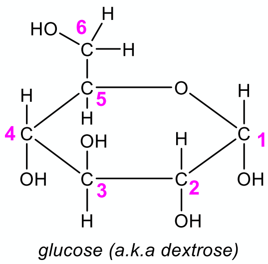
Carbohydrates: Starch is made of sugar

Model 1.



Glucose is a simple sugar - it contains only one *ring* and is rapidly metabolized in the body for energy. Glucose contains 6 carbons which are numbered as shown on the structure seen at the left.

Starch is made of chains of glucose molecules. To utilize the starch as a source of energy, we must break the large starch molecule down into glucose molecules.

Figure 18.1. Glucose, a simple sugar

Carbohydrates are molecules made of one or more sugars. The most common sugar we find in food is *glucose* (i.e. dextrose) – $C_6H_{12}O_6$, but there are many sugars with similar molecular formulas and structures.

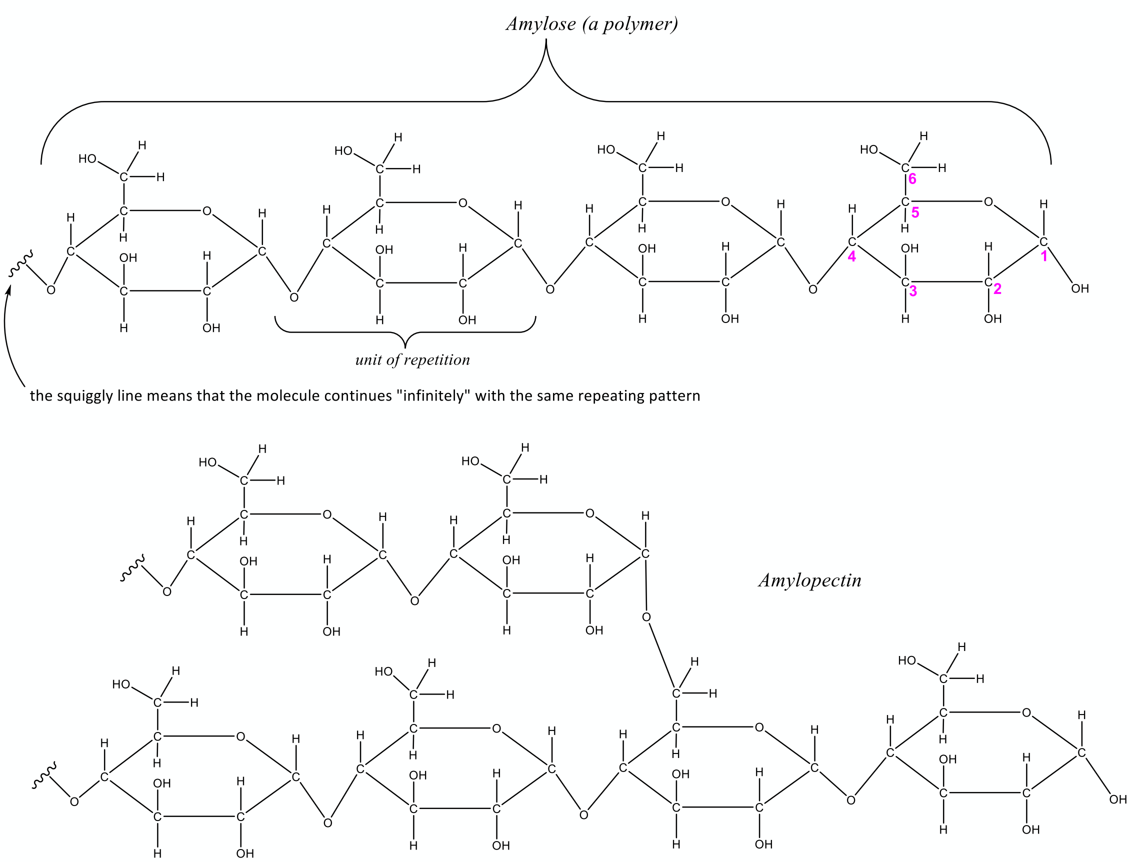


Figure 18.2. Amylose and Amylopectin. Two types of starch.

Starch is a *carbohydrate*. In nature, starch is found most often in one of two forms: *amylose* or *amylopectin*. If you examine the structure of *amylose* or *amylopectin* in Figure 18.2, you will notice that each is a combination of repeating units. The same molecular piece is repeated over and over again. *Amylose* and *amylopectin* are *polymers* – where *poly* = "many". The unit of repetition is called a *monomer*. In *amylose* and *amylopectin*, the *monomer* unit is a glucose.

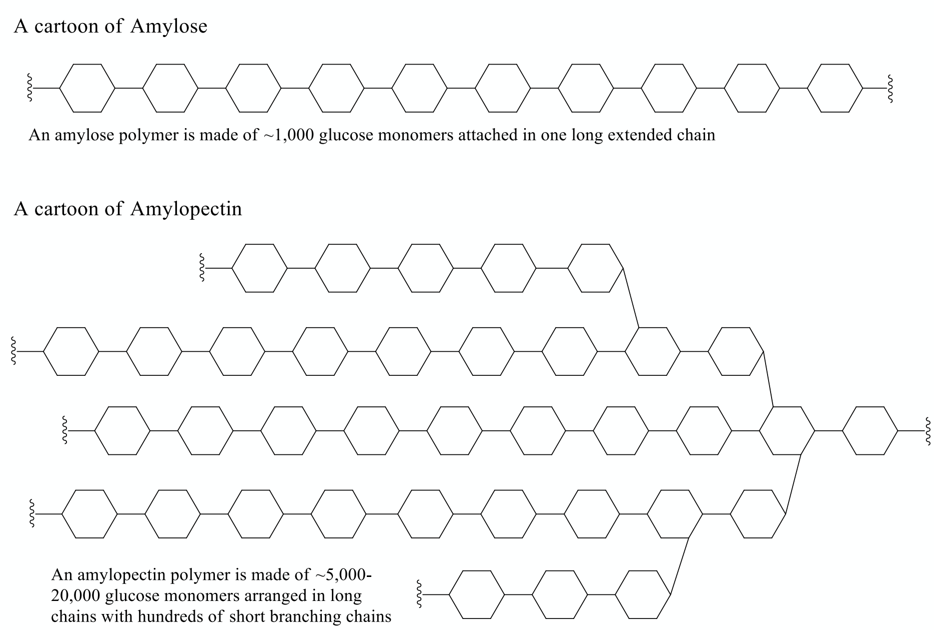
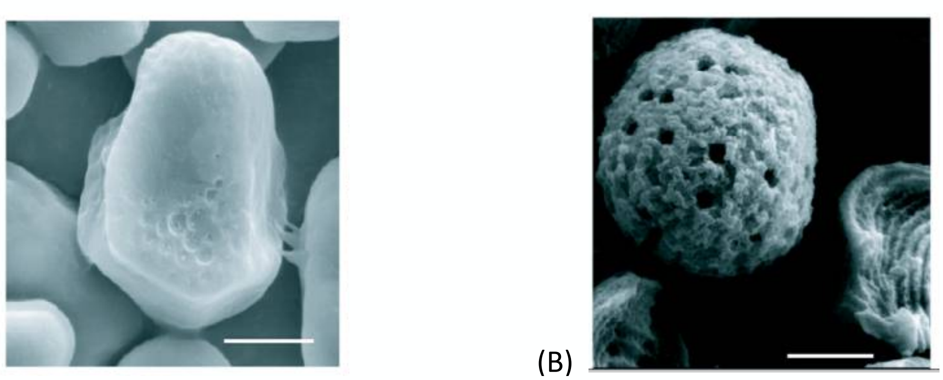


Figure 18.3. Cartoons of large amylose and amylopectin polymers



(A) A powerful microscope image of a starch granule

(B) A powerful microscrope image of a starch granule after exposure to the enzyme, *alpha amylase.*

Figure 18.4. Microscope images of a wheat starch granule before after digestion. [1]

[1] Images are from J Insect Sci. 2009; 9: 43 and are used here under the Creative Commons Attribution License

Plants deposit starch molecules in microscopic solid granules. The size, shape, amylose and amylopectin ratios and cooking qualities of starch granules vary depending on the species of the plant. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin.

The enzyme *alpha amylase* (present in flour, egg yolk, etc) is able to break starch molecules down into individual glucose units. In addition, the human body can break down *amylose* and *amylopectin* into individual glucose molecules using *enzymes* called *glycosidases*.

The *glucose* molecule is an essential source of energy for human metabolism. When glucose ($C_6H_{12}O_6$) is broken down via *aerobic respiration* to provide energy for the body, the glucose is converted to carbon dioxide and water in an *oxygen dependent* series of *enzyme catalyzed* reactions. One gram of carbohydrate broken down by *aerobic respiration* yields ~4 calories (~16 kilojoules) of energy.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \text{ (+ 16.7 kilojoules of energy per gram)}$$

1. Consider the structure of glucose. Each has the basic molecular formula $C_nH_nO_n$ where n = the number of each atom. Record that formula in the table below. Now, rewrite the molecular formula in the following format: $C_n(H_2O)_n$

Molecular formula for glucose

	Glucose
$C_nH_nO_n$	$C_6H_{12}O_6$
$C_n(H_2O)_n$	$C_6(H_2O)_6$

Using this information, explain why glucose is an example of carbo*hydrate*?

hydrate of Carbon

2. Using Figures 18.2 and 18.3, compare the structure of *amylose* to that of *amylopectin*.
   a. Explain why amylose is called a *1,4-linked* polymer of glucose

   Bonded between C_1 of one molecule and C4 of another

   b. Explain why amylopectin is called a *1,4* and *1,6 linked* polymer of glucose?

   Has bonding described above and C1 to C6

c. Are your answers consistent with the fact that amylose is a *linear* ("like a line") polymer of glucose while *amylopectin* is a *branched* polymer of glucose? Explain how.

Yes, 1-6 linkage causes branching

3. Compare Parts (A) and (B) of Figure 18.4. Explain the chemical reasoning behind the difference in physical appearance of the starch granule in part (A) vs. part (B).

Granule broken down by alpha amylose.

4. Does the equation for aerobic respiration abide by the *law of conservation of mass*? Explain.

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5. The word *aerobic* means "requiring air". Explain how this definition is consistent with the equation for the breakdown of glucose by *aerobic respiration*.

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18B. Gelation of starch

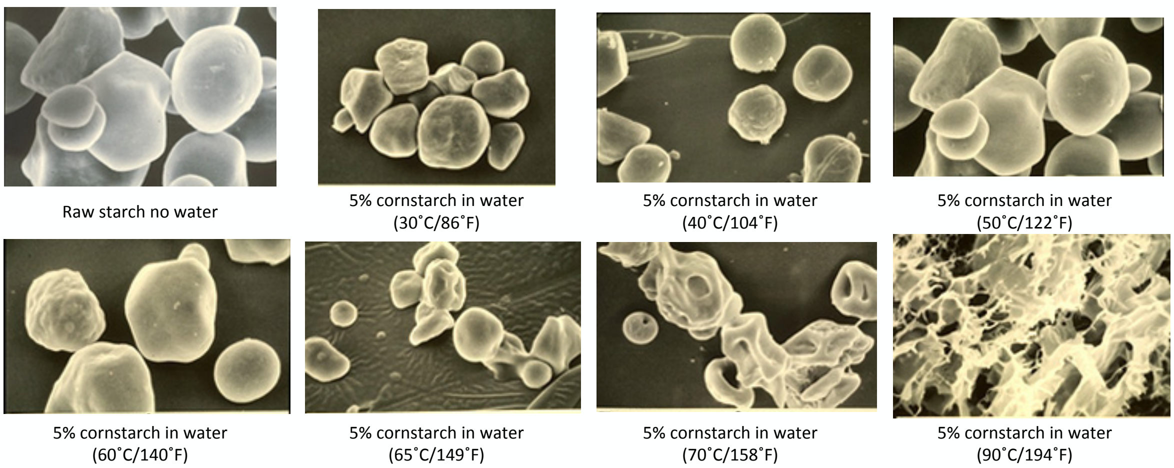

Figure 18.5. Starch in water at increasing temperatures[2]

Table 18.1. Types of common thickening starch and their properties[3]

Type	Gelation Temperature	Thickening power	% amylose[4]	Avg granule size	Additional factors that affect thickening power
Wheat	126-185°F, 52-85°C	+	26%	17µm[a] (50%), 7µm (20%), other (30%)	High protein content (~10-12%), variable granule size inhibits good amylose gels
Corn	144-180°F, 62-80°C	++	28%	14µm	Opaque gels
Potato	136-150°F, 58-65°C	++++	20%	36µm	Amylose polymers are unusually long > improves gels
Tapioca (cassava root)	126-150°F, 52-65°C	++	17%	14 µm	Forms clear gels, but stringy
Arrowroot	140-187°F, 60-86°C	++	21%	23µm	Forms clear gels, but stringy

[a] µm = micrometer, or one millionth of a meter

When starch granules are mixed with water at room temperature not much happens to the starch. But if the starch in water mixture is heated, eventually the temperature gets high enough that the granule begins to swell up as water penetrates into the center. Eventually, the granule absorbs enough water and swells to such a degree that it breaks

[2] Dr. ZoeAnn Holmes, Professor Emeritus, Oregon State University. *Used with Permission.*
[3] On Food and Cooking, McGee p.615, Functional Properties of Starches by Morton Satin (FAO Agricultural and Food Engineering Technologies Service)
[4] For example, 20% amylose means a 20/180 ratio of amylose to amylopectin.

apart into a network of starch molecules mixed with water. These networks of long starch molecules with water in between are called *gels*. The temperature at which the starch granule falls apart into this matrix of water and starch molecules is called the *gelation temperature*.

The *gelation temperature* of starch is dependent on the kind of starch it is. The amount of amylose, the size of the amylose chains, and the size of the starch granule are all factors in the thickening power. Amylose forms stronger *gels* than amylopectin – this is because amylose has a linear (thread like) structure, while amylopectin has the bushy branched structure. The threads of amylose more readily form *gels*: 3-dimensional networks of polymer that has trapped water molecules between the polymer chains. Hydrogen bonds between the straight amylose chains hold them together. Amylopectin molecules will form gels, but the gels are softer and less stable because the bushy amylopectin molecules cannot stack closely and form stable hydrogen bonds with each other as easily. When the starch granules are large, they are easily trapped in the 3-dimensional network of starch chains and water, and therefore increase the viscosity of the liquid. The tightly ordered clusters of amylose molecules require higher temperatures, more water and longer cooking times to *gel* (separate into a network filled with water molecules). Clusters of amylopectin molecules gel at lower temperatures.

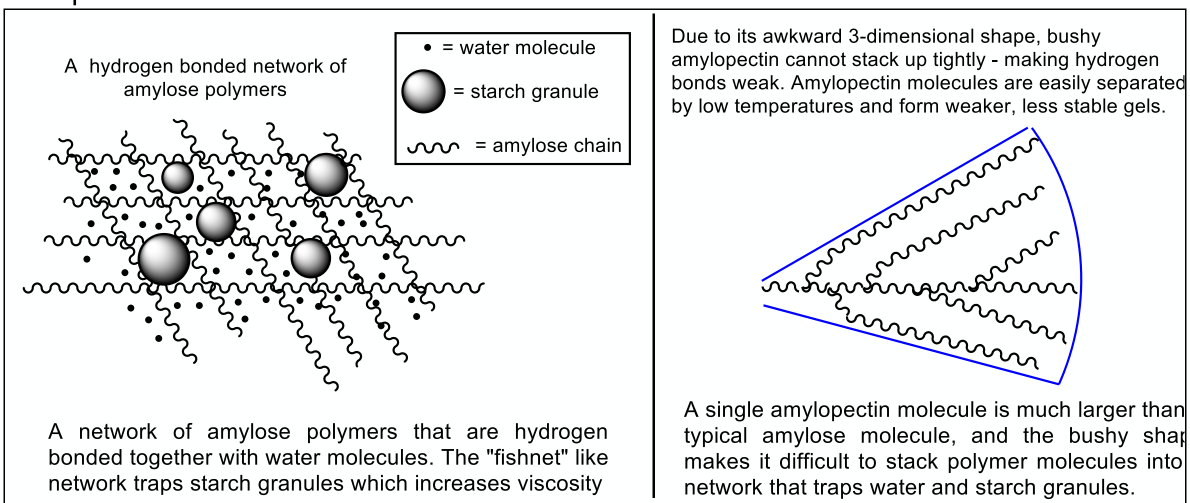

Figure 18.6. Gelation of amylose. The bushy shape of a molecule of amylopectin.

When a cook adds starch to a liquid and then heats it to form a gel, the starch molecules leak out of the starch granules and the sauce thickens. When the sauce is thick enough, the cook will turn off the heat and the mixture will cool. As the temperature falls, there is less energy for the molecules to move and groove, consequently they move less and form more stable hydrogen bonding networks with each other and with the water molecules interspersed among the polymer chains. If the temperature gets low enough, the starch molecules will *congeal* or solidify into a solid gel. Amylose chains reform their tightly packed hydrogen bonded structures quickly because their linear shape makes tight packing easy and hydrogen bonding strong. If there is little water, then the amylose chains will pack into a hard *crystalline* solid instead of a moist gel. Amylopectin molecules take longer to reassociate into hydrogen bonded networks upon cooling because their bushy shape makes tight packing difficult, and they form weaker networks (softer gels) compared to amylose.

This process of heating starch to gelation temperatures and then cooling the gelled network into a solid is called *retrogradation*. The *retrograded* starch is *more compact* (i.e. harder) that the native starch. This is what happens when pie fillings, puddings and other gel-like solids are made. It also explains why cooked rice turns hard in the refrigerator overnight.

Questions:

6. Medium grain rice Starch is 18% amylose with average granule sizes of 5µm. Would you predict rice starch to be better or poorer thickening agent when compared to cornstarch? Why?

   Poorer ⇒ less amylose and smaller granule

7. Considering the gelation temperature of cornstarch (table 18.1), explain what is happening in Figure 18.5.

   At 180°F, gelation is complete but you can see it beginning by 150°F

8. Arrowroot starch is a common substitute for cornstarch in recipes. Explain the chemical reasoning behind the similar thickening power of arrowroot and cornstarch.

Less amylose but larger granule size

9. The stacking of linear amylose chains versus bushy amylopectin chains is mediated by hydrogen bonds. Using the structures of amylose and amylopectin and your knowledge of hydrogen bonding – explain which atoms are able to form hydrogen bonds with each other and with water molecules, and why formation of these hydrogen bonds is dependent on the 3D shapes of amylose and amylopectin.

The O-H groups on the amylose + amylopectin

The shape dictates how well the molecules fit together

10. There is constant disagreement among cooks as to whether or not you should mix cornstarch with hot water or mix it with cold water before adding it to a hot sauce that you wish to thicken. What do you think? Which is preferred or does it matter?

Putting it all together:

11. The making of bread dough requires yeast to produce carbon dioxide gas. Yeast require glucose to make carbon dioxide, and the food source for the yeast comes from the flour itself in the form of starch and the enzyme, alpha amylase. Explain how the yeast are able to make carbon dioxide from this food source.

Starch $\xrightarrow[\text{amylase}]{\text{alpha}}$ glucose $\xrightarrow{\text{yeast}}$ CO

12. Rice comes in 3 basic varieties shown below which vary in their amylose/amylopectin ratios.

<table>
<tr><td>Rice</td><td>% Amylose[5]</td><td rowspan="5">All rice is cooked by boiling in water, which heats the starch granules up, causing them to swell and leak starch. In the table to the right, 22% amylose means a 22/78 ratio of amylose to amylopectin. So a 0% amylose starch has 100% amylopectin.</td></tr>
<tr><td>Long grain</td><td>22%</td></tr>
<tr><td>Medium grain</td><td>18%</td></tr>
<tr><td>Short grain</td><td>12%</td></tr>
<tr><td>Waxy (“sticky”)rice</td><td>0-1%</td></tr>
</table>

Using the % amylose information and your knowledge of gelation in high amylose starches, explain why long grain rices have a “firm, springy texture” when cooked and get inedibly hard when refrigerated overnight, while “sticky rice” has a softer, stickier texture and hardens much less during overnight refrigeration.

can make strong gel which constricts when cold.

13. When rice is refrigerated overnight and gets really hard (think leftover take-out Chinese food), you can fix the problem by simply microwaving the rice with a little added water – i.e. after microwaving the rice becomes soft and edible once more. Based on your knowledge of starch gelation and retrogradation, what is the chemical explanation behind this phenomenon?

Swells the gel by expanding and rehydrating

14. To use wheat starch as a thickening agent, the cook must overcome the high protein concentration in wheat flour (most of it glutenin and gliadin!) that interferes with starch gelation. Furthermore, the protein will also absorb water and form elastic, insoluble gluten – great for bread, but it will give your sauce chewy lumps (bleck!). To use wheat flour as a thickener, the cook should cook the flour first in some kind of oil or fat – this is called making a *roux*. Once the flour has cooked in the oil for a minute or two, the cook can slowly add liquid and bring the mixture to a boil. How does making a *roux* fix the problems associated with using the starch in wheat flour as a thickening agent?

Oil prevents gluten formation

15. When potatoes are boiled, professional cooks recommend cooking the potato slices at ~160˚F for ~20-30 minutes followed by *cooling them down* while standing (i.e. don’t mash or otherwise disturb the potatoes) for 30 minutes. You can then finish the cooking process by briefly reheating the potatoes by steaming or simmering followed by gentle mashing. This process of heating > cooling > then briefly reheating avoids the gluey texture that mashed potatoes can sometimes get. What is the cooling accomplishing? And why does this fix the “gluey” problem?

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[5] On Food and Cooking, McGee p. 459