Introduction to Agar

Introduction

Agar, more correctly known as agar-agar, has been used in the East for several hundred years and certainly since the seventeenth century. Agar is traditionally claimed to have been discovered by Tarazaemon Minoya in 1658 in Japan.

Agar is typically a strong gelling polysaccharide derived from red seaweeds and is characterised by its chemical repeat units of 3-6,anhydro L-Galactose. Agars also contain sulphate esters in low levels and some methoxy groups.

Agar is eaten extensively in Asia has a flavoured jelly where the brittle texture is appreciated. However for western tases, brought up on gelatin, this is less acceptable. Agar is useful in the food industry as a gelling and thickening agent with particularly good properties in acidic dairy products where it is used as a stabiliser. Another key property of agar is the large hystersis between the melting and setting temperatures which is unusual for a polysaccharide. One of the single biggest users of agar in the west is in the baking industry where the very high melting points of the agar gels make them particularly suitable to the baking process. Agar has good compatibility with sugar and can be used in very high sugar environments that would precipitate most other gums. Agar is often used to provide structure to high sugar systems such as doughnut icing.

Structure

The original structure of agar was was believed to be a simple sulphated poly galactose. However in in 1937 showed that agar consisted of at least two separate polymers that could be fractionated. One was called agarose and the other agaropectin. Essentially agarose is the gelling fraction of agar. Later in 1957 agarose was assigned a linear polymer structure consisting of alternating D-galactose and 3,6 anhydro-L-galactose as shown in figure 1. However agar is actually a very complex polysaccharide and varies considerably depending on the source. In 1991 showed that at least eleven different agarobiose structures could be identified in different agar bearing weeds depending on gender, species environmental conditions and time of the year. In summary agar can be considered to consist mainly of alternating β-(1-3)-D and α-(1-4)-L linked galactose residues. Most of the α-(1-4) residues are modified by the presence of a 3,6 anhydro bridge. The other modification that can be found are mainly substituents of sulphate, pyruvate, uronate or methoxyl groups. Modern alkalie treatment methods tend to increase the level of anhydro bridging in the molecule which subsequently improves the gelstrength. The level of methoxy content appears to be one of the main structural moieties that determines the gel setting temperature with very low methoxy contents giving the lower setting temperatures.

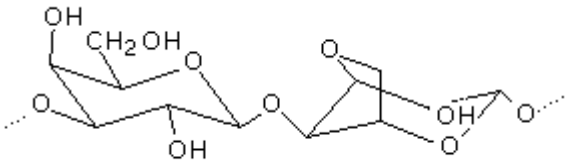

Figure 1. Original structure of agar repeat unit

Agarose is typically high in molecular weight and low in sulphate. Agaropectin is typically a lower molecular weight and also higher in sulphate at about 5-8%. Xylose has been found in some agars

Production

Agar producing seaweeds are available from a wide variety of sources (table 1). Agar weeds are typically wild harvested although commercial farms have been used in Chile and Namibia.

Table 1. Primary agar producing species

Acanthopeltis Japonica	Japan
Gelidiella Acerosa	Japan, India
Gelidium Amansii	Japan
Gelidium Cartilagineum	USA, Mexico, South Africa
Gelidium Caulacanthum	New Zealand
Gelidium Corneum	South Africa, Iberia, Morocco
Gelidium Liatulum	Japan
Gelidium Ligulatum	Japan
Gelidium Pacificum	Japan
Gelidium Pristoides	South Africa
Gelidium Sesquipedale	Portugal, Morroco
Gracilaria Conferviodes	South Africa
Pterocladia Capillacea	Egypt, Japan, New Zealand
Pterocladia Lucida	New Zealand

Agar can be extracted in a variety of ways but the basic methodology revolves around dissolving the agar from the seaweed with hot water, separating the agar from the cell wall residues by filtration and then isolating the agar from the dilute solution. Various methods have been developed to isolate the agar from solution, the traditional method relies on cutting the gel into strips and allowing it to freeze overnight and thaw out the next day in the sun. Due to the high level of syneresis produced in an agar gel the strips loose water on each freezing and cooling cycle until a dry strip is formed. this strip is known in Japanese as *Kanten* which literally translates as "Frozen sky".

Industrially Agar can be made in several ways. One method involves freezing agar solutions in ice tanks in a simply scaled up version of the traditional method. A newer method, which only works for agar types that have significant syneresis such as gracillaria, involves forming a blocks of gel wrapped in clothes and literally pressing the water out of the blocks. The pressing is usually done with large static concrete weights. The pressed agar is then usually pressed again in hydraulic presses to reduce the water content even further prior to drying. A variation of the gel pressing method involves pumping broken agar gel into large filter presses and using the pressure from the feed pumps to force water out of the matrix. This technology was pioneered by Hispanagar in the 1960's and is now the

dominant method of pressing agar. Another methodology involves roller drying the extracted agar. This method has the advantage in that it can utilise a variety of agar species including gelidium which cannot be pressed easily.

Agar gel strength can be improved by removing some of the ester sulphates from the agar chain by alkali treatment. Alkali treatment also increases syneresis and makes pressing the agar easier.

Traditional agar is sold in strip or block form. Commercial agar is normally milled into a coarse powder. The agar gel press method is the basis for gel repss methods used in the newer carrageenan processing techniques. As in carrageenan processing not all agar weed types can be pressed and some of the weeds favoured for their low syneresis such as gelidium types are very difficult to press. Very low syneresis agar is favoured in microbial plates.

Properties

Agar gels due to the presence of the agarose fraction in the crude agar at typical concentrations between 0.5% and 2.0%. Unlike carrageenan agar does not require the presence of any particular ions to gel. One of the classic uses of agar is for the preparation of microbial plates where the combined properties of low syneresis, ion independent and a low set temperature make agar ideal.

Agar has a uniquely large hysteresis between its melting and setting temperature. Typically agar need to be heated above 90^{o}C to form a good solution and depending on the seaweed source the setting temperate can be as low as 30^{o}C and is typically between 30-45^{o}C for a 1.5% solution. To overcome the very high dissolution temperature of agar several companies manufacture a form of agar that has been specially dried to allow the agar to dissolve at lower temperatures.

According to Rees agar forms antisymmetric double helices on cooling that hydrogen bond to form clumps of helices. These clumps can then form larger groupings that from a large porous gel structure. Agar is known to form a very porous gel and the pore size can be roughly measured by assessing the size of particulates that are excluded from the gel in a gel permeation experiment. It has been shown that agar gels can allow molecules up to 30M daltons in size to percolate through it structure. An agar gel as the unusual property of behaving like a sponge. An agar gel of a particular shape can be dried and upon rehydration it will swell to its original size and shape.

Agar synergy's are not as commercially important as they are for xanthan or carrageenan and tend to be rather small in magnitude. *Gelidium* agar is known to form a small synergistic interaction with locust bean gum that is not seen in products based on *gracilaria*.

Agar forms a synergistic interaction with sucrose and is used in some confectionery products. Tannic acid on the other hand may actually inhibit gelation. Agar is reasonably acid stable compared to other polysaccharides and does not show any protein reactivity. Agar can be used in acidic dairy products such as yoghurts where carrageenan would cause excessive flocculation due to the protein reactivity of the carrageenan. Recently a synergy has been reported between low gel strength agar and guar gum in patent by Rachid Lebbar of Setexam

Agars all have negative optical rotations whereas carrageenans are positive. This can be used to distinguish the two when identification is tricky. Sulphate level is often used and whereas a low sulphate level would indicate an agar you cannot definitively say that a high sulphate level is always a carrageenan.

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