CHAPTER I
GENERAL INTRODUCTION
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CHAPTER-I
GENERAL INTRODUCTION

1.1 POLYSACCHARIDES

Carbohydrates - a major class of organic compounds figure prominently in the dynamics of man's day to day life. They are responsible for many important biological processes starting from cell metabolism to energy requirements of man. Polysaccharides, which are long chain carbohydrate polymers, are playing a key role in human growth as well as in the growth of many industries from which man derives his comfort.

In the renaissance period, plant gums were found to have excellent solution properties and hence man exploited them for various industrial applications such as textiles, food cosmetics, papers and explosives. Because of their large volume applications, there is a constant search for new sources of gums to meet the growing demands by various sectors of users. Often native gums are unable to meet the property requirements of a specific end use. In such cases, specialty needs are met by modifying the gums by physical or chemical methods.

Till now over 300 gums have been identified and many of them and their derivatives are of commercial importance. Presently, gums and their derivatives are used in huge quantities in various industries.
1.2 GUM

The term gum was originally applied to plant exudates which were slimy and had adhesive properties. Now the term gum embraces a group of naturally occurring substances which are water soluble or swellable and which give viscous solutions. Gums have high molecular weight. When dispersed in water they give colloidal sols and as such are termed "Hydrocolloids". Gums are natural products derived from a wide variety of plants such as seed-bearing plants and sea weeds. They may be obtained as exudates or isolated from seeds, modified stems and roots. The major constituent of these plant parts is polysaccharide which is accompanied by other components such as fats, nitrogenous compounds and salts.

1.3 SOLUTION PROPERTIES OF POLYSACCHARIDES

Solution property of a polysaccharide is the manifestation of its basic structure. There are about 300 gums which have varied structures consisting of different repeating units. The primary reason for their conspicuous solution properties is the high molecular weight or degree of polymerization. The building blocks of polysaccharide are monosaccharides which have an abundance of hydroxyl groups. The latter form the sites for strong hydrogen bonding. Polysaccharides have linear or branched chain structures having neutral, acidic or basic groups.
In the dry state, the polysaccharide chains of a gum are oriented randomly and hence it has large amorphous regions. Many hydrogen bonding sites, because of intermolecular and spatial arrangements, are not satisfied. Nevertheless, at normal temperature and humidity a section of bonding sites which are otherwise free, have strong affinity for water. Hence a gum, at normal temperature and humidity, is known to contain 10-12% moisture.

When a gum is placed in water it gets hydrated and swells to form viscous or gel structure. The extent to which a gum swells is dependent upon its macro structure and the nature of its building blocks.

When in water, the hydration of polysaccharides is conceived as penetration of water molecules to the amorphous region which has numerous hydrogen bonds. This results in the immobilization of cluster of water molecules around the chains, tearing apart intermolecular and spatial forces. When chains are pulled apart due to hydration, new hydration sites which were inaccessible before hydration are exposed and consequently will be hydrated. As the hydration of polysaccharide continues, the amount of free water molecules, which act as lubricant between gum particles, goes on decreasing while viscosity of the solution goes on increasing till all the chains are fully hydrated. This state of a gum represents the viscous or gel structure.
The ease with which free water molecules penetrate the gum structure is, as described earlier, the manifestation of the basic structure of the gum itself, which also governs other allied properties viz. viscosity and solubility.

A perfectly neutral and linear polysaccharide, obviously has a tendency of forming more compact and oriented molecular chains. Molecules of such nature generally are homopolymers (homopolysaccharides e.g. homoglucans), which have a single repeating unit all along their linear structure. The chains of such polymers tend to associate with each other through hydrogen bonds and consequently have regions of high order although there are some amorphous or low order regions. Such polysaccharides do not hydrate very easily in water because of the high energy required to solvate or disrupt the structural network. They are insoluble in water even at elevated temperatures. However, should these polysaccharides be dissolved by overcoming the hydrogen bonds, by high temperature or action of an alkali, it has been observed that lowering of temperature or neutralizing the alkali causes the dissolved linear molecules to precipitate. This happens because of the collision of molecular segments. Such collisions shear away the water molecules resulting in the chain segments to cling to each other. The best example of such a linear polysaccharide is cellulose which has linearly arranged β-D-glucopyranosyl units. In general linear and neutral polysaccharides are insoluble in water, they do not have
tackiness and give poor solution stability under normal conditions.

A branched polysaccharide, on the other hand, differs greatly in the ease of dissolution and in its viscosity property. In comparison to linear polysaccharides which dissolve slowly, if at all, branched molecules of the same average molecular weight, dissolve more readily but will form solutions that at equal concentrations have much lower viscosity though both may hydrate equally in the solution. As linear molecules gyrate, they sweep larger amounts of water than branched molecules, which is shown in Fig.1.1.

Branched polysaccharides have a high degree of disorder resulting in large amorphous regions. Hence, when a branched polysaccharide is dispersed in water it gets easily hydrated because the disordereded chains are more accessible for hydration. In solution, limbs of branched molecule collide with each other and may entangle, if the concentration is high, resulting in the formation of a gel. Extensive association between the chains is not possible because the chain segments come in the way. Hence, solutions of branched polysaccharides are stable and do not undergo precipitation or slow retrogradation as do solutions of linear polysaccharides. Branched polysaccharides because of entanglement with each other can produce tacky pastes if concentration is sufficiently high.
Fig. I.1 Artists Conception of the Space Occupied by the Gyration of Extended Linear and Branched Polymers of Equal Molecular Weight
When solutions of branched polysaccharides are dried, the molecules do not form strong intermolecular associations. Hence, if water is added to the dry material, the polysaccharide redissolves and reconstitutes, softening quickly to a tacky solution or paste. This property makes many of the branched polysaccharides useful as remoistening gums or adhesives. Highly branched polysaccharides form only brittle films and consequently have no applications as self-supporting sheets, although in low concentration with linear molecules they may have limited applications. Therefore, for good solution property, a polysaccharide should have a long linear chains with short branches.

Polysaccharides having ionic groups undergo hydration in three ways i.e. electrostatic hydration around the ionic group, the hydrophobic hydration around the non polar groups and hydrogen bonding around polar groups. Polysaccharides containing basic and acidic groups show good solution properties.

Solubility of polysaccharides is also affected by the nature of glycosidic linkages and the type of sugar unit they contain. The different linkages in polysaccharides and the solution properties are given in Tables-1.1 and 1.2.

However, the solubility of polysaccharide gums are different from that of crystalline substances like salts and organic substances of low molecular weight inasmuch as polysaccharides neither exhibit properties like melting, boiling, freezing nor have crystal properties.
TABLE 1.1
EXAMPLES OF POLYSACCHARIDES IN DIFFERENT SOLUBILITY GROUPS

<table>
<thead>
<tr>
<th>Solubility Group</th>
<th>Linkage</th>
<th>Polysaccharide</th>
<th>Sugars Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least</td>
<td>1→ 4</td>
<td>Cellulose</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chitin</td>
<td>2-acetamido-2-deoxy-β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Xylan</td>
<td>β-D-xylopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amylose</td>
<td>α-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mannan (ivory nut)</td>
<td>β-D-mannopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pectic acid</td>
<td>-D-galacturonopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alginic acid</td>
<td>-L-guluronopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1→ 3</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cellose (callan)</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Paramylan</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pachyman</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td>1→ 3 (mainly)</td>
<td>Laminaran</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td>1→ 6 (minor)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate</td>
<td>1→ 6</td>
<td>Pustulan</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td>1→ 3 1→ 4(1:1)</td>
<td>Nigeran</td>
<td>-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td>1→ 3 1→ 4(1:3)</td>
<td>Lichenan</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td>Easily Soluble</td>
<td>1→ 4, 1→ 6(2:1)</td>
<td>Pullulan</td>
<td>-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td>1→ 4 main chain</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1→ 6 branches</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1→ 4, 1→ 3(2:1)</td>
<td>Cereal glucan (branched?)</td>
<td>β-D-glucopyranosyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anionic Polysaccharides</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Source</td>
<td>Chemical Type</td>
<td>Characteristics</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------</td>
<td>------------------------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>Irish Moss</td>
<td>Complex Polysaccharide</td>
<td>Adds stability to emulsions, short inelastic gels</td>
</tr>
<tr>
<td>Sodium Alginate</td>
<td>Sea Weed</td>
<td>Long Chain Linear Polysaccharide</td>
<td>High viscosity gels at low pH (3-3.5)</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>Acacia Tree</td>
<td>Complex Polysaccharide</td>
<td>Ease of solution, excellent adhesive properties</td>
</tr>
<tr>
<td>Guar</td>
<td>Guar Plant</td>
<td>Nonionic, Neutral Polysaccharide Galactomannan</td>
<td>High viscosity, stable over wide pH range</td>
</tr>
<tr>
<td>Locust Bean Gum</td>
<td>Locust Bean Tree</td>
<td>Neutral, Water Soluble Polysaccharide Galactomannan</td>
<td>High viscosity, good stability, compatibility</td>
</tr>
<tr>
<td>Karaya</td>
<td>Sterculia Tree</td>
<td>Acetylated Polysaccharide</td>
<td>Relatively insoluble, marketed as textile gum, 15-18%</td>
</tr>
<tr>
<td>Tragacanth</td>
<td>Astragulus Plant</td>
<td>Complex Mixture Polysaccharides</td>
<td>High viscosity, stability</td>
</tr>
<tr>
<td>British Gum</td>
<td>Corn Starch Modification Polysaccharide</td>
<td>Highly dispersible, high viscosity, alkali stable</td>
<td></td>
</tr>
</tbody>
</table>
1.4 GALACTOMANNANS

Galactomannans are polysaccharides having a backbone of \( \beta-D-(1 \rightarrow 4) \) linked \( \beta-D \)-mannopyranosyl residues with side stubs of single \( \alpha--D \)-galactopyranosyl units. Galactomannans are the main constituent of many seeds belonging to Leguminosae family. Some galactomannans have also been reported from microbial sources. These contain furanoid sugars. Many of the plant derived galactomannans are edible and are used as additives in food. The chemistry of galactomannans has been reviewed by many authors.

In 70 species of the plant family Leguminosae, galactomannans have been found. The galactomannans differ from each other in the ratio of \( \text{D-galactose to D-mannose units} \), nature of distribution of galactose units along the mannan backbone and the degree of polymerization of the polymer.

The solution properties of galactomannan polysaccharides are influenced to great deal by the degree of branching. More the branching on the backbone, greater is the solubility in water. In solution, galactomannans are reported to be in a random coil conformation. Since galactomannans are nonionic their solution viscosity is stable, over a wide range of pH. However, the viscosity is affected when gum solutions are treated with a strong acid or alkali.

Among a large number of galactomannans that occur in nature
guar and locust bean gums are the most important and their chemistry has been studied in great detail.

1.5 GUAR GUM

India and Pakistan are the main producers of guar gum. The geographical areas growing guar and other particulars of agriculture have been documented. Of the many gums known today, guar gum is the most popular and is abundantly used in many industries.

Guar has been grown in India for centuries, both for animal and human consumption. But during the last 20-25 years, guar has assumed great importance as a cash crop owing to the development of guar gum industry in India. A major portion of the gum is exported to the United States of America.

Before World War II, locust bean gum was used in many industries like food, textiles, paper etc. During the second world war locust bean gum could not be imported into the U.S. from Europe and therefore a substitute for locust bean gum became an urgent necessity. Guar gum ultimately emerged as a suitable substitute and rival to locust bean gum. After the introduction of guar gum in different industries, the importance of guar gum progressively increased because of its ability to get hydrated rapidly in cold water to form very viscous colloidal dispersions and other useful properties. Presently, guar gum has taken a firm root in the international trade and it is unlikely that any synthetic
gum would be able to compete with this relatively inexpensive product. In India, guar gum is used in textiles, paper, adhesives, paints, cosmetics, oil well drilling, mining and pharmaceutical industries.

Guar gum is derived from the seeds of guar (Cyamopsis tetragonolobus) a hardy annual belonging to the family Leguminosae, sub-family Mimosoideae. Guar plant is draught-resistant and grows to a height of three-six feet with vertical stalks. The fruits of this plant (pods) grow in clusters along the vertical stem. The length of the pod is about 1-2 inches and contains 6-7 seeds which are considerably smaller than locust bean seeds. In India, guar gum is grown in Rajasthan, Haryana, Punjab, Gujarat and Uttar Pradesh. The annual production of guar gum in India constitutes about two thirds of world's production (60,000/1,10,000 tonnes). Through foreign exchange India earns about 30 crores of rupees annually.

The guar seed is composed of hull, which is the seed cover, endosperm and the germ. The actual gum is the endosperm which is between hull and the germ. The endosperm is separated by taking advantage of the differences in hardness of the seed components. By steaming and differential grinding, including that by hammer mill, the guar seed components are separated from each other. The properties of the gum are influenced by variations in the processing techniques. The proximate analysis of guar gum is given in Table-1.
**Table-1.3**

**Composition of the Components of Guar Seed**

<table>
<thead>
<tr>
<th>Seed Part</th>
<th>Protein (N x 6.25)</th>
<th>Ether Extract, %</th>
<th>Ash, %</th>
<th>Moisture, %</th>
<th>Crude Fiber, %</th>
<th>Type of Carbohydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hull (14-17%)</td>
<td>5</td>
<td>0.3</td>
<td>4</td>
<td>10</td>
<td>36.0</td>
<td>D-Glucose</td>
</tr>
<tr>
<td>Endosperm (35-42%)</td>
<td>5</td>
<td>0.6</td>
<td>0.6</td>
<td>10</td>
<td>1.5</td>
<td>Galactomannan</td>
</tr>
<tr>
<td>Germ (43-47%)</td>
<td>55.3</td>
<td>5.2</td>
<td>4.6</td>
<td>10</td>
<td>18.0</td>
<td>D-Glucose</td>
</tr>
</tbody>
</table>

Endosperm is ground to a fine particle size (mesh) and is marketed as guar gum in many grades. Food grade guar gum is comparatively pure endosperm which is edible. The industrial grade gum is sold after incorporating additives for modifying its properties and for preservation. The viscosity of industrial grade gum is generally less than that of food grade gum.

Many workers have reported the Purification preparation and properties of guar gum. In the laboratory, for chemical studies, guar gum is purified by dissolving it in water, precipitating it in alcohol and exchanging with solvents such as ether and petroleum ether. Freeze drying of an aqueous solution may also be used as a method of purification.

1.6 **Structure of Guar Gum**

Studies on the structure of guar gum received considerable attention in the nineteenfifties and several research papers appeared. Simultaneously, studies on the development of
useful products derived from guar gum and their applications in food and other industries were also initiated. Studies were also undertaken on the comparative properties of guar gum and locust bean gum. Some of the relevant information is given in Table-1.4

On the basis of above information, guar gum is considered to have a backbone of $\beta$-D mannose units linked with each other by $1\rightarrow4$ glycosidic bonds and on this mannan backbone single residues of D-galactose, linked by $1\rightarrow6$ bonds occur as branches. The ratio of galactose to mannose is 1:2. Recently, the structure of guar gum has been reviewed by Whistler and others. The structure of guar gum is given in Fig. 1.2 and an artist's conception of guar chain in Fig. 1.3

1.7 MOLECULAR WEIGHT OF GUAR GUM

Molecular weight of guar gum has been determined by various techniques such as, light scattering, friction reduction and gel permeation chromatography. The results have shown that the molecular weight of gum is in the range of 1,60,000 to 2,20,000.

1.8 PROPERTIES OF GUAR GUM

Guar gum exhibits excellent solution properties, particularly it is able to get hydrated quickly in cold water, and this property is responsible for its wide commercial exploitation in various industries.
Fig. I.2 Structure of Guar

Fig. I.3 Artist's Conception of Guar Molecule
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Experimental</th>
<th>Observation</th>
<th>Inference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(a) Selective fermentation organisms were cultured &amp; many reserve carbohydrates of leguminosae seeds were fermented to get the galactose units unaffected</td>
<td>Many reserve carbohydrates of Leguminosae (galactomannans) seeds contain galactose and mannose. The ratio of mannose to galactose differs from gum to gum (species). In case of locust bean and guar gum the ratio is 4:1 and 2:1 respectively</td>
<td>Guar gum and locust bean gums are heteropolysaccharides</td>
<td>23-25</td>
</tr>
<tr>
<td></td>
<td>(b) Acid hydrolysis and chromatography of the hydrolyzate were carried out</td>
<td>2.3.4.6-tetra-o-methyl galactose, 2.3.6-tri-o-methyl mannose and 2,3 di-methyl mannose were characterized from the hydrazate</td>
<td>1→4 linkages in these polysaccharides were indicated</td>
<td>26,27*</td>
</tr>
<tr>
<td>2.</td>
<td>Purified galactomannans from reserve carbohydrates of leguminosae seeds were oxidized with Malaprade reagent and the oxidatively cleaved products were hydrolysed</td>
<td>The galactomannans consumed one mole of oxidant per anhydro-pyranose unit and the cleaved product after hydrolysis yielded glyoxal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Acetylation followed by methylation of locust bean gum, methanalysis of the methylated product, hydrolysis and identification of hydrolyzate fractions were carried out</td>
<td>2,3,4,6 - tetra-o-methyl galactose, 2,3,6 - tri-o-methyl mannose and 2,3 di-methyl mannose were characterized from the hydrazate</td>
<td>1→5 or 1→4 linkages were proposed But, on the normal stability of polysaccharides, 1→4 linkages were suggested as favourable one</td>
<td>28</td>
</tr>
</tbody>
</table>

(contd.)
### TABLE-1.4 (contd.)

**STRUCTURAL STUDIES ON GUAR GUMS**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Experimental</th>
<th>Observation</th>
<th>Inference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.</td>
<td>Purified galactomannans were tosylated followed by thiocyanation and iodination</td>
<td>Two different tosyl esters of guar gum, when thiocyanated yielded derivatives with thiocyanate content varying from 0.44 to 0.52 equivalents per anhydro hexopyranose units</td>
<td>Depending upon the reactivity of primary -OH groups, the replacement of tosyl groups by thiocyanate and iodine indicated that at least half of the hydroxy groups (primary) are involved in (1→6) linkages</td>
<td>29</td>
</tr>
<tr>
<td>5.</td>
<td>Fractionation in water and alkali; hydrolysis by acid and enzyme; derivatization of hydrolyzed monomers to phenylhydrazones; optical rotation of monomer derivatives, acetylation and X-ray studies of guar gum were carried out</td>
<td>The derivatives (monomers) of galactose and mannose, obtained after hydrolysis, showed optical rotations corresponding to D-series. Film properties showed amorphous X-ray pattern</td>
<td>Both monomers, constituting the gum, are of D-series from X-ray pattern. It was suggested that guar molecule is highly linear but has either a random distribution of D-galactose chains and that the chains are very short.</td>
<td>30-32</td>
</tr>
<tr>
<td>6.</td>
<td>Methylation of guar gum, methanalysis of the methylated product, fractional distillation of the mixture and identification of the fractions were carried out</td>
<td>Identified three products viz. 2,3,4,6 tetra-O-methyl galactose and other two as trimethyl and dimethyl derivatives of mannose</td>
<td>A branched chain structure was proposed on the basis of results obtained from methylation products</td>
<td>33</td>
</tr>
</tbody>
</table>
### TABLE 1-4 (contd.)

**STRUCTURAL STUDIES ON GUAR GUMS**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Experimental</th>
<th>Observation</th>
<th>Inference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.</td>
<td>Guar gum was oxidized with periodate</td>
<td>1 mole of formic acid was produced per 2.7 anhydro units</td>
<td>Branched chain structure in guar gum was conceived</td>
<td>34</td>
</tr>
<tr>
<td>8.</td>
<td>Guar gum was fractionated, oxidized with sodium periodiate, methylated and methanolysis of the methylated product was carried out</td>
<td>Paper chromatography revealed about eleven derivatives (including tetra, tri, di and monomethyl derivatives), Three crystalline compounds were identified, similar to locust bean gum (27), viz., 2,3,4,6 tetra-O-methyl D-galactose, 2,3,6-tri-O-methyl D-mannose</td>
<td>Guar gum structure consisting of D-mannose and D-galactose (2:1) as a large molecule having repeating units of two (units) of D-mannose and a D-galactose unit was proposed</td>
<td>35</td>
</tr>
<tr>
<td>9.</td>
<td>Methylation of guar gum, methanolysis of methylated product, fractional distillation of mixture and identification of fractions were carried out</td>
<td></td>
<td>On the basis of these facts, structure of the gum was proposed as 1→4 linked anhydro D-mannopyranose units with a single unit of D-galactose unit linked 1→6 to half of mannose units. The structure is compared to locust bean gum</td>
<td>36,37</td>
</tr>
<tr>
<td>10.</td>
<td>Enzymatic hydrolysis of guar gum with diastase was carried out. The hydrolyzate was analysed by paper chromatography</td>
<td>After the enzymatic degradation, the viscosity of the paste reduced and reducing</td>
<td>Further support to the branched structure was given</td>
<td>38</td>
</tr>
</tbody>
</table>
With the accumulated facts, final structure of guar gum was suggested as D-Manno-pyranosyl units as backbone of the polysaccharide and a single D-galactopyranosyl units in branches linked to mannose chain at 6 position.

Another support for the branched structure of the gum was given.

Isolated two crystalline disaccharides viz. O-β-D-galactopyranosyl (1→6) β-D-mannopyranose & 6(α-D-galactopyranosyl) β-D-mannopyranose

Further support to the branched structure of the galactomannan was given.

The consumption of periodate decreased as the degree of substitution of cyanoethyl group increased.

Two crystalline tri saccharides were isolated. They were O-α-D-galactopyranosyl(1→6) β-D-mannopyranosyl (1→4) β-D mannopyranose and O-β-D-Mannopyranosyl (1→4) /β-D Mannopyranosyl (1→4) β-D Mannopyranosyl (1→4) β-D Mannopyranose (Mannitriose)

With the accumulated facts, final structure of guar gum was suggested as D-Mannopyranosyl units as backbone of the polysaccharide and a single D-galactopyranosyl units in branches linked to mannose chain at 6 position.
## TABLE-1.4 (contd.)

**STRUCTURAL STUDIES ON GUAR GUMS**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Experimental</th>
<th>Observation</th>
<th>Inference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.</td>
<td>Purified fractions prepared by hot water extractions &amp; centrifugation, were characterized by physical and chemical techniques</td>
<td>The galactose to mannose ratio was 1:2 in all fractions</td>
<td>- do -</td>
<td>44-45</td>
</tr>
<tr>
<td>15.</td>
<td>Guar was oxidized with periodate. Varying the time of oxidation, the distribution of galactose residues in guar was studied</td>
<td>The oxidation of guar gum containing 36% galactose residues, virtually stopped after 58% of D-mannose residues had been oxidized</td>
<td>This effect was traced to the formation of inter-residual, stable hemiacetal linkage between aldehyde group of the oxidized residue and the -OH-group at C6 of the unoxidized residue. The distribution of galactose on mannan is discussed</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>Guar gum and locust bean gums were purified, primary p-tosyl derivatives were prepared. Methylation hydrolysis, derivatization and characterization of derivatives were carried out by g.l.c</td>
<td>The gas chromatography results showed the expected ratio of galactose to mannose</td>
<td>The distribution of 50,51 galactose residue on the mannan chain is discussed. Structure of the gum is a regular repetition of the 4-D-(6-O-α-D-galacto pyranosyl/β-D- mannopyranosyl)/β-D-mannopyranose</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>Both ¹H and ¹³C NMR studies were carried out</td>
<td>The spectral assignments indicated the distribution of galactose residues on the mannan chain according to earlier report.</td>
<td>The distribution of 52,53 galactose units on the mannan chain is discussed</td>
<td></td>
</tr>
</tbody>
</table>
1.8.1 Viscosity and Solubility

Solubility of guar gum is a manifestation of its physico-chemical structure. When compared to other galactomannans of commercial importance, guar gum has more branches of D-galactose units on the mannan chain. The higher (twice) number of galactose branches in guar gum as compared to locust bean gum explains higher solubility of the former.60

When dispersed in water guar gum forms a very viscous sol due to the hydration of chains. Although the rate of hydration of guar gum is rapid in cold water, maximum viscosity is attained only when enough time is allowed for its complete hydration. It is customary to take the viscosity readings of gum solutions after 24 hrs of hydration. Viscosity development as a function of time is shown in Fig. 1.4

Viscosity of guar gum is dependent upon its molecular weight57,61-63 and on the history of processing. Hence, different guar products sold in the market have seldom the same viscosity. Aqueous solutions of guar gum are susceptible to biodegradation but can be preserved by addition of 0.1-1% of a preservative such as sodium pentachlorophenate, formaldehyde, citric acid, sodium benzoate and sorbic acid.

The viscosity of guar gum, as is true for other gums, is affected by temperature, concentration, pH, shear, ionic strength and presence of sugars. These aspects are discussed below.
Fig. 1.4 Viscosity Development as a Function of Time

Fig. 1.5 Effect of Shear on the Viscosity of Guar Gum Solution
1.3.2 Shear

Solutions of guar gum are non-Newtonian and pseudoplastic. They thin reversibly as their solutions are sheared. Viscosity decreases sharply as the shear rate is increased and then levels off as shown in Fig. 1.5 In other words, solutions of guar gum have zero yield value at the most commonly used concentrations and that they begin to flow as soon as the slightest shear force is applied. When the viscosity decreases to the minimum limiting value, it is independent of time but depends on the concentration. It makes no difference whether the final rate of shear is approached from low shear rate to high shear rate or vice versa, provided the shear rates are not high enough to degrade the molecular structure. The molecular structure can be irreversibly degraded by high shear rates, as for example, in pumping of solutions. At low concentrations/at low viscosity the effect of shear is not pronounced i.e. the behaviour of gum solutions at low concentration approximates to Newtonian fluids.

1.8.3 Temperature

Temperature influences the rate of hydration and in turn the viscosity. Solutions prepared at higher temperatures get faster hydration and attain maximum viscosity when compared to those solutions prepared at low temperatures. Because of the higher temperature, the chains are given energy for
greater degree of mobility in solution resulting in the lowering of viscosity when compared to the viscosity of the same concentrated solution at lower temperature. The viscosity changes as a function of temperature is shown in Fig. 1.6. These changes may be reversible. However, degradation of gum solution takes places with time when an elevated temperature is maintained.

1.8.4 Exponent of Hydrogen Ion Concentration (pH)

Since guar gum is a non-ionic polymer its aqueous solutions are stable over a wide range of pH. However, presence of basic or acidic substances will affect the hydration of polymer chains. The maximum viscosity is attained at pH 8-9. The effect of pH on the viscosity of guar gum is shown in Fig. 1.7.

1.8.5 Concentration

In dilute solutions the viscosity of gum increases linearly with concentration (upto 0.5% concentration). Thereafter, the gum solutions behave as non-Newtonian fluids. The effect of concentration on viscosity is shown in Fig. 1.8.

1.8.6 Ionic Strength

Guar gum is a non-ionic polymer compatible with a wide range of electrolyte concentrations. Viscosity of the solution increases with an increase in the concentration of mono-, di- and trivalent cations, and nitrate, chloride and
Fig. 1.6 Viscosity Changes as a Function of Temperature

Fig. 1.7 Effect of pH on the Viscosity of Guar Gum Solution
Fig. 1.8 Effect of Concentration on the Viscosity of Guar Gum Solution
FIG 1-9 Effect of Salts on Viscosity of Guargum

FIG 1-10 Effect of Sugar on Viscosity of Guargum Solution
Fig. I.11 Percent Friction Reduction as a Function of Concentration of Guar Gum
sulfate anions. The effect of these is shown in Fig. 1.9. With calcium and borate ions, which form complexes with cis-OH groups, the viscosity increases. However, with aluminium sulfate viscosity of guar solution decreases. With borate ions the gum forms gels, depending upon the temperature and pH. Optimum pH for gel formation is 7.5 to 10.5 and it collapses below 7 pH.

1.8.7 Effect of Sugar & Other Gums

In presence of sugar, viscosity of gum solution decreases which is shown in Fig. 1.10. With the addition of other gums like xanthan, the viscosity of guar gum increases synergistically i.e. the viscosity is higher than either of the individual gum solutions at the same concentration. Many papers and reviews on the factors affecting the viscosity of guar gum have been published.

1.9 FRICTION REDUCTION AND FILM FORMING PROPERTIES

Guar gum, with its long chain, reduces and minimises the frictional pressure losses of water when in turbulent flow, which is dependent upon the concentration of gum itself (Fig. 1.11). Because of such a property it is being used in oil-well drilling.

Guar forms tough, pliable films that are sensitive to water. The properties of films of guar and its acetates is reported elsewhere.
I. 10 MODIFICATION AND REACTIVITY OF GUAR GUM

Because of improved physicochemical properties, as required by end use, the modified gums find increasing applications as compared to native gum. Chemical modification of guar gum alters its properties such as solubility, viscosity, stability of solutions, biodegradability, and compatibility with salts. The reactions that guar gum undergoes are typical of a polysaccharide. It can undergo substitution, oxidation, hydrolysis and thermal degradation. Modification of guar gum is also done by crosslinking and by physical mixing with other gums and additives to get products suitable for specific applications.

Reactions like carboxymethylation, hydroxyalkylation, oxidation, crosslinking, quaternization are of importance for preparing products of industrial applications.

When reacted with 2-chloroethanol or ethylene oxide and propylene oxide, guar gum gives hydroxyethyl and hydroxypropyl derivatives, respectively. These derivatives exhibit better solution properties like miscibility with organic solvents, electrolyte compatibility, and lower COD and BOD.

When reacted with quaternary ammonium compounds and haloacetic acids, guar gum gives cationic and anionic derivatives respectively. Introduction of charged groups in the gum modifies many of its properties with respect to reaction on cellulose surface and with dyes and minerals.
Oxidized guar gum is used as thickener in textile and paper industries. Crosslinking with many organic and inorganic reagents improves the viscosity of guar gum paste. The use of mixed ethers i.e. carboxymethyl and hydroxyethyl groups possessed by a gum, is gaining attention.

Besides these important derivatives, numerous other miscellaneous guar derivatives have been reported. Surprisingly, little is known about the ester derivatives of guar gum.

I.11 INDUSTRIAL APPLICATIONS OF GUAR GUM AND ITS DERIVATIVES

Originally tried as a substitute for locust bean gum, guar gum has become the most important industrial gum due to its many desirable properties. In many applications such properties of guar gum as thickening, dispersing, film forming, stabilizing and binding are made use of. Moreover, its solution stability within a wide range of pH has favoured its use as dispersant, film former, flocculant, floatation reagent, stabilizer, suspending agent and water sealer. Of the total quantity of guar gum used in industrial applications, about 25% is used in food whereas 75% is used in other industries like paper, textile, oil-well drilling, tobacco processing, mining and explosives.

Versatility of guar and its derivatives has been reviewed by many authors.²⁸,⁷⁰
Although many publications and patents have appeared in the literature on applications of guar gum, only a few important ones are mentioned below:

I.11.1 Oil-Well Drilling

The main use of guar and its derivatives in the oil-well industry is in oil exploration as a drilling agent. Its functions are to control viscosity and water loss of the mud; to suspend the mud materials; to reduce friction and to lubricate and cool the drilling bit. Guar gum, which has high molecular weight, satisfies the requirements of an effective friction reducer. In fact, friction reductions of as much as 70% are readily attainable with guar gum itself. However, depolymerized guar gel contains about 10% residue which can cause formation damages. Hydroxyalkylated guar gums have low percentage of residue. When hydroxyalkylated guar gums are crosslinked with either organic or inorganic reagents, superior fracturing fluids compared to conventional guar gums are obtained. Gels from crosslinked gums are less sensitive to changes of either shear or temperature.

The patents covered in this area are:

- Additives for drilling fluids
- Hydroxypropyl guar gum in fracturing fluids of deep and hot formations
- Guar gum in treating a well using a volatile hydrocarbon
- Flocculation of clay in drilling fluids
- As thermal viscosity stabilizer for non-clay well bore fluids
Guar for plugging leaks from oils

Guar and other friction reducers as thickeners for drilling agents

Guar gum with fused potassium pyroantimonate in drilling oil-wells

Guar gum with boric acid and magnesium oxide, to provide stable viscosity in oil-well fracturing

Gelling of aqueous well drilling fluids

Sodium thiosulfate stabilized solutions of guar to control the viscosity of oil-well drilling fluids

Borate cross-linked guar in drilling operations

Guar gum with xanthan gums in oil drilling fluids

Guar in drilling fluids to reduce the tendency to filter through the pores of subsurface earth formation

As suspension agent in treatment fluids for drilling wells

Hydroxyalkyl guar gum to reduce friction and increase permeability

Guar as a thickening agent in drilling mud and in drilling fluids

Guar derivative for well stimulation

Guar gum in drilling fluid additives containing methylene blue, activity indicator

Carboxymethyl guar gum for oil-well fracturing fluids

Hydroxyalkyl and carboxymethyl guar gum in formation of bore hole plugs

Hydroxyalkyl guar gum to prepare ultra thick fracturing fluid

Hydroxypropyl guar with xanthan gum in oil-well drilling

Hydroxyalkyl guar gum in the preparation of clay free well bore fluids
Hydroxypropyl guar gum with glyoxal to control the blow out of an off-shore platform development cell.

### 1.11.2 Paper

Guar gum is used in paper making as a wet end additive. It is added to the pulp suspension before the sheet is formed and the addition of gum helps either in replacing or supplementing the hemicelluloses which are removed along with lignin during pulping. Advantages gained by addition of gums are:

- Increased fold strength
- Increased tensile strength
- Increased pick
- Increased Mullen bursting strength
- Increased machine speed with maintenance of test results
- Increased flat crush of corrugating medium
- Improved finish
- Decreased porosity.

Patents covering the applications of guar and its derivatives in paper industry are:

- Oxidized guar gum to improve strength properties of paper
- Guar to increase the strength of photographic paper
- Guar gum and paraformaldehyde for wet strength of paper
- Guar gum treated with peracetic acid to improve the binding properties in the formation of paper sheets
- Crosslinked guar gum in paper sizing
- Aminoethyl guar gum in increasing dry strength of paper
I.11.3 Explosives

Guar gum and its derivatives are used in this industry because of their ability to efficiently thicken ammonium nitrate solution, the basic component of explosive formulations, under a variety of conditions. These gums are readily crosslinkable to form stable water resistant gels. The patents covering this area of application of guar and its derivatives are:

- Hydroxyalkyl guar gum in non-aqueous slurry compositions
- Hydroxypropyl guar gum in nitroglycerin free semi-gelatinous explosives and to aerate NH₄NO₃ explosives
- In ammonium nitrate based gelled non-sticky blasting explosives
- Guar gum as thickening agent in blasting slurries
o Cyanoethyl guar gum as thickening agent for explosive mixtures

o Blasting agents containing guar gum

o Crosslinked guar gum in thickened water containing explosives

o Modified guar gum in stabilized air bubble containing explosive compositions

o Guar gum in safety explosives

o Guar derivatives in explosives

I.11.4 Textiles

Guar gum is a good and economic replacement for other gums used in sizing, printing and finishing of textiles. When used in sizing, it increases the warp strength by about 35-40% resulting in reduced breakages. Carboxymethyl and hydroxyalkyl derivatives are reported to give good results in printing. Patents covering this area of application are:

o Guar gum in textile printing colour paste extenders

o Guar gum with acrylamide for textile printing

o Guar gum with xanthomonas gum as a thickener

o Guar gum derivative for textile printing

o Dye thickened with borax crosslinked guar carboxyalkyl, hydroxyalkyl and carbanylalkyl ethers

o Guar gum thickeners for carpet colouration

o Guar gum derivatives in printing and dyeing

o Guar gum in printing composition for disperse dyes
I.11.5 Mining

Guar gum gets adsorbed on the hydrated mineral particles and this property is made use of in the mining industry where it is used as a flocellulant to produce liquid-solid separation by filtration, settling or clarification of mineral particles. It is used also as a floatation agent in mining. Patents covering this area of application are:

- Guar gum and its derivatives as filtration aids in the treatment of uranium ores
- With paraformaldehyde in the flocculation of slimes
- Aminoethyl guar gum in the settling of the fine particles
- In the separation of potassium chloride from salt mixtures
- As a flocculating agent for slimes in water
- As a settling agent for concentrating ores
- As a dewatering agent for foundry sand slimes
- A modified guar together with sodium sulfate as a sedimenting agent suitable for drinking water
- Flocculants based on guar gum
- Guar, dextrin and lignosol blend in recovery of gold from active carbonaceous ores
1.11.6 Tobacco

Guar is used as a binder for fragmented tobacco fines in the manufacture of reconstituted tobacco sheets. Tobacco fines, gum, water and humectant are blended together and converted into a sheet with same thickness as that of tobacco leaf. This sheet can be further blended with leaf tobacco. Patents covered in this area of applications are:

- Guar gum used to convert tobacco fines into usable and water resistant sheets\(^{157,158}\)
- Guar gum and humectant in production of tobacco sheets to reduce irritant properties\(^{159}\)
- Guar gum used as a strengthening agent in tobacco sheets\(^{160}\)
- Guar gum in foams and sponge sheets for cigarette manufacture\(^{161}\)

1.11.7 Building

Guar gum is used as a water-proofing agent in concrete\(^{162}\), thickening agent in plaster\(^{163}\), foam stabilizer for foamed cement materials\(^{164}\) and in water resistant texturized wall coverings\(^{165}\).

1.11.8 Pharmaceuticals and Cosmetics

In drug industry guar gum functions as binder and disintegrator for certain compressed tablets\(^{166a-d}\). Patents covering this area of application are:
o Guar gum prescribed and used in treatment of gastrointestinal disorders and gastric hyperacidity.

o Along with bismuth salts, guar gum is used in the treatment of gastrointestinal ulcers.

o Guar gum is reported to have an antidiabetic action and reduces cholesterol content in the blood.

o Guar gum is used in the microencapsulation of drugs and to stabilize water soluble preparations of vitamin B₁₂ and vincamine.

o Guar gum is used in lozenges for the treatment of oral infection.

o Guar gum is used for slow release of drugs making use of its hydration properties.

o Guar gum is used in cosmetics as a thickener. Hydroxypropyl guar gum is used in shampoo.

I.11.9 Food

Guar gum in combination with other gums is used as a binder and stabilizer in many frozen food preparations like ice cream, juices, and lollies because of its ability to inhibit ice crystal formation and water holding properties. It increases the shelf-life in industrial bread making. A guar solution added to the dough while kneading increases the yield considerably. The dough thus produced has greater resilience and a less flabby appearance. Guar improves the elasticity and spreadability of bread slices. Guar gum eliminates whipping and improves the texture in cold pack cheese products. Guar gum in combination with other gums
is an excellent stabilizer for dairy desserts and acidified dairy products. It is an acid-resistant free water binder in sauces and pickles and functions as an emulsion stabilizer by increasing the viscosity of aqueous phase and thus reducing the separation between oil and water phases. It is a fast, cold dispersible, thickening and texturising agent used in instant sauces and a good suspension agent in powdered chocolate mixes. It is used to stabilize carbonate and bicarbonate in the production of carbonated drinks to prevent premature decomposition. Out of many guar derivatives, carboxymethyl guar is used in food as thickener.

I.11.10 Miscellaneous

Other than the major areas, following are miscellaneous applications of guar gum:

- Guar as a binding agent in insecticide composition
- Guar as stabilizing agent in dithiocarbonate slurries used as agricultural fungicides
- Guar in fertilizers, as coating agent, to prevent aggregation
- Guar oxidized with periodic acid is used for hardening photographic gelatinous layers
- Guar as a lubricant for concrete surfaces
- Guar and its derivatives as emulsions and binders
- Guar gum containing isocyanates as emulsions in manufacture of sheets and molded boards
- Guar in dry enzyme composition having improved pH stability
- Guar in dentifrice composition
- Derivatized guar in glass fibre mat preparation
- Guar gum with decyl sulfate and ammonium phosphate as viscosity stabilizers in fire-fighting solutions
- Guar borax and boric acid used for shock impregnation pressure inside shock area
- Guar gum to improve the film forming properties of paints.
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