Xanthan – A Versatile Gum

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Natural gums occur in all life forms. We use gum Arabic for sealing envelopes and for sticking postal stamps. The better consistency to ice-cream is often provided by gelatin or dextran. The delicious jellies and jams can be moulded into beautiful shapes using China grass (sea weed, agar). Gum tragacanth gives desirable flow property to the toothpaste. Many types of gums can be obtained from plant sources. Their collection is costly and requires skilled labourers. Moreover, seasonal variations affect the quality and quantity of plant gums. The polysaccharides for scientific and industrial applications are obtained more conveniently from microbial sources due to several factors. They can be produced under controlled conditions from selected species using renewable sources and are biocompatible and biodegradable. These factors have accelerated the use of microbial gums such as pullulan, curdlan, scleroglucan, dextran and xanthan. Chemically gums are carbohydrate polymers or polysaccharides. (However, gelatin is a protein). Polysaccharides are present in all life forms. They have a number of unique chemical and physical properties. They serve as structural material to the plant kingdom, as energy reserves, adhesives and also information-transfer agents. Microbial polysaccharides are composed of regular repeating units of simple sugars like glucose, mannose, fructose, etc. These polysaccharides are sometimes termed as slime or exopolysaccharides.

Why do Microorganisms Produce Gums?

Most phytopathogenic bacteria do not form spores. Many of them are resistant to desiccation and survive under dry conditions for more than 50 years at normal surrounding temperature. This is due to the protective layer of the 'ooze' or exudates produced by the bacteria. The layer is nothing but a coating of specific gum that is chemically a polysaccharide. This coating may act as a barrier against attack from bacteriophage, and also

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helps identification of appropriate sites on the host plant for colonization of the bacteria. *Xanthomonas campestris* synthesizes the xanthan gum. It is a gram negative, yellow-pigmented bacterium and several species of *Xanthomonas* pathogenize specific plant hosts. For example, cabbage is attacked by *X. campestris*, sugar cane by *X. vasculorum*, strawberry by *X. fragaria* and walnut by *X. juglandis*. Xanthan gum is a cream coloured powder that is soluble in hot or cold water with a high viscosity even at low concentrations. The molecular weight of xanthan is determined by light scattering, quasi-elastic light scattering and band sedimentation analysis. These methods however have revealed a wide variation between 2 million to 62 million in the molecular weight of xanthan. The explanations for these variations in the reported values were provided by the quasi-elastic light scattering techniques. Hydrogen bonding appears to be important in stabilizing the aggregates of xanthan in water. In 4 molar urea solution, a lower molecular weight of 2 million was obtained.

Backbone of Xanthan

The main chain of xanthan is built up of D-glucose units linked through the b-1 position of one unit with 4th position of the next unit, a linear backbone identical to the chemical structure of cellulose. The primary structure of xanthan consists of a pentasaccharide repeating units (*Figure* 1). The presently accepted structure of xanthan consists of $(1\rightarrow 4)$-β-D-glucopyranose units. Trisaccharide side-chains are attached to alternate sugar residues on the main chain at the C-3 position. The side-chain consists of two mannose residues and a glucuronic acid residue. The terminal β-D-mannopyranose residue is $(1\rightarrow 4)$ linked to the β-D-glucuronic acid residue, that in turn is $(1\rightarrow 2)$ linked to non-terminal α-D-mannopyranose residue. The 6-OH group of the non-terminal D-mannopyranose residue is present as acetic acid ester. Pyruvate acetal groups are located on the D-mannopyranosyl end groups of side-chains. The influence of different glycosidic (or other) linkages in the backbone of any polysaccharide is an important feature in modifying polysaccharide chain conformation and its characteristics. It is not surpris-

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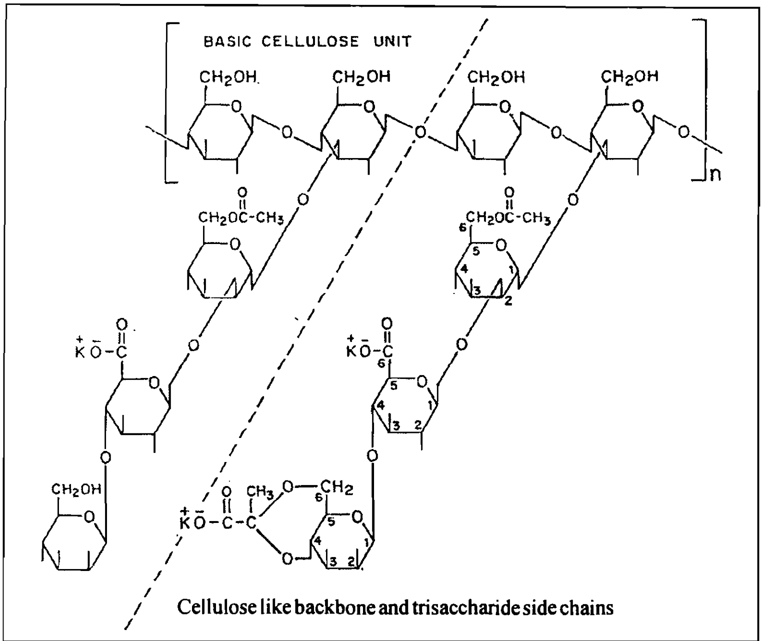

Figure 1. Structure of xanthan gum.

ing that xanthans of different pyruvate levels (that is 1 to 6 %) display different rheological (flow) properties. Pyruvic acid attached to the terminal carbohydrate of the side chains adds another carboxylate group. The percent composition of xanthan proposed for industrial use is as follows: Glucose 37, mannose 43.4, glucuronic acid 19.5, acetate 4.5 and pyruvate 4.4%.

Production of Xanthan

The biosynthesis of microbial heteropolysaccharides such as xanthan is a complicated process involving a multienzyme system. The initial step in the biosynthesis of xanthan is the uptake of carbohydrate, which may occur by active transport or facilitated diffusion. This is followed by phosphorylation of the substrate with a hexokinase enzyme that utilizes adenosine 5'-triphosphate. The biosynthesis involves conversion of the phosphorylated substrate to the various sugar nucleotides required for assembly of the polysaccharide-repeating unit via enzyme such as UDP-Glc pyrophosphorylase. UDP-glucose, GDP-mannose and UDP-glucuronic acid are necessary for the synthesis of xanthan with the appropriate repeating unit.

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In the biosynthesis of xanthan on the cabbage plant by *X. campestris*, the cabbage provides the carbohydrate substrates, proteins and minerals for cell growth. In the laboratory conditions or commercial fermentation, carbon sources, nitrogen sources, trace minerals and pH conditions are provided in a way that simulates natural conditions.

Industrial Production

The industrial scale production of xanthan is carried out using inexpensive substrates and nutrients. Carbohydrate sources such as sucrose; sugarcane molasses and whey have been successfully used in the production medium. Whey also provides adequate nitrogen and some growth factors. Efficient conversion of carbon source to the desired polysaccharide production requires a high carbon to nitrogen ratio. Inorganic nitrogen sources like ammonium or nitrate salts are suitable, and a wide variety of complex nitrogen sources like yeast extract, soy-meal peptone and soybean whey are also useful for xanthan production. The nutritional requirements of *X. campestris* necessitate the presence of phosphorus and this is usually added in the form of a phosphate buffer. Beneficial production is achieved using cereal grains. Generally batch cultivation with complex media is favoured. However, simple synthetic media can be used. The batch growth cultivation requires two days. Although, most often, a stirred-tank reactor is used with batch fermentation operation, there is no uniformity with regard to the operational conditions employed such as temperature, oxygen mass transfer, pH, and the composition of the culture medium. The production is generally carried out using a temperature range of 25 to 35°C. Oxygen mass transfer is influenced by both agitation speed and airflow rate.

Proper maintenance of *X. Campestris* stock culture is important for consistency in the production of xanthan, as variation is a recognized characteristic in *Xanthomonas* species. During the initial growth phase polysaccharide accumulation starts and continues after growth. The pH decreases during the fermentation due to the formation of organic acids. If pH falls below 5.0, the formation of xanthan drastically reduces. Thus, it is necessary to control the fermentation medium at the optimum pH of 7.0 using a buffer or addition of base during process. Adequately designed agitation is necessary to disperse the introduced air evenly throughout the medium. Agitation of the medium is useful for enhancing the rate of transport of nutrients across the cell membrane, which in turn supports the growth rate of the microorganism.

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Isolation of the Gum

The fermentation broth of the xanthan gum is apparently very viscous. The crude broth contains bacterial cells, and after solidifying the gum, their weight will be about 15 g per 100 g of xanthan gum. The removal of the cells is essential if the gum is to be used in optically clear food products and cosmetics. In the 'Enhanced Oil Recovery ' application, the presence of the cells in the polymer is undesirable because such polymer fluid causes the plugging of the pores in the oil-bearing rocks. The separation of cells from viscous broth by centrifugation, filtration or by flocculations is very expensive. In the laboratory method, the culture broth is diluted with 33% ethanol to 100 cP (Centipoise, a unit of viscosity). The cells are removed by centrifugation and 1% KCl is added to the broth. Precipitation of the gum is achieved by the addition of 3 volumes of chilled 95% ethanol. Solvent precipitation, precipitation using divalent metal ion salts of the polymer at alkaline pH, precipitation as a quarternary ammonium complex at acid pH, or precipitation as fatty amine complex at acid pH have been successfully attempted. Whole broth containing xanthan can be spray or drum dried. However, the final product is highly coloured because the bacteria possess a yellow pigment in the wall, which is extractable only with organic solvents. The gum itself is colourless

Unique Properties

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the xanthan gum can be explained on the basis of its helical structure. The viscosity of xanthan in solution instantaneously and reversibly decreases as the shear rate increases. Most aqueous solutions of other polysaccharides show a sharp decrease in viscosity as the temperature is increased. Xanthan exists in solution at moderate temperature in a native, ordered conformation. On increasing the temperature of an aqueous solution of xanthan, the viscosity increases suddenly, suggesting a conformational change. A xanthan solution in presence of salts like sodium or potassium chloride can maintain its ordered structure and viscosity up to 100°C. Generally, at a low ionic strength, polyelectrolytes adopt a highly expanded conformation. On the addition of salt, the conformation collapses to form a more compact coil due to charge screening. Xanthan solutions (0.2-0.5%) show an increase in viscosity with an addition of 0.1% sodium chloride solution due to stabilization of the xanthan structure in the ordered form, giving rise to intermolecular association.

The measurement of optical rotation of a salt free xanthan gum solution has shown that the viscosity increase is exactly parallel to a decrease in the optical rotation. This is consistent with the unwinding of the ordered conformation such as helix into a random coil with a consequent increase in resultant shape and size of the molecules. This alters the viscosity of the solution.

At low temperatures, xanthan has a compact conformation that undergoes a transition to an expanded form at a specific temperature, reported to be 55°C. By NMR spectroscopy it is demonstrated that there is an ordered conformation for xanthan below 55°C and a disordered random coil at higher temperatures. These changes have also been examined by circular dichroism spectroscopy. Fourier transform IR spectroscopic investigation of xanthan solution showed that an order-disorder transition occurs, as the temperature is increased. This is correlated with the sharp increase in viscosity in the same temperature range.

A Tight Relationship!

There is a special relationship between plant polysaccharides and xanthan gum. A synergistic viscosity rise is observed when the xanthan is added to the solutions of plant polysaccharides such as locust bean gum and guar gum. The galactomannans of these gums link with helices of xanthan to form a more rigid molecular structure of a gel. It is this particular property that facilitates use of xanthan gum in many daily applications such as ice cream, pasteurized process cheese dips and spreads as well as a variety of frozen desserts. Locust bean gum is preferred over guar gum as it has fewer galactose side chains. A greater proportion of guar gum (80:20) is required for optimal synergy compared to locust bean gum (50:50). On heating up to 55°C and cooling, such solutions form thermally reversible stable gels with a three dimensional network. These are true gels, which do not flow and do not recover from mechanical damage.

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Many Applications...!

The major applications of xanthan gum are in food industry as a suspending and thickening agent for fruit pulp and chocolates. United States Food and Drug Administration have approved xanthan on the basis of toxicology tests for use in human food. Many of today's foods require the unique texturization, viscosity, flavour release, appearance and water-control properties. Xanthan gum improves all these properties and additionally controls the rheology of the final food product. It exhibits pseudoplastic properties in solutions, and has less 'gummy' mouthfeel than gums with more Newtonian characteristics (see *Box* 1).

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Xanthan has wide applications in the chemical industry (*Table* 1). A mixture of xanthan and locust bean gum can be used in deodorant gels. A special gel of xanthan can form in presence of borate. This combination has been used for preparation of explosives. The ability of xanthan to impart the desired dispersion stability at rest, and low viscosity under application is used to obtain a right consistency to the toothpaste. Ceramic glazes

Application	Properties
Food Industry	
Juice, drinks, chocolates, pickles, fruit pulp,	Suspending and thickening agent particulate suspension (for chocolate)
Canned food, jams, jellies, milk products	Shear thinning properties ensures favourableviscosity under processing conditions. Good gelling agent, easy pouring due to high pseudoplasticity.
Frozen foods, sauces, gravies	Provides favourable emulsion, suspension,stability and viscosity, improves freeze-thaw stability of starch thickened products.
Bakery products	For better texture to bread, mouth feel and release. Xanthan can replace gluten.
Cheese, creams, meat products, margarine	Combination of xanthan with plant gums like locust bean gum, guar gum is suggested
Industrial Chemicals	
Agriculture	Longer contact with crops, clings during spraying and controls drift of fungicide, herbicide, pesticide and fertilizers.
Paints and inks	Stabilizer, emulsifier for thixotropic paints, compatible with other thickeners and water based emulsion inks, prevents sagging and allows easy and even application.
Ceramics	Suspending agent for heavy particles in ceramics glazes. Maintains proper viscosity and lubricating power of suspension.
Paper manufacturing	Clay coating for paper finish. As a rheology modifier for high size press, roll coating.
Textile	Suspending agent for dyes, pigments, controlling agent for printing.
Abrasives, adhesives, polish, toothpastes, cosmetics, gelled explosives	Viscosity control, flow modifier,
Enhanced oil recovery	Flocculent, stable to pH and temperature changes and to high salt concentrations, effective lubricant, high pseudoplasticity. allows easy injectability.

Table 1. Applications of xanthan.

Box 1. What it Means?

Rheology: This is the science that deals with the deformation of matter when subjected to an applied force. The magnitude of the applied force may range from the gravitational force on a single, small, suspended particle to the very high shear rates encountered in high-speed mixing or homogenization.

Newtonian system: The solution where the dissolved material is low in molecular weight, non-associating, and with limited solute-solvent interaction or solvation, the characterization of flow is simple. Flow is directly proportional to the force applied, and the system is said to be Newtonian. If the viscosity of a Newtonian solution is measured at varying shear rates and shear stresses, and a graph is plotted, then we will get a straight line that passes through the origin. The slope of the line is constant.

Non-Newtonian system: More complex solutions tend to respond in a non-linear manner to applied stress. Here, the dissolved or solvated molecules are large. The tendency to entangle and/or reassociate is high and the solvent must exert some solvating force to maintain the polymer in solution. Such solutions are classified as non-Newtonian. Here, the response to shear stresses is not linear. The viscosity for these systems is not a constant value.

contain suspension of heavy particles. Xanthan gum solution maintains proper viscosity and lubrication power of the suspension.

The special rheological properties of xanthan are technologically suitable for the 'Enhanced Oil Recovery' (EOR) application. At low concentration, the gum forms high viscosity solution that exhibits pseudoplasticity. The oil is held in the tiny pores of the small sand stone rocks. For the efficient displacement of oil, the pumping of xanthan gum solution in the rocks is necessary. As a result, oil held in the pores of the sand stone rocks is displaced.

The microbial polysaccharides have gained a significant commercial importance during the last 10 years. The applications of xanthan are based on its ability to alter the rheological properties of aqueous solutions. However, carboxymethyl cellulose and polyacrylamides are also competitive to xanthan because of their lower price. The commercial production of xanthan requires a very high level of engineering and technical expertise as well as marketing skill. Only those firms engaged in developing a whole range of microbial products, for example Tate and Lyle or Kelco Company, presently produce xanthan.

Suggested Reading

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