust
- English Muffins
- Pretzels
- Pasta
- Hand-Held Crust Appetizers
- Breakfast and Lunch Wraps
- Ready-to-Drink Beverage

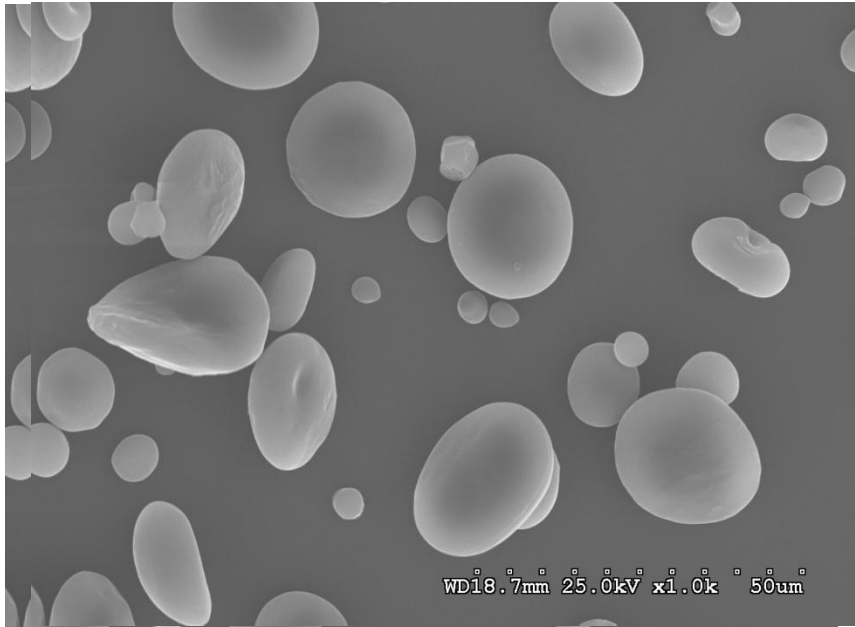


Native Wheat Starch Granules

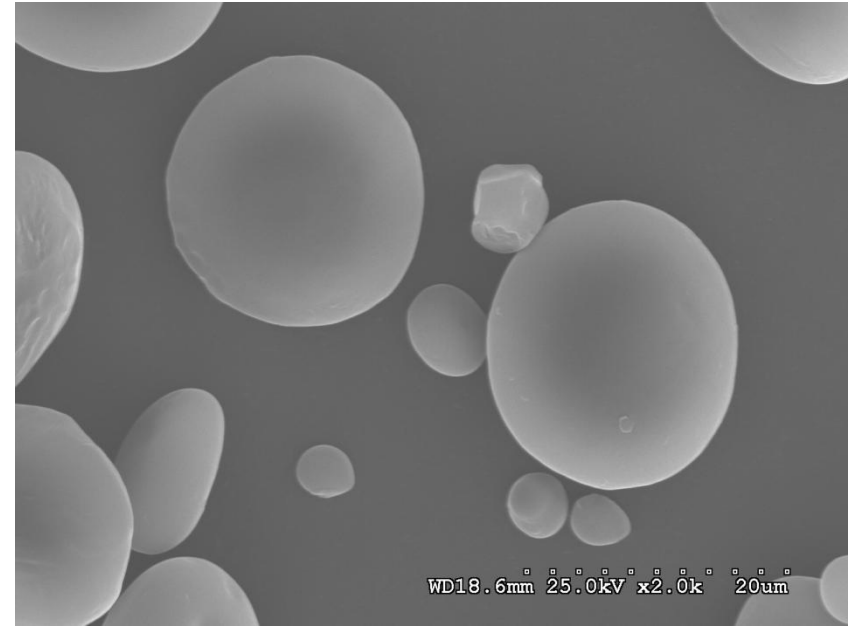


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RS4-Type Resistant Wheat Starch Granules (Fibersym[®] RW)



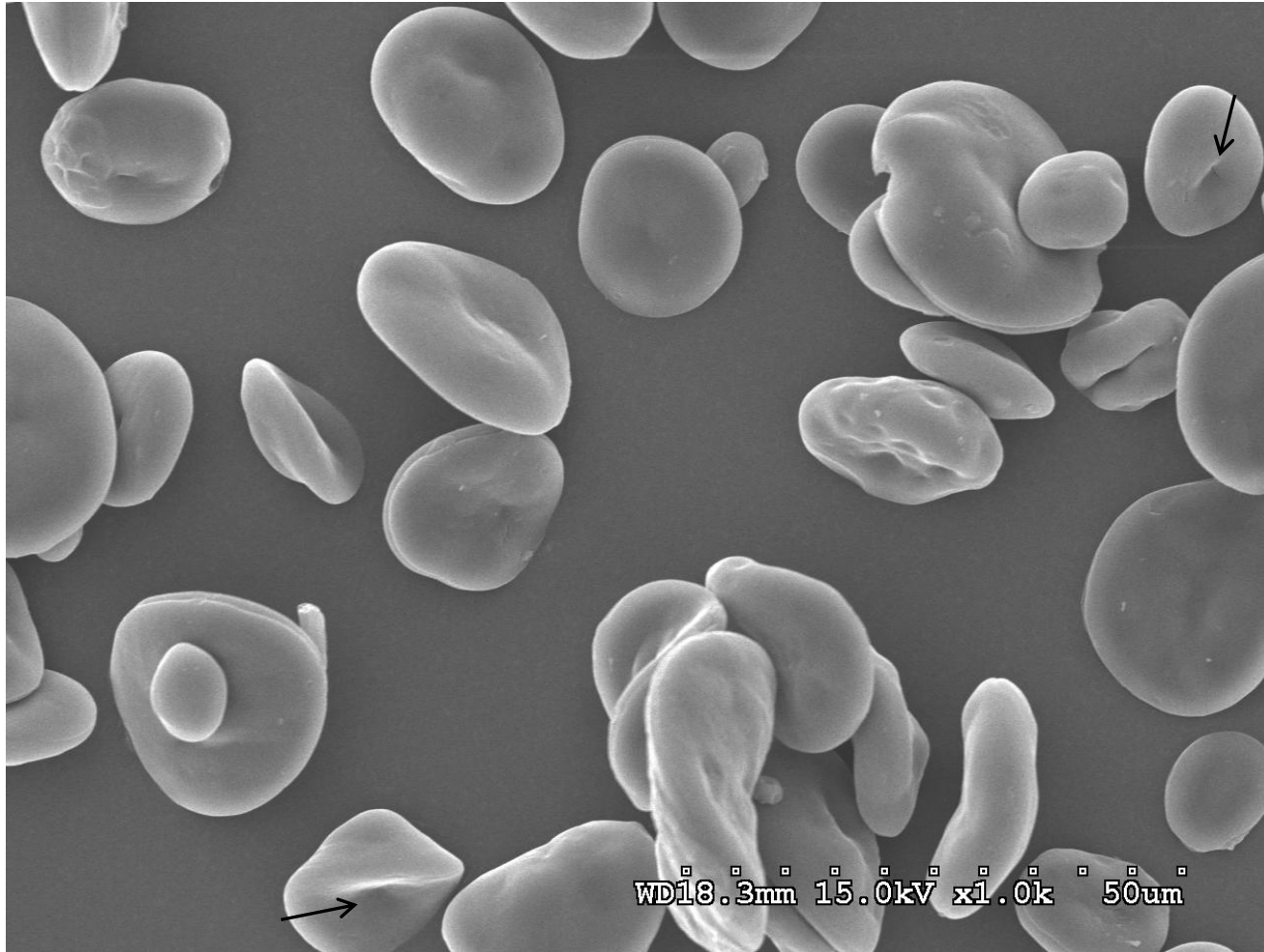
X 1, 000



X 2, 000

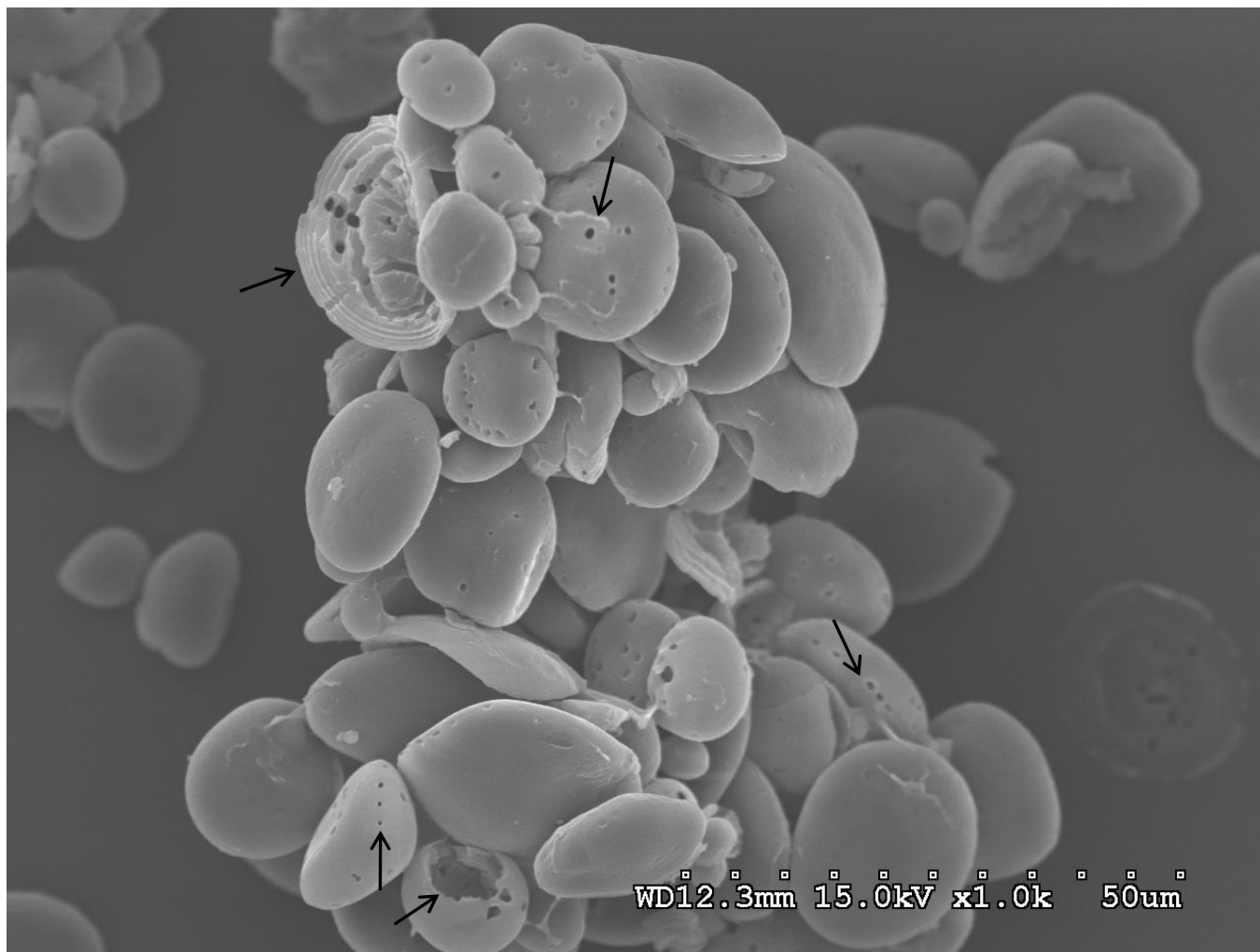


Cooked (Gelatinized) RS4-Type Resistant Wheat Starch Granules (FiberRite® RW)



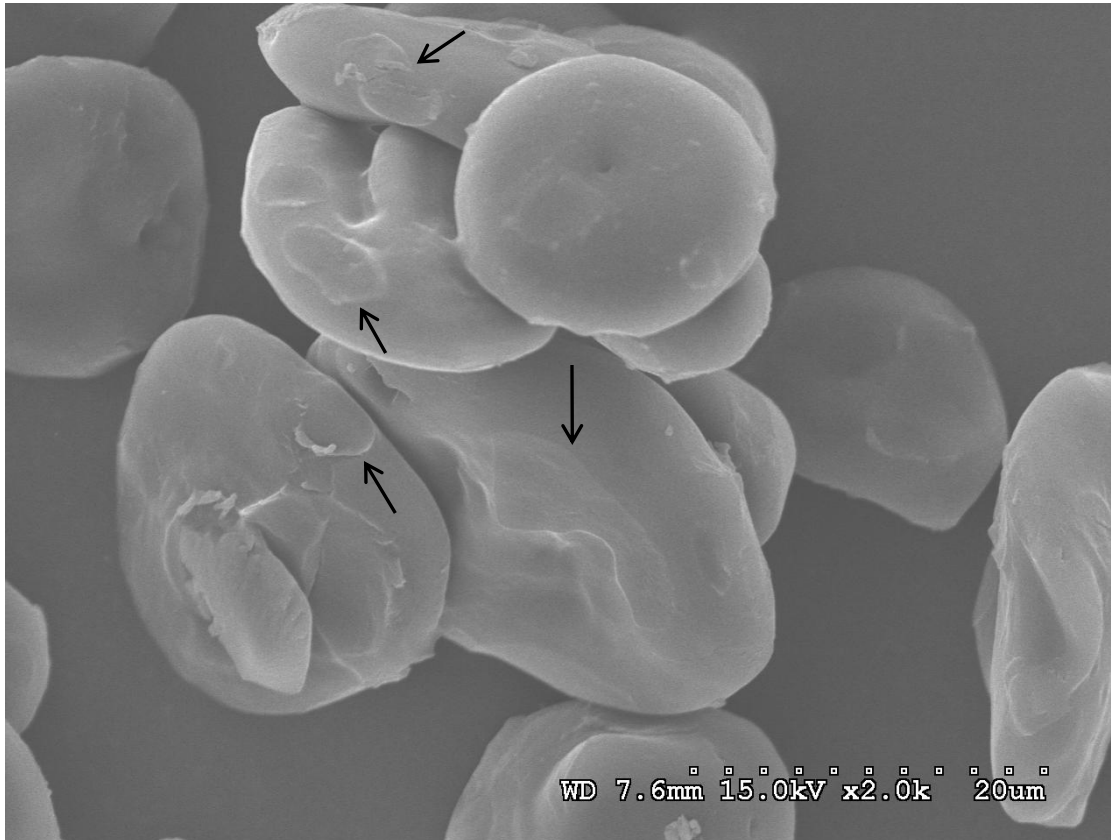
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Indigestible Residue from Native, Ungelatinized Wheat Starch (after alpha-amylase, protease, and glucoamylase digestion at 25°C and pH 7 for 16h)





Indigestible Residue from Fibersym® RW (after alpha-amylase, protease and glucoamylase digestion, AOAC Method 991.43)

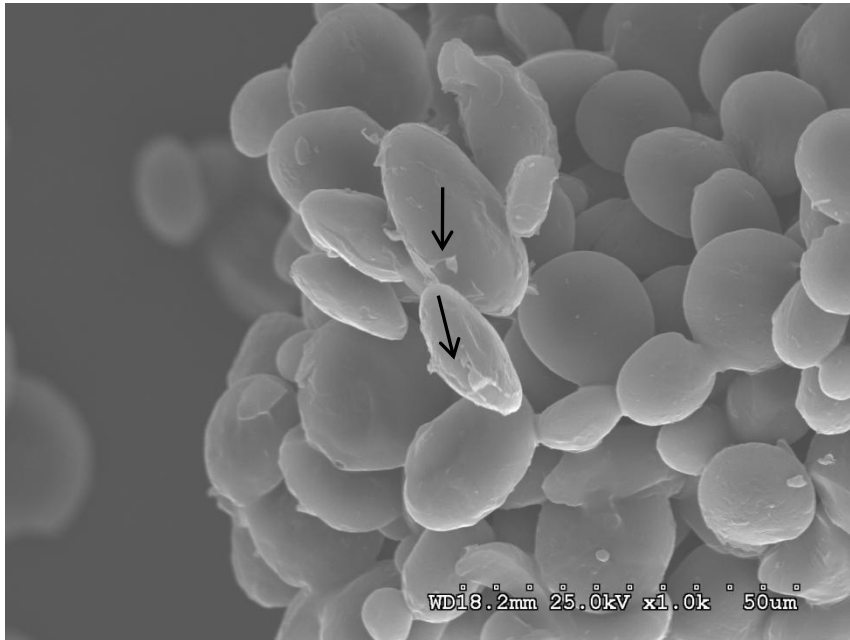


Alpha-Amylase
95 - 100 °C
pH 8.2
35 min.

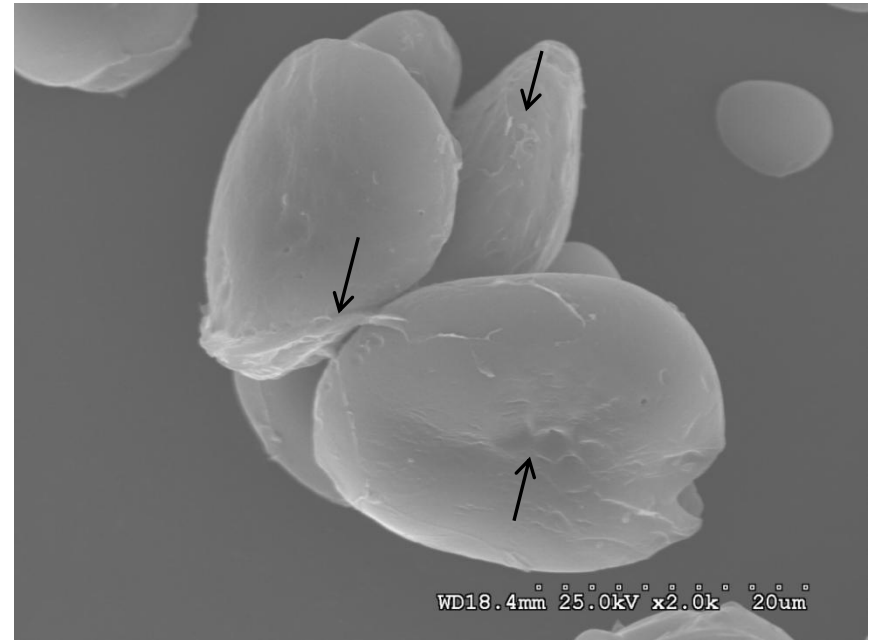
Protease
60 °C
pH 8.2
30 min.

Glucoamylase
60 °C
pH 4.5
30 min.

Indigestible Residue from Fibersym® RW (Englyst Method, 20 min, SDS+RS)



X 1,000



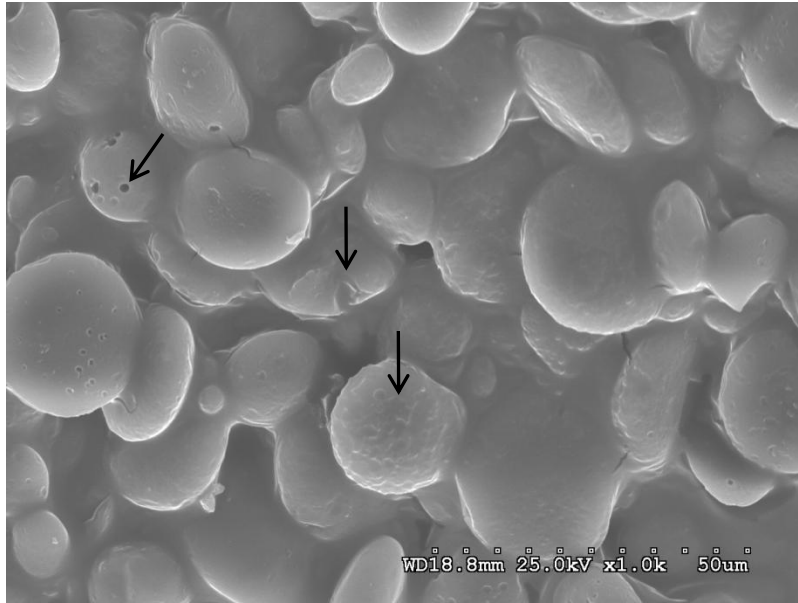
X 2,000

Pepsin 37 °C, pH 2, 30 min.

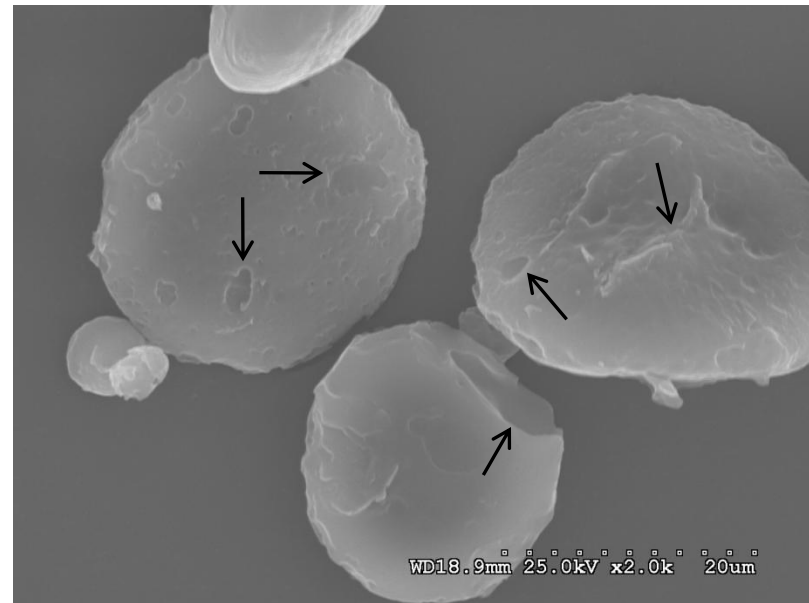
Amyloglucosidase, Pancreatin, Invertase, 37 °C, pH 5.2, 20 min.

Digestion method by Englyst et al 1992

Indigestible Residue from Fibersym[®] RW (Englyst Method, 2 h, RS)



X 1,000

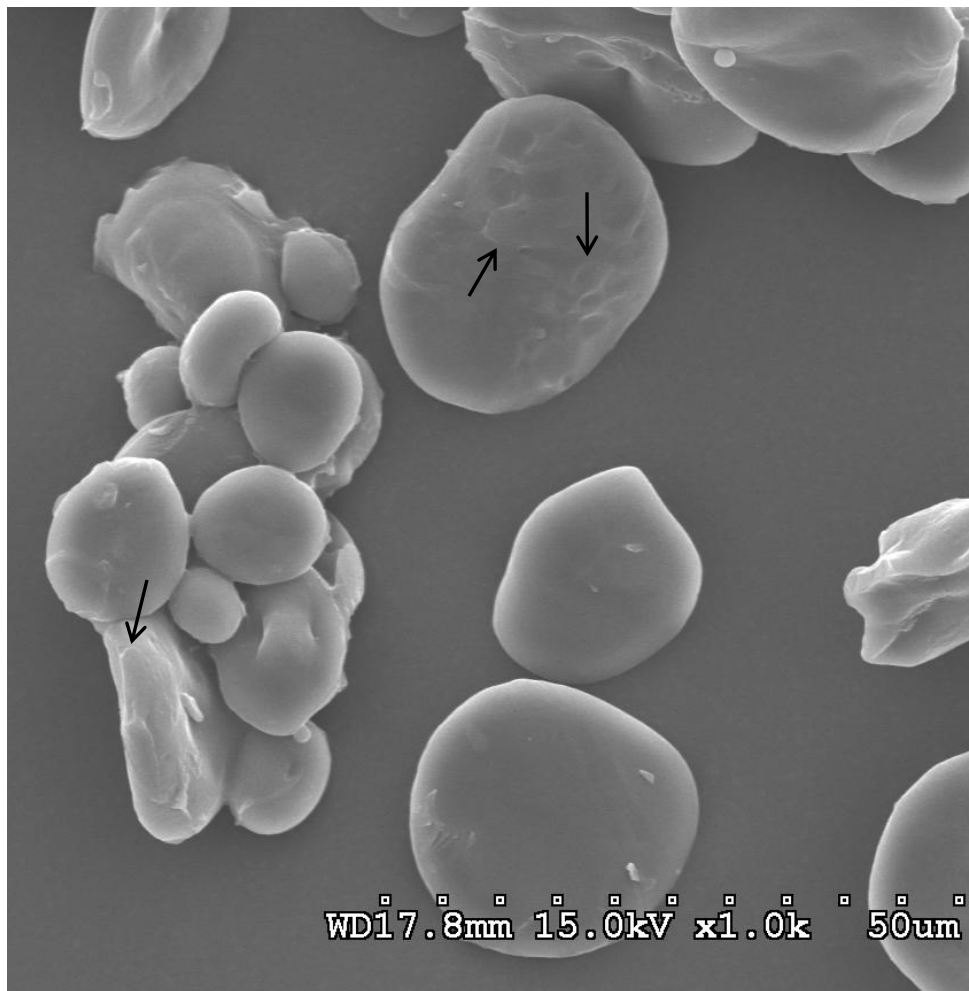


X 2,000

Amyloglucosidase, Pancreatin, Invertase, 37 °C, pH 5.2, 120 min.

Digestion method by Englyst et al 1992

Indigestible Residue from Fibersym® RW (after *in vitro* pepsin and pancreatin digestion)



Boiling water bath
30 min.

Pepsin-HCl
37 °C
pH 2.0
3 hrs.

Pancreatin-Bile
37 °C
pH 7.5
12 hrs.

Digestion method by
Trinidad et al 1996

RS4 – Type Cross-Linked Resistant Starch

- Surface erosion is the primary mode of enzyme attack; endo-corrosion is not evident
- Blocklets on surface are probably the most susceptible to enzyme attack
- Numerous phosphate cross-linking bonds stabilize granular structure; restrict granular swelling during heat treatment
- Surface pores and channels are blocked or obstructed by phosphate groups
 - Inhibit the diffusion of enzyme molecules
- Phosphate groups sterically hinder the formation of enzyme-starch complex
- Enzymatic procedure and gelatinization of resistant starch affect mode of enzyme attack
- Botanical source has limited effect on mode of enzyme attack