Technical Article

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. Durvillea and ascophyllum species tend to be high in mannuronic acid and hence form softer gels whereas alginate sources such a laminaria hyperborea stems tend to have a higher guluronic acid content an hence form much more rigid gels.

Fucus type brown seaweed

Alginate bearing weeds are typically found in temperate or cold water. Major commercial sources of alginates are the giant kelp from California (*Macrocystis pyrifera*) and *Ascophyllum Nodosum* from the north Atlantic. The major manufacturers are based near the weed sources in San Diego, Scotland and Norway. More recently manufacturers have been developing in Asia. Other weed sources from around the world are shipped to the major factories and include several types of Laminaria, Ecklonia, Lessonia and Sargassum.

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 in figure 1. 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.

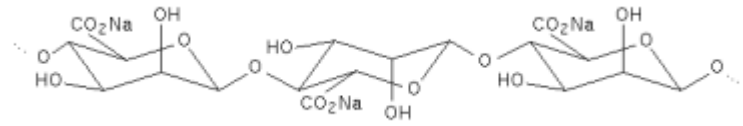

Figure 1. Sodium polymannuronic acid

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

Despite the stronger gel strength of the high guluronic acid containing weeds the major application for this product is in pet food. Most of the alginate sold into food and pharmaceutical applications today tends to be low in guluronic acid.

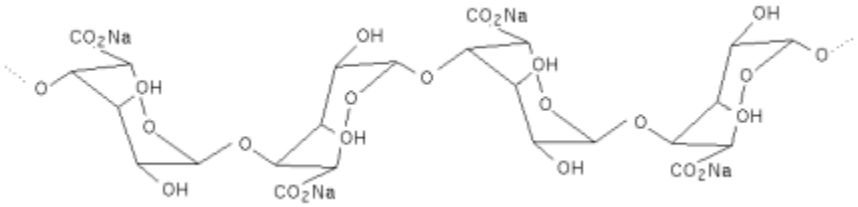

Figure 2. Sodium polyguluronic acid

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.

Mixed weeds at low tide

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.

Shore cast Laminaria

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.

Shore cast Laminaria

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 thinly 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.