Asian Journal of Chemistry; Vol. 24, No. 10 (2012), 4823-4824

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

NOTE

Preparation and Characterization of Novel Schiff Base Obtained from Dialdehyde Galactomannan and Aniline

G. UMAMAHESWARI[1,*], SWARNA V. KANTH[2] and M.J. UMAPATHY[1,*]

[1]Department of Chemistry, College of Engineering, Anna University, Chennai-600 025, India
[2]Central Leather Research Institute, Adyar, Chennai-600 020, India

*Corresponding authors: Tel.: +91 44 22203140; E-mail: mj_umapathy@yahoo.com; uma.gunasekar@gmail.com

(*Received*: 11 November 2011; *Accepted*: 15 May 2012) AJC-11504

Guar gum is a straight chain galactomannan, obtained from the endosperm of leguminaceae plant, *Cyamposis tetragonalobus*. The modification of guar gum is carried out by periodate oxidation, it specifically cleaves the vicinal glycols in galactomannan to form dialdehyde galactomannan. The product was then reacted with aniline to form yellow coloured Schiff base characterized by the shift in UV-Visible spectroscopy and the formation of aldehydic and imine functional group was endorsed by FTIR. Thermal studies of guar gum, dialdehyde galactomannan and imine show decrease in decomposition temperature from the guar gum to imine. This could be explained due to the cleavage of glycosidic linkage.

Key Words: Guar gum, Dialdehyde galactomannan, Periodate oxidation, Schiff base.

Guar gum is a non-starch polysaccharides (NSPs), obtained from the endosperm of leguminaceae plant, *Cyamposis tetragonalobus*. It is a heteropolysaccharide consisting of a linear chain of (1→4)-linked β-D-mannopyranosyl residues to which are attached varying proportions of (1→6)-linked α-D-galactopyranosyl groups as single unit side chains[1,2] (Fig. 1).

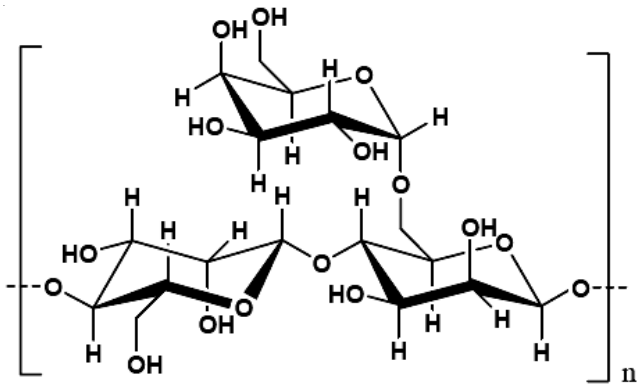

Fig. 1

It shows better solubility in water, low cost, easy processing and film forming property makes it viable in various industrial and medical applications. Some of the applications are mining, paper, textile, ceramic, paint, cosmetic, pharmaceutical and explosive. This polymer has proven particularly useful for colon delivery as it can be degraded by the specific enzymes present in this tract of the intestine[3,4]. Oxidation is a chemical modification to functionalize the polysaccharides, it can be done with various oxidising agent but preferably periodate is used as oxidising agent for its selectivity. This leads to the selective cleavage of C_2-C_3 bond of the monosaccharide unit results in dialdehyde derivative. In the present work guar gum is oxidized with sodium metaperiodate to give dialdehyde galactomannan. It is an open chain polymer containing aldehyde groups.

Formation of Schiff base is the characteristic reaction of aldehyde, the formation of imine (-CH=N-) results in the yellow colouration hence shift in absorption was measured from UV-Visible spectroscopy. The conversion of functional group from alcoholic to aldehyde and from that to imine was clearly seen in IR spectroscopy. Thermal analyses shows decrease in Tg due to oxidation and further decrease in the imine, as oxidation involves the cleavage of glycosidic linkage and further reaction makes the polymer flexible.

Guar gum was obtained from SD Fine Chemicals, India. Sodium metaperiodate was obtained from Qualigens fine chemicals, Bombay, India. All the reagents used were of analytical grade

Preparation of dialdehyde galactomannan: Dialdehyde galactomannan was synthesized according to the reported procedure[5]. Guar gum was dispersed in 500 mL of distilled

water by stirring it with 1000 rpm for 0.5 h and the dispersion has been kept overnight for complete swelling of guar gum. Sodium metaperiodate was added to the dispersion while stirring with a magnetic stirrer. The reaction was performed in the dark at 35 ºC for 48 h. The reaction mixture was poured into three volumes of *t*-butyl alcohol, dialdehyde product was precipitated out, it was filtered dried and again redissolved in water to remove soluble impurities and precipitated the pure dialdehyde galactomannan with *t*-butyl alcohol.

Preparation of Schiff base: Purified dialdehyde product was dissolved in 50 mL of methanol and stirred at room temperature for 1 h. Pre-dissolved aniline in methanol was added in the ratio of 1:2 (v/v). This reaction was kept for overnight stirring, yellow colouration reveals the formation of imine. The product was concentrated in a rotatory evaporator under vacuum and washed with water to remove the unreacted dialdehyde galactomannan if any, filtered and dried at room temperature.

The absorbance of oxidized product and Schiff's base was recorded using Perkin Elmer UV-Visible spectrometer. Nicolet impact 400 Fourier transform infrared (FT-IR) spectrometer was used to examine the structure of guar gum, dialdehyde galactomannan and imine. The solid samples were recorded by making pellets with potassium bromide (E-Merck, IR grade). Thermogravimetric analysis was performed to assess the relative thermal stability of the natural polymers. Thermograms were obtained using a TA instruments Q100 series Thermogravimetric analyser.

Dialdehyde galactomannan was completely soluble in water and partially soluble in methanol, it was colourless solid reacts with aniline to form yellow coloured Schiff base. The maximum absorbance of dialdehyde galactomannan is at 202 nm, it was shifted to 256 nm in UV-Visible spectroscopy. The FT-IR spectrum of guar gum and dialdehyde galactomannan were shown in Fig. 2, comparing the spectrum of guar gum with dialdehyde galactomannan, a new band at 1725 cm^{-1} characteristic stretching of aldehyde carbonyl (C=O). The occurrence of sharp band at 2937 cm^{-1} due to the C-H stretching of aldehydic (-CHO). The intensity of (-OH) broad band slightly decreased and narrowed at 3568 cm^{-1} as the oxidation of guar gum to dialdehyde galactomannan reduces the number of hydroxyl groups, Fig. 3 shows the IR of Schiff base, a strong absorption band at 1603 cm^{-1} attributed to the -CH=N- vibrations characteristic of imines, which is not observed in dialdehyde galactomannan. The broad peak at 3419 cm^{-1} corresponds to the stretching vibration of -NH and -OH bonds shifted to higher frequency and changed from doublet band of $-NH_2$ to a single band for -NH indicates the formation of Schiff's base from dialdehyde galactomannan and aniline.

Thermal analysis: The decomposition of guar gum started at 286 ºC whereas it decreased to 221 ºC for dialdehyde galactomannan, this could be explained that oxidation results in the open chain polymer and further decrease in decomposition temperature was observed in the case of Schiff base to 174 ºC.

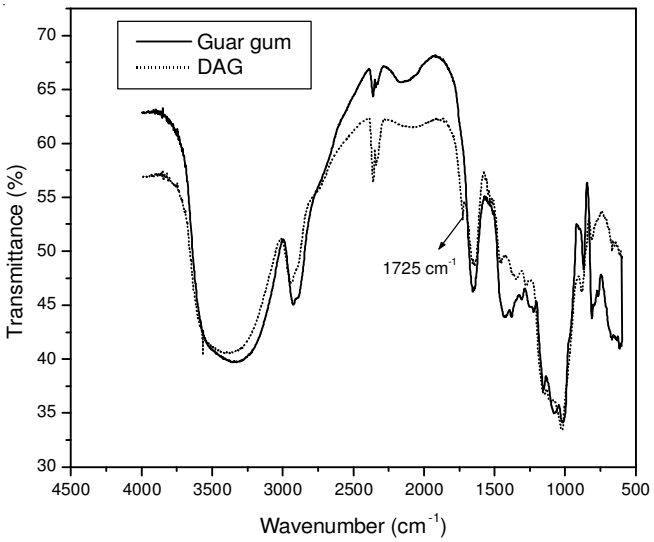

Fig. 2

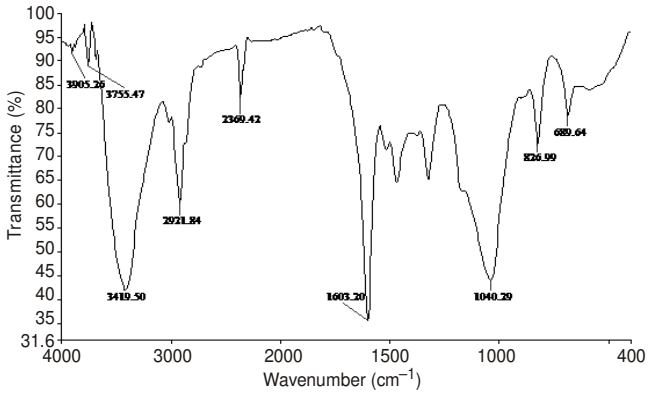

Fig. 3

In conclusion, a novel Schiff base was synthesized by the reaction of dialdehyde galactomannan with aniline. The shift in λ_{max} indicates the formation of Schiff base and the functional group was endorsed by FT-IR and the decrease in decomposition temperature of the product reveals that glycosidic ring got cleaved during oxidation resulting in an open chain polymer.

ACKNOWLEDGEMENTS

The authors thank Ms. A.Yasothai, Central Leather Research Institute for her timely help.

REFERENCES

1. I.C.M. Dea and A. Morrison, *Adv. Carbohyd. Chem. Biochem.*, **31**, 241 (1975).
2. B.V. McCleary, A.H. Clark, I.C.M. Dea and D.A. Rees, *Carbohyd. Res.*, **139**, 237 (1985).
3. Y.S.R. Krishnaiah, P.V. Raju, B.D. Kumar, V. Satyanarayana, R.S. Karethikeyan and P. Bhaskar, *J. Control. Rel.*, **88**, 95 (2003).
4. Y.S.R. Krishnaiah, R.S. Karethikeyan, P. Bhaskar and V. Satyanarayana, *J. Control. Rel.*, **83**, 231 (2002).
5. A.J. Varma, S.P. Kokane, G. Pathak and S.D. Pradhan, *Carbohyd. Polym.*, **32**, 111 (1997).