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Guargum: A Versatile Polymer for Application

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Abstract: Guargum is a natural polysaccharide composed of the sugars galactose and mannose. It is extracted from the refined endosperm of cluster bean seeds, chemically classified as galactomannan. It is basically composed of a straight chain of D mannose units, united by β(1-4) glycoside linkages and bearing a single D-galactose unit on approximately every alternate mannose, joined to it by an α(1-6) glycoside linkage. Due to its unique rheology modifying properties, it is being widely used across a broad spectrum of industries viz. oil well drilling, textile,paper, paint, cement, cosmetic, food, pharmaceutical etc. India is the major producer of guar in the world and its contribution to the world- production is around 80%.India is a major exporter of guar gum; the country's export of guar gum was 186,718.4 MT worth Rs. 10.50 Billion (US$ 235 Million.In this article, an attempt has been made to collect and compile the information on various aspects of guar- from its harvesting to industrial applications alongwith the chemical and functional properties.

Key words: Guargum · Galactose · Galactomanan · Mannose · D-mannopyranosyl · D-galactopyranosyl

INTRODUCTION

Guar also known as cluster bean (*Cyamopsis tetragonoloba* (L.) Taub) a drought hardy leguminous crop. Guar is being grown for seed, green fodder, vegetable and green manuring. It is an annual plant, about 4 feet high, vertically stalked, with large leaves and clusters of pods. Each pod is about 5-8 cm long and has on an average 6-9 small grayish-white pea shaped seeds. The pods are used as a green vegetable or as a cattle feed besides the industrial extraction of guar gum. Guar grows best in sandy soils. It needs moderate, intermittent rainfall with lots of sunshine. The crop is sown after the firstrains in July and harvested in October-November. It is a short duration crop and is harvested within 3-4 months of its plantation. Guar is a rain dependent crop; rainfall influences the yield of the crop. Its seed consists of seed coat (14-17%), endosperm (35-42%) and germ (43-47%). It has attained an important place in industry because of its galactomannan rich endosperm. Even if guar gum and its derivatives are well-known for a wide range of applications, like other polysaccharides, they evidence some drawbacks, such as uncontrolled rates of hydration, pH-dependent solubility and high susceptibility to microbial attack. Chemical modification provides an efficient route not only for removing such drawbacks but also for improving swelling and solubilization. Possible processing methods for guar gum depend on the chemical modifications aimed at developing functional characteristics that make this material versatile and useful in a variety of applications. Native guar gum can be modified into various water-soluble derivates by using reactive groups, to substitute the free hydroxyl groups along the macromolecule backbone. Upon dissolution in water, guar gum may give rise to as much as 10-14% insoluble residue, as depending on gum purity. The formation of such residues, mainly composed of heavily intertwined polysaccharide chains, proteins and ashes, together with the tendency of guar gum to form aggregates in solution, are indesirable characteristics in some applications. Natural gums are biodegradable and nontoxic, which hydrate and swell on contact with aqueous media and these have been used for the preparation of dosage form. Cyamopsis tetragonolobus. It has been investigated as controlled release carrier and regarded as nontoxic and nonirritant material [1].

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Fig. 1: Guar-gum plant

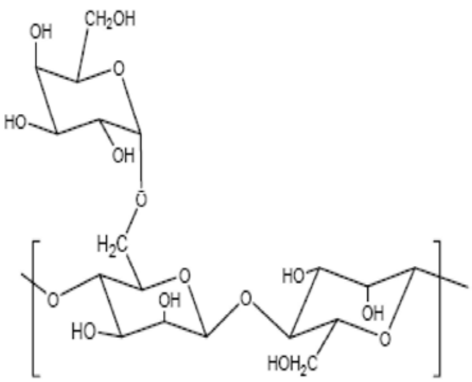

Fig. 2: Structure of sodium alginate

Properties of Guargum: The most important property of guar gum is its ability to hydrate rapidly in cold water to attain uniform and very high viscosity at relatively low concentrations. Apart from being the most cost-effective stabilizer and emulsifier it provides texture improvement and water binding, enhances mouth feel and controls crystal formation.

The main properties of guar gum are:

- It is soluble in hot and cold water but insoluble in most organic solvents.
- It has strong hydrogen bonding properties.
- It has excellent thickening, emulsion, stabilizing and film forming properties.
- It has excellent ability to control rheology by water phase management.
- The viscosity of guar gum is influenced by temperature, pH, presence of salts and other solids.

Chemically, guar gum is a straight chain galactomannan, which is 75-85% of the endosperm, has a chain of (1?4)-linked-β-D-mannopyranosyl units with single α-Dgalactopyranosyl units connected by (1?6) linkages to, on the average, every second main chain unit. The ratio of D-mannopyranosyl to D-galactopyranosyl units is about 1.8:1. The average molecular weight of guaran is in the range of 1-2 ×106 dalton. The *cis*-position is important since adjacent hydroxyl groups reinforce each other in hydrogen bonding reactions[2].

Guar gum is analyzed for

Test	Testmethod	Test	Testmethod
Colour	TP/09	acid-insoluble residue	TP/113
Viscosity	TP/04/110	fat content	TP/18
Granulation	TP/21	ash content	TP/12
Moisture	TP/01/09	gum content	TP/23
Protein	TP/ 05	heavymetals	TP/03
Insoluble ash	TP/ 11	filterability	TP/20A

Guar Gum Powder Standards:
HS-Code- 130 232 30
CAS No.- 9000-30-0
EEC No. - E 412
BT No.- 1302 3290
EINECS No. - 232-536-8
IMCO CODE- harmless

Major Growing Area of Guargum: It is mainly grown in areas of India (Rajasthan, Haryana, Gujarat and Punjab), Pakistan, Sudan and USA. India produces 6.0-7.5 lakh tons of guar annually. It contributes to around 80% share in the world's total production. In India, Rajasthan and Haryana states contribute 85% of the total production. In Rajasthan, the districts where guar production is done are Churu, Bikaner, Jaisalmer, Barmer, Nagaur, Hanumangarh, Jodhpur, Ganganagar, Jaipur, Sirohi, Dausa, Jhunjhunu and Sikar. The districts in Haryana indulged in the production of guar are Bhiwani, Sirsa, Mahendragarh and Rewari and the districts in Gujarat are Kutch, Banaskantha, Mehsana, Sabarkantha and Ahmedabad. Jodhpur city in Rajasthan is one of the major processing centers of guar gum in India[3].

Manufacturing and Processing of Guargum Seed: Various exporters and manufacturers export guar splits, guar gum powder and itsderivatives all over the world. India's export of guar gum has witnessed a 45 per centincrease between the years 2000-01 and 2005-06. The country's export of guar gumwas 186,718.4 MT during the year 2005-06. The net worth of the Indian exports is estimated around INR 10.5 Billion. The consumption of guar seeds is largely influenced by the demands from the petroleum industry of United States of America and China. Guar and Guar derivatives are quite useful in the petroleum drilling and fracturing industries. The major importing countries of guar gum and its derivatives are USA, Germany, Italy, China, Denmark, France, UK, Netherlands, Japan and South Africa [4].

Processing of Guar Seeds: The gum is commercially extracted from the seeds essentially by a mechanical process of roasting, differential attrition, sieving and polishing. The seeds are broken and the germ is separated from the endosperm. Two halves of the endosperm are obtained from each seed and are known as undehusked guar split (Fig. 3). When the fine layer of fibrous material, which forms the husk, is removed and separated from the endosperm halves by polishing, refined guar splits are obtained. The hull (husk) and germ portion of guar seed are termed as guar meal. The refined guar splits are then treated and finished into powders (known as guar gum) by a variety of routes and processing techniques depending upon the end product desired [5].

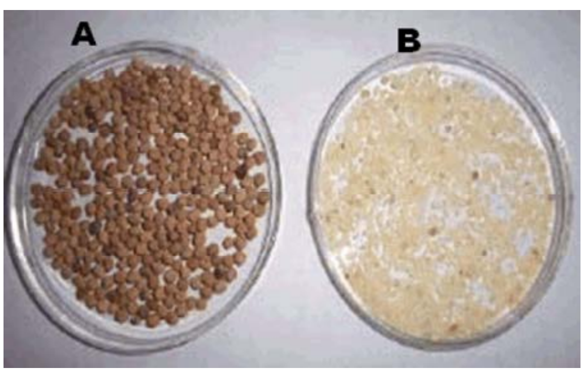

Fig. 3: (A) Guar seeds (B) Guar

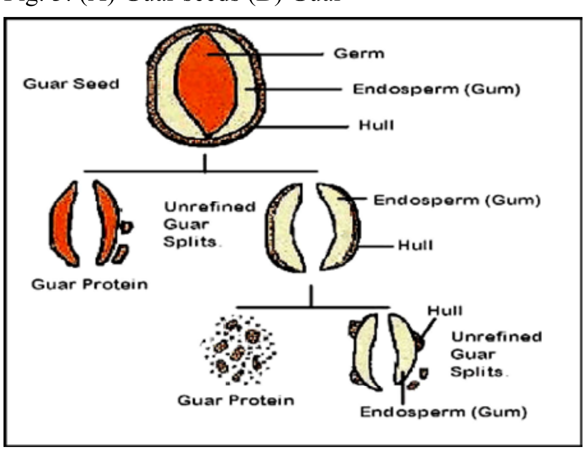

Fig. 4: Processing of Guar Seed

Fig. 5: Structure of Guar Seed

Research Work Conducted on Guar Gum: Guar gum is always a favorite agro-based commodity, attracting wide interest of researchers all over the world. Following is the research work conducted during the last 10 years on guar gum in many national and international laboratories to repare value added products from this renewable source of hydrocolloid. Grafting of poly (*N*-isopropylacrylamide) (PNIPAAm) was carried out onto *O*carboxymethyl- *O*-hydroxypropyl guar gum (CMHPG) in aqueous solutions by using potassium persulfate (KPS) and *N*,*N*,*N*,*N*'-tetramethylethylene diamine (TMEDA) as the initiation system, resulting in new stimuli-responsive grafted polysaccharides. The resulting grafted polysaccharides showed lower critical solution temperatures in aqueous media.The rheology of binary mixtures of two alginates and one carboxymethyl guar (CMG) was determined. Two reactive dyes were printed from pastes based on thesemixtures. The printing and the final print (color yield, levelness and fabric stiffness) were assessed. From the results, it can be concluded that mixture of CMG with alginates can be used in reactive printing.With a view that hydroxypropyl guar (HPG) may replace hydroxyethyl cellulose (HEC) from water based paints, chemical modification of guar gum via hydroxypropylation was carried out at lab/commercial level. The comparative study reveals that HPG is a perfect choice of rheological agent, which governs excellent properties for aqueous paints. This product has similar/ better properties of HEC. Graft copolymerization of methacrylic acid (MAA) onto guar gum was carried using potassium persulfate (PPS) as free radical initiator. Using PPS, the maximum percent grafting was ascertained to be 241 at the optimum conditions of 60°C reaction temperature, 3 h of reaction time, 1.1 mmol of PPS and 0.058 mol of MAA. The prepared graft copolymer could find applications in drug delivery systems. Chemical modification of guar gum was carried out through substitution and grafting reactions and products so obtained were tested against kaolin suspension to check their efficacy as flocculants. It was found that flocculation efficiency of the chemically modified products is better than Deftech and has potential to replace synthetic flocculants. Flocculants were also synthesized by grafting of polyacrylamide (PAM) onto hydroxypropyl guar gum (HPG) using a ceric ion-induced solution polymerization technique. Flocculation efficiency of grafted products was determined against kaolin, iron ore and silica suspensions. Among the series of graft copolymers, the one with fewest but longest PAM chains shows the better performance. Graft copolymerization of various monomers like *N*-vinyl-2-pyrrolidone, 4-vinylpyridine, acrylamide and acrylic acid onto guar gum was carried out by using initiator systems viz. potassium peroxymonosulfate / glycolic acid, potassium monopersulfate / thioacetamide, Cu+2-mandelic acid redox couple and peroxydiphosphate-silver (I) respectively. The effect of different reactants along with reaction time and temperature were studied by determining the grafting parameters:grafting ratio, efficiency, conversion, add-on, homopolymer and rate of grafting. It was observed that the graft copolymers were thermally more stable than the pure gum. Guar gum / poly (acrylic acid) semi-interpenetrating polymer network (IPN) hydrogels have been prepared via free radical polymerization in the presence of a crosslinker of *N*,*N*'-methylene bisacrylamide (MBA). Hydrogels showed enormous swelling in aqueous medium and displayed swelling characteristics, which were highly dependent on the chemical composition of the hydrogels and pH of the medium (ionic strength I = 0.15 mol/L) in which hydrogels were immersed. *Pandey et al,* 2006 modified guar gum by graft copolymerization with acrylic acid in aqueous medium using vanadium (V)–mercaptosuccinic acid redox system. The optimum reaction conditions affording maximum grafting ratio, efficiency, add on and conversion were vanadium(V) concentration 1.0 × 10-2 mol dm-3, mercaptosuccinic acid concentration 2.0 × 10-2 mol dm-3, acrylic acid concentration 20.0 × 10-2 mol dm-3. The grafting ratio, add on and conversion increase, on increasing the H+ ion concentration from 1.5 × 10-1 to 6.0 × 10-1 mol dm-3. On increasing the guar gum concentration the grafting parameters increase. The optimum time and temperature for the grafting reaction was 120 minutes and 35 °C respectively. The water uptake behavior of barium ions crosslinked sodium alginate/carboxymethyl guar gum bipolymeric beads in the media of varying pH was also studied. The beads swelled to nearly 15±4% in simulating gastric fluid (SGF) of pH 1.2 in 3 h. On transferring the hydrogel into simulated intestinal fluid (SIF) of pH 7.4, the swelling was enhanced to nearly 310±12%. When loaded with the model drug vitamin B12, the 8 total release in SGF in 3 h was nearly 20%, while nearly 70% was released in SIF in the next 7 h. The percent entrapment was nearly 50% when the beads were crosslinked with a 5-6% (w/v) BaCl2 solution. Guar gum was chemically modified by sulphonation using chlorosulphonic acid (ClSO3H) as a reagent. Activated partial thromboplastin time (APTT) assay showed that the guar gum sulphate could inhibit the intrinsic coagulant pathway. The anticoagulant activity strongly depended on the degree of substitution (DS) and molecular weight (Mw) of polysaccharides. DS>0.56 was essential for anticoagulant activity. The guar gum sulphate with the DS of 0.85 and the Mw of 3.40×104 had the best blood anticoagulant activity. *T*he optimum reaction conditions for affording maximum percentage of grafting for grafting of acrylonitrile (AN) onto sodium salt of partially carboxymethylated guar gum (DS 0.497) using ceric ammonium nitrate (CAN) as a redox initiator, in an aqueous medium, by successively varying reaction conditions such as concentrations of nitric acid, ceric ammonium nitrate, monomer (AN) as well as reaction time, temperature and amount of substrate was also established by an expert. The IR-spectroscopic, thermal (TGA/DSC) and scanning electron microscopic (SEM) techniques were used for the characterization of the graft copolymer. Using microwave (MW) irradiation grafting of polyacrylonitrile (PAN) onto guar gum in water was done without using any radical initiator or catalyst within a very short reaction time. The extent of grafting could be adjusted by controlling the reaction conditions and maximum percentage grafting (%G) of about 188% was obtained under optimum conditions in 1.66 minutes.Grafting of acrylamide onto guar gum is achieved by Ce(IV) induced free-radicalpolymerization to prepare interpenetrating polymer network (IPN) beads of polyacrylamide-*g*-guar gum with sodium alginate by crosslinking with glutaraldehyde. Two widely used pesticides, solid chlorpyrifos and liquid fenvelarate, were loaded up to 60-70% efficiency in the IPN beads. Equilibrium swelling experiments indicate that the swelling of the beads decreases with an increase in crosslinking, as well as an increase in pesticide loading. The action of a cationic polyelectrolyte (ammonium hydroxy-propyl-trimethyl chloride of the polysaccharide guar gum, commercially know as cosmedia guar, CG) in aqueous alumina suspension was investigated. This polymer was used aiming to find alternatives for synthetic polymers, as for instance, sodium polyacrylate- PANa, normally used as a deflocculating agent of alumina suspension. The measurements of particle size, as a function of time, showed that the addition of this polyelectrolytic macromolecule (CG) keeps the particles dispersed for a longer time, in comparison with the suspension containing only alumina. *T*he ceric-ammonium-nitrate-initiated graft copolymerization of polyacrylamide onto hydroxypropyl guar gum by solution polymerization technique was studied. The synthesized products were then characterized by various instrumental techniques like viscometry, elemental analysis, IR, thermal, XRD and SEM studies. The percentage of grafting increases with increasing catalyst concentration and decreases with monomer concentration taking other parameters constant. A mild method for microencapsulation of sensitive drugs, such as proteins, employing a suitably derivatized carboxymethyl guar gum (CMGG) and multivalent metal ions like Ca2+ and Ba2+ was reported. The swelling data of Ca2+ and Ba2+ crosslinked beads suggest that Ba2+ crosslinks CMGG much more efficiently than Ca2+. The drug loading efficiency of these Ba2+/CMGG beads, as a function of concentration of both metal ion as well as drug, was then determined using Bovine Serum Albumin as a model drug. Results indicated that Ba2+ crosslinked carboxymethyl guar gum beadscould be used for gastrointestinal drug delivery [6].

Use of Guargum in Pharmacology: Guar gum is a food additive shown to reduce serum cholesterol. It appears to have positive effects on blood glucose. Do not use guar gum to promote weight loss.

Animaldata: Research reveals no animal data regarding the use of guar gum for hyperlipidemia.

Clinicaldata: Guar gum has been shown to have positive effects on cholesterol at doses ranging from 12 to 15 g/day. Most short-term studies (< 1 year) in patients with mild to moderate hypercholesterolemia have demonstrated a decrease in serum total cholesterol levels ˜?6.5% to 15% and in low density lipoprotein-cholesterol (LDL cholesterol) by between 10.5% and 25%, without any effect on triglycerides or high density lipoprotein-cholesterol (HDL cholesterol) levels. A long-term study in 40 patients illustrated that the effects of guar gum on total cholesterol and LDL cholesterol are sustained with continued use over a period of 24 months. A comprehensive review of the lipid-lowering effects of guar gum described a general hypothesis for the mechanism of this action: Guar reduces cholesterol absorption and increases bile excretion leading to increased hepatic turnover of cholesterol. It has been suggested that the effects of guar on LDL cholesterol metabolism are similar to those of the bile-sequestering agents.

Guar gum also has been used as an adjunct to more conventional lipid-lowering therapy. Coadministration with lovastatin resulted in a larger decrease in total cholesterol levels (44%) compared with lovastatin alone (34%) after 18 weeks of treatment. Guar gum has an unpleasant flavor. Placebo-controlled trials have used a number of methods in an attempt to mask this; using uncoated granules, powders, crispbreads and other flavored formulas.

Diabetesmellitus: The ability of guar to alter viscosity and thus affect GI transit results in delayed absorption of glucose and may contribute to its hypoglycemic activity.

Guargum in Pharmaceutical Inndustry: Guar gum or its derivatives are used in pharmaceutical industries as gelling viscosifying thickening, suspension, stabilization, emulsification, preservation, water retention water phase control, binding, clouding/bodying, process aid, pour control for suspensions, anti-acid formulations, tablet binding and disintegration agent, controlled drug delivery systems, slimming aids, nutritional foods etc.Guar gum is an important non-caloric source of soluble dietary fiber. Guargum powder is widely used in capsules as dietary fiber. Fiber is a very important element of any healthy diet. It is useful in clear the intestinal system since fiber cannot be digested. This keeps the intestines functioning properly and also improves certain disorders and ailments. All natural fiber diet works with body to achieve a feeling of fullness and to reduce hunger. Its synergistic mix of guar gum and fiber mixture when taken with water expands in stomach to produce a feeling of fullness [7].

Industrial Applications of Guar Gum: Guar gum and its derivatives are widely used in various industries as per its needs. It is used in industries such as food, textile, pharmaceuticals, personal care, health care, nutrition, cosmetics, paper, explosives, mining and oil well drilling. Guar gum mainly functions as a thickener, emulsifier, stabilizer, binding agent, gelling agent,natural fiber, flocculant, fracturing agent etc. in the above-mentioned industries [8].

Applications of Food Grade Guar Gum Powder/ Derivatives

Food Industry: In food Industry guar gum / derivatives is used as gelling, viscosifying, thickening, clouding and binding agent as well as used for stabilization, emulsification, preservation, water retention, enhancement of water soluble fiber content etc. Some food products in which guar gum powder is used are:

- Ice cream, soft drinks and concentrates, puddings
- Chocolate milk, flavored milk
- Pet Foods
- Bread, biscuit and other baked foods
- Ham and sausages
- Soft cheese and cheese spreads
- Canned or retorted food of fish and meat
- Myonnaise, ketchup, sauce and dressings
- Noodles and pasta

In frozen food products-guar gum reduces crystal formation; act as a binder and stabilizer to extend shelf life of ice cream. In baked food products- guar gum provides unparallel moisture preservation to the dough and retards fat penetration in baked foods. In dairy products- guar gum improves texture, maintains uniform viscosity and color. In sauces and salad preparations- guar gum acts as a water binder in sauces and salad dressings and reduces water and oil separation [8].

In confectionary-guar gum controls viscosity, bloom, gel creation, glazing and moisture retention to produce the highest-grade confectionary. In beverages- guar gum provides outstanding viscosity control and reduces calories value in low calories beverages.

In pet food-guar gum forms gels and retains moisture, acts as a thickening, stabilizer and suspending agent for veterinary preparations [9].

Cosmetic Industry: Guar gum or its derivatives being used as a thickener, protective colloid and conditioner in hair/skin care products, creams, shampoos and lotions. Beside this, these are also used in toothpaste and shaving cream for easy extruding from the container tube [10].

Applications of Industrial Grade Guar Gum Powder/ Derivatives: In industrial applications, guar gum powder/derivatives utilized as thickening agent, sizing agent, wet-end strength additive, gelling agent and water barrier, flocculation aid for waste water treatment, as emulsifier, binder. Also used for mud formulations, enhanced oil recovery, polymer flooding, well treatment, lost circulation plugging etc. Guar gum industrial grade powder is used in industries such as textile printing and sizing, fire fighting, ceramics, pharmaceuticals, printing inks, mosquito mats, synthetic resins, paper industry, battery electrolytes, water treatment, floatation agent, water paint, carpet printing, oil well drilling, explosives, mining etc [11].

Paper Industry:

- Guar gum provides better properties compared to substitutes.
- It gives denser surface to the paper used for printing.
- Guar gum imparts improved erasive and writing properties, better bonding strength and increased hardness.
- Due to improved adhesion, it gives better breaking, mullen and folding strengths[12].

Textile Industry:

- Guar gum gives excellent film forming and thickening properties when used for textile sizing, finishing and printing.
- It reduces warp breakage, reduces dusting while sizing and gives better efficiency in production[13].

Oil Field Industry:

- Industrial grade guar gum powder/derivatives are use in oil well fracturing, oil well stimulation, mud drilling and industrial applications and preparations as a stabilizer, thickener and suspending agent.
- It is a natural, fast hydrating dispersible guar gum and is diesel slurriable.
- In the oil field industry, guar gum is used as a surfactant, synthetic polymer and deformer ideally suited for all rheological requirements of water-based and brinebased drilling fluids [14].

- High viscosity guar gum products are used as drilling aids in oil well drilling, geological drilling and water drilling.
- These products are used as viscosifiers to maintain drilling mud viscosities that enable drilling fluids to remove drill waste from deep holes.
- Guar gum products also reduce friction in the holes and so minimizing power requirements. Some guar gum derivatives act to minimize water loss should occur in broken geological formations [15].

Metallurgical and Mining Industry:

- Guar gum is widely used as a flocculants to produce liquid solid separation.
- Guar gum is also used in flotation. It acts as a depressant for talc or insoluble gangue mined along with the valuable minerals.

Explosive Industry:

- Gelling agent for gel sausage type explosives and pump able slurry explosives.
- Water blocking agent in nitro-glycerine, slurry explosives, ammonium nitrate and dynamite explosives- by mixing guar gum in ammonium nitrate, nitro-glycerine and oil explosives, even in wet conditions, explosive property is maintained. This is due to the better swelling, water blocking and gelling properties of guar gum [16].

CONCLUSION

As a natural product, it is a good polymer and pharmaceutical product as it is use in reducing serum controlled and positive effects on blood pressure. The ability of guar to alter viscosity and thus affect GI transit results in delayed absorption of glucose and may contribute to its hypoglycemic activity.It is a versitle polymer as it is used in different industries like pharmaceutical, paper,textile,oil, Metallurgical and Mining Industry, Explosive Industry.

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