

Introduction to Alginate

What is Alginate?

Alginate is found in a wide variety of brown seaweeds and is present as a structural polysaccharide. Alginate is made up of a linear block copolymer of α -L-guluronic acid and β -D-mannuronic acid. The blocks vary in size and alternating M and G segments as well as random blocks may also be present. The type of structure is influenced by the seaweed source as well as the growing conditions of the weed. The block structure ultimately dictates the gelling properties of the alginate produced. *Durvillaea* and *Ascophyllum* species tend to be high in mannuronic acid and hence form softer gels whereas alginate sources such as *Laminaria hyperborea* stipes tend to have a higher guluronic acid content and hence form much more rigid gels.



Alginate bearing weeds are typically found in temperate or cold water with the exception of *Sargassum*, which also grows in warmer waters. Commercial sources of brown seaweed that are used for alginate extraction vary around the world. The most common species used are *Ascophyllum*, *Durvillaea*, *Ecklonia*, *Laminaria*, *Lessonia*, *Macrocystis*, *Saccharina* and *Sargassum*. Processors often utilise a local source of brown seaweed but in many cases, it is supplemented with other materials that are brought in and which may have different properties.

← *Ascophyllum nodosum*

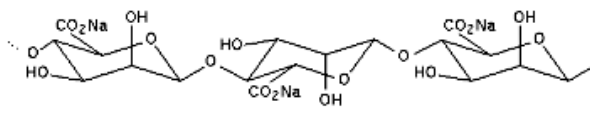
Alginate can also be produced from a bacterial source (*Azobacter vinelandii*). However, the block structure in bacterial alginate tends to give a product with poor gelling characteristics and the expense of production means the product has never been commercialised and remains of academic interest only.

Structure of Alginate

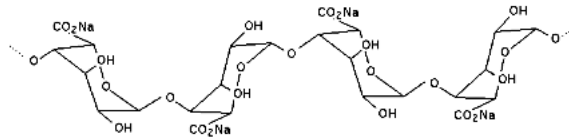
Alginate was originally thought to consist of a uniform polymer of mannuronic acid as shown below. However later studies showed the presence of guluronic acid residues and it is now understood that alginate is a linear co-polymer of β -D-Mannuronic acid and α -L-Guluronic acid.

Depending on the weed source and growing conditions the ratio of mannuronic and guluronic acid can vary. It is also known that the block structure within the alginate can vary significantly. The poly guluronic acid blocks bind significantly more effectively with calcium ions than the poly mannuronic acid blocks. The weed types with the higher guluronic acid levels are normally the ones that show the strongest interaction with calcium and hence the strongest gel strength. However, it is not quite that simple and only guluronic acid blocks over a certain size can be involved in calcium crosslinking and the larger the

block the stronger the cross link. Hence to identify the alginate with the strongest calcium gel not only high guluronic acid levels are required but also significant block structures.



Sodium polymannuronic acid



Sodium polyguluronic acid

Production of Alginate

There are essentially two processes for the preparation of alginates. They all start off with similar extraction procedures but vary in the methods used to precipitate the alginate at the end of the process, usually via the addition of calcium salts or with acid.

Extraction

Raw or dried weed is washed with acid to remove crosslinking ions that cause the alginate to be insoluble. The acid washed weed is then dissolved in alkali, typically sodium hydroxide, to produce a viscous solution of alginate and cell wall debris which contains a lot of cellulose. The solution is filtered to remove the cell wall debris and maybe treated to remove colour. Finally, a clear, clean alginate solution is left.

Calcium Precipitation

This the most common and versatile of precipitation methods is the calcium method. In this method calcium salts are added to the filtered liquor to produce a fibrous precipitate. This fibre is then left to harden' before being recovered. One method of recovery involves blowing air into the tank and skimming the floating the fibrous mat off the surface.

The recovered mat of calcium alginate is then treated with more acid to remove the calcium ions and leave an insoluble alginic acid fibre. This fibre can then be mixed with various alkali salts eg sodium carbonate to form sodium alginate.



Beach cast kelp ↑

Acid Precipitation

Another and more direct method of precipitation is by using acid directly. This method has the advantage that the calcium addition and subsequent removal is avoided making an inherently simpler process. However, it will only work with certain strong gelling types of weeds. With weeds such as *Ascophyllum* the acid precipitate formed is too soft too press and dewater and cannot be used. So in terms of seaweed types that can be used this process is much less flexible.

Properties of Alginate

Roughly speaking the M to G ratio of the alginate largely controls functionality. Work has shown that a more sophisticated approach linking gel properties to block size produces a better correlation. Higher G containing polymers tend to form more rigid gels at a very specific concentration of cations whereas higher M polymers tend to form softer gels and over a wider range of conditions. As alginate is a linear polymer the viscosity is determined by the molecular weight and the rigidity and extension of the chain.

Laminaria digitata →



The most common alginate gel used is the calcium alginate gel. Alginate will gel with most di and trivalent salts, but the calcium gel is really thin one used in the food industry. The texture of a straight alginate gel is not very good for a lot of food applications but has found a niche in the area of restructured products such as fruits and meats. Alginate is also used as a stabiliser for the ice cream industry.



One advantageous property of alginate is in the ability to formulate controlled set gels by manipulation of the calcium ion availability. This can be used in cold whip products where the gel set is delayed by a few minutes until the alginate is dissolved.

PGA (propylene glycol alginate) is the only, commercially available, chemically modified alginate. PGA is made by contacting a partially neutralised alginic acid with propylene oxide gas under pressure. The propylene oxide reacts exothermically with the alginic acid to form a mixed primary/secondary ester. The PGA market can be split into two main areas: The highest clarity and ester content PGA is used in the beer industry as a head retention aid. Lower grade products are typically used in salad dressings, in conjunction with xanthan gum and fruit juice based products as a stabiliser.

← ***Laminaria hyperborea***

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