Carbohydrate Polymers **11** (1989) 279–292

Guar Gum Derivatives. Part I: Preparation and Properties

H. Prabhanjan*, M. M. Gharia & H. C. Srivastava‡

Ahmedabad Textile Industry's Research Association, Ahmedabad — 380015, India

(Received 7 October 1988; revised version received 6 January 1989; accepted 10 January 1989)

ABSTRACT

O-(2-Hydroxyethyl), O-(2-hydroxypropyl) and O-carboxymethyl derivatives of guar gum have been prepared under different experimental conditions. Several properties such as moisture regain, rate of hydration, solubility, viscosity and rheology of these derivatives have been studied. The properties depend upon polysaccharide chain length, and the nature and degree of chemical modification. The effect of alkali and alkaline hydrogen peroxide on the properties of guar gum have also been studied.

INTRODUCTION

Guar gum is a galactomannan, derived from guar (*Cyamopsis tetragonolobus*) seeds. The product of commerce is a dirty white powder which has very high affinity to water, so much so that its sols in water have the highest viscosity of all the natural carbohydrate polymers that have been discovered to date. The galactomannan of guar gum has a backbone of β(1-4)-linked D-mannopyranose units to which, at intervals, are attached single units of D-galactopyranose by α(1-6)-glycosidic bonds (Ahmed & Whistler, 1950; Rafique & Smith, 1950). There is some controversy as to the distribution of galactose units across the mannan backbone. In the publications by Ahmed and Whistler (1950) and Rafique and Smith (1950), it was envisaged that the branches of D-galactose units occur at regular intervals. However, Painter *et al.*, (1979) and Grasdalen and Painter (1980) have suggested that the guar galactomannan is a block

---

*Present address: Central Food Technological Research Institute, Mysore, India.
‡To whom correspondence should be addressed.

copolymer containing a galactose-rich region and an unbranched mannan region. Be that as it may, the guar galactomannan has the unique property of imbibing large quantities of water, resulting in dispersions of extremely high viscosity. High viscosity coupled with branched character of the polymer is responsible for adhesion of guar gum to hydrophilic surfaces. Because of these properties, guar gum is used for a large number of industrial and food applications. However, in many cases, the native gum has been found wanting in certain end-use properties. To overcome this, the gum is chemically modified to meet the property requirements for special applications. Thus the gum is modified by one or more reactions such as depolymerisation, oxidation, hydroxyalkylation, carboxymethylation, cyanoethylation, quaternisation and sulphation. Although hydroxyalkyl derivatives have been used for industrial and food applications for the past several decades, no systematic information seems to have been gathered on the changes in the properties of guar gum that take place with increasing substitution and the correlation of nature and degree of substitution with end-use applications. This paper attempts to fill in a few of these gaps. The changes in the solution properties of the derivatives have been correlated with the nature and degree of chemical modification. Furthermore, as all modification procedures involved the use of alkali as a catalyst, the effect of alkali on the gum has also been studied.

MATERIALS AND METHODS

Materials

A commercial grade guar gum used in the present study had the following analysis: moisture, 12·8%; fat, 0·6%; protein, 2·1%; viscosity, 8500 centipoise-seconds (cPs) (Brookfield, 1% soln.); and turbidity, 36 nephelo turbidity units (NTU). Ethylene oxide (NOCIL), ethylene chlorohydrin (BDH), propylene oxide (Fluka) and monochloroacetic acid (BDH) were of laboratory grade and were used without further purification.

Derivatisation

Guar gum was converted to *O*-(2-hydroxyethyl), *O*-(2-hydroxypropyl) and *O*-carboxymethyl derivatives (abbreviated, respectively, as HEG, HPG and CMG) by reacting it with ethylene oxide, propylene oxide and monochloroacetic acid, respectively. The reaction was carried out by two methods, namely, slurry and semi-dry or wet method. In the slurry method, gum (100 g), contained in a 2-litre round-bottom flask, was suspended in 75% aqueous isopropanol (400 ml) and reagent and catalyst (sodium hydroxide) were added with stirring. The mixture was heated in a water bath (50–70°C) for 1–1·5 h after which period the products were cooled, neutralised (acetic acid), washed successively with 75% aqueous isopropanol and air dried.

In the semi-dry or wet method, sodium hydroxide, dissolved in the minimum amount of water, was mixed with the gum (100 g) in an electric blender. After adding the reagent, the mixture was stirred in the blender and the reaction was allowed to proceed for the required length of time (1–1·5 h). After the reaction, the product was suspended in 75% aqueous isopropanol, neutralised with acetic acid and further processed as described for the slurry reactions. For hydroxyethylation, ethylene oxide was added portionwise during the reaction whilst for hydroxypropylation, propylene oxide was added and the reaction was carried out under self-generated pressure by sealing the stopper of the reaction flask with an adhesive tape. Concentration of alkali for hydroxyalkylation was 4% on the weight of gum; for carboxymethylation it was varied depending on the degree of substitution required.

Alkaline degradation

Alkaline degradation experiments were performed as blank sets in which all the steps of derivatisation were followed except that the addition of reagent was omitted. To study the effect of reaction parameters, alkaline degradation experiments were carried out varying the concentration of alkali (4% and 8%), time of alkali treatment (up to 8 h) and temperature (34°C, 50°C and 70°C) by both the semi-dry and slurry methods. The effect of treatment of gum with alkali under a nitrogen atmosphere was studied by bubbling nitrogen gas into the slurry at the rate of 25–30 bubbles per min. Degradation of the gum with alkaline hydrogen peroxide was carried out by the semi-dry method employing 4% or 8% sodium hydroxide and 30% solution of hydrogen peroxide (4%, on the weight of the gum).

Degree of chemical modification

Molar substitution (MS) for hydroxyalkyl groups was determined by the method of Lortz (1956). Degree of substitution (DS) of carboxymethyl groups was determined according to the method described in Indian Standard No. 3520 (1966). The method is briefly described here.

Accurately weigh about 1 g of the material and place in a 250-ml beaker. Add 10 ml hydrochloric acid and stir occasionally for 10 min. Add 20 ml water and neutralise with sodium hydroxide using phenolphthalein as indicator. The sample should be completely dissolved. Add about 0·2 ml sodium hydroxide in excess. The product is then precipitated by adding 160 ml of 95% alcohol under vigorous agitation. Stir for 15 min. Transfer quantitatively to an accurately weighed dry-sintered glass filter crucible of porosity G3 and filter by suction. Wash the residue with 95% alcohol and then with ether. Dry carefully with air and then at 105°C.

From the above material about 0·5 g is carefully burnt in a crucible. Dissolve the ash in water and titrate against 0·1 N sulphuric acid using methyl red as an indicator. The DS is calculated as follows.

$$\mathrm{DS} = \frac{0{\cdot}162\,B}{1 - 0{\cdot}08\,B}$$

where $B = 0{\cdot}1\,b/C$, b = volume in millilitres sulphuric acid required, and C = mass in grams of residue taken.

Viscometry

A 1% (w/v) solution of gum in water was made; after 24 h, viscosity of the solution was measured on a Brookfield (Synchro-Lectric) viscometer, Model LVT using spindle No. 2 at 12 rev/min. Viscosity values reported in this paper are of 1% solution unless otherwise stated.

Rheology

Rheotest-2 (VEB MLW) was used for studying rheology of gum solutions, at different concentrations (0·5–2·5%). Shear rates ranged between 3 and 1312 reciprocal seconds. Readings were taken after shearing the paste for 30–40 s.

Solubility

Solubility of gums in water was measured indirectly by measuring the turbidity of the solution, employing a Nephalo Turbidity Meter. The instrument was calibrated with formazine or with standard colloidal aqueous solution.

Moisture regain

Gum was desorbed at 110°C for 6 h and then placed in a desiccator containing saturated solution of an electrolyte having the desired relative humidity. After equilibrium was reached, the increase in weight due to moisture absorption was noted.

RESULTS AND DISCUSSION

Alkaline degradation

Earlier, the effect of alkalis on polysaccharides has been studied by many workers (Evans, 1942; Lindberg, 1956; Sowden, 1957). Based on the products obtained by alkaline degradation, many reaction mechanisms have been proposed (Whistler & BeMiller, 1958; BeMiller, 1965). However, the main reaction that takes place is peeling of the polysaccharide chain from the reducing end, the cleaved sugars appearing as saccharinic acids. A similar mechanism has been proposed for the alkaline degradation of guar gum (Whistler & BeMiller, 1961). Hui and Neukom (1964) have reported that addition of alkali to guar gum solution decreases its viscosity by dissociation of the aggregates. Addition of alkali to polysaccharide solution is reported to disturb the water–chain interaction pattern, ultimately reducing the viscosity (Rowland, 1977). Whistler and BeMiller (1961) have found that guar gum undergoes degradation to saccharinic acids even in oxygen-free alkali solution. Therefore, to assess to what extent the lowering of viscosity and other changes in solution properties of guar gum are due to alkaline degradation and to derivatisation, blank experiments were carried out in this study.

The effect of alkali on the viscosity of guar gum at different alkali concentrations, time periods and temperatures is shown in Figs 1 and 2. In both the semi-dry and the slurry methods the degradation is quite high as reflected by fall in the viscosity of alkali-treated gums. At both 4% and 8% alkali concentration at 34°C, the degradation is comparatively less but the maximum degradation takes place during the first 3 h. At higher temperatures there is a precipitous fall in viscosity during the first hour after which the rate of fall in viscosity is reduced. After 6 h only watery solutions were obtained. When guar gum was heated at 70°C for 24 h in the absence of alkali, not much change in the viscosity was observed. This indicates that, primarily, alkali is responsible for the degradation of gum which is accelerated at higher temperatures.

Studies by earlier workers (Richards & Sephton, 1957, and Whistler & BeMiller, 1961) have shown that alkaline degradation of poly-

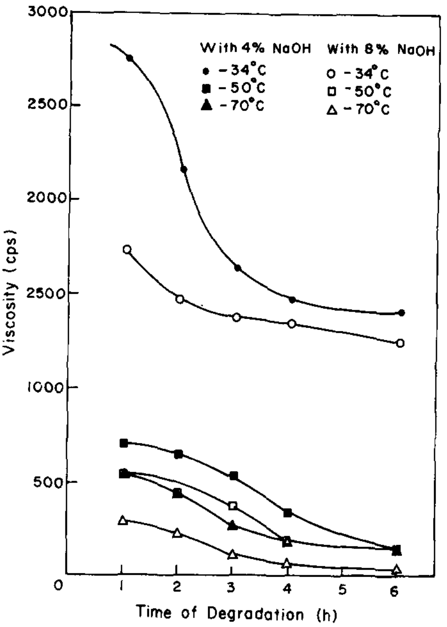

Fig. 1. Alkaline degradation of guar gum in the slurry state.

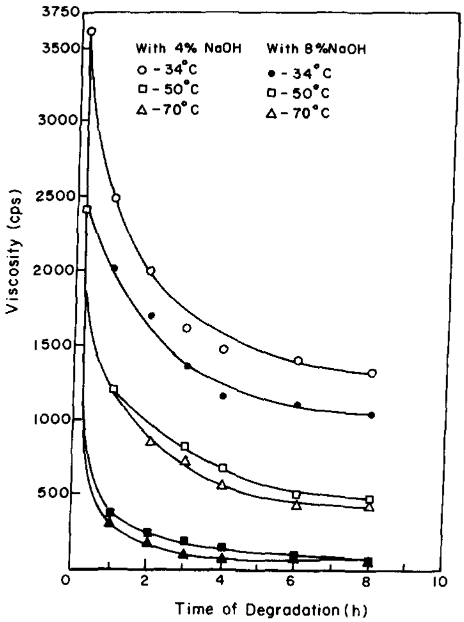

Fig. 2. Effect of alkaline degradation of guar gum in the semi-dry state on its viscosity as a function of time.

saccharides does not lead to complete depolymerisation to saccharinic acids but that a 'stopping of the reaction' mechanism comes into play by the formation of D-glucometasaccharinate terminals. Our results show that both in the slurry and semi-dry states, especially at 34°C, the viscosity levels off after a steep fall indicating that 'stopping of the reaction' mechanism is also operating here. However, at higher temperatures the stopping reaction seems to be inhibited resulting in extensive degradation of the gum.

In order to find out the effect of oxygen in air on alkaline degradation, guar gum was treated with 4% and 8% sodium hydroxide at 34°C, 50°C and 70°C in an atmosphere of nitrogen and in air. The results on the viscosity of a 1% solution of the gum (Table 1) show that under a nitrogen atmosphere, the degradation is very much less compared to that in air. Whatever degradation has taken place is due to higher temperatures, higher concentrations of alkali not affecting the viscosity of all.

Degradation of guar gum with alkaline hydrogen peroxide was also studied. The results, given in Fig. 3, show that very extensive degradation of the gum takes place in the first 2 h. The degradation is much more at 50°C and with 8% alkali.

TABLE 1
Alkaline Degradation of Guar Gum in Air and in Nitrogen Atmosphere

Temperature (°C)	*Concentration of alkali (%)*	*Viscosity (cPs 1% solution)*[a]	
		Air	N_2
34-35	4	2 755	8 400
34-35	8	1 740	8 400
50	4	700	7 400
50	8	560	7 000
70	4	550	6 500
70	8	300	6 500

[a] Viscosity of undegraded gum: 8 500 cPs.

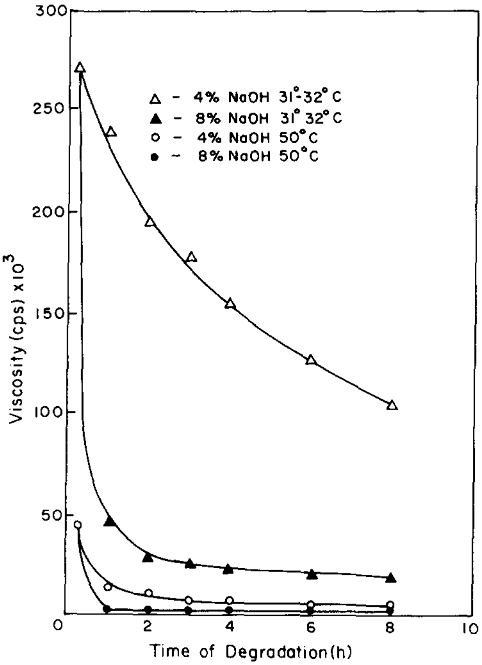

Fig. 3. Degradation of guar gum with alkaline hydrogen peroxide.

Substitution effects on solution properties of guar gum

Morton and Hearle (1962) have reviewed the association of water molecules with polymer network. For cellulose, the association depends on ambient humidity and hydroxyl groups of the polysaccharide chains for hydrogen bond formation (Urquhart, 1960). The number of hydroxyl groups in a polysaccharide network available for hydration depends on the structure of the polysaccharide in terms of ordered/amorphous regions, chain length, branching and ionic groups (Whistler, 1971, 1973). However, all polysaccharides contain a minimum level of moisture confined to the periphery of its network (bound water) which is neither freezable nor desorbable (Rowland, 1977; Deodhar & Luner, 1980). At increasing moisture levels, water molecules break intermolecular associations in polysaccharides which have a less ordered supramolecular structure. Thus starches, exudate gums and seed gums give viscous solutions. The solution properties are modified by introduction of substituent groups in the polysaccharide structure.

Figure 4 shows the effect of various substituent groups on the viscosity of guar derivatives. It is found that up to a certain value of MS/DS, viscosity of the derivatives increases almost linearly and thereafter further modification leads to a drop in the viscosity of the derivatives.

According to the theory of flow behaviour in amorphous polymers of high molecular weight (Graessley, 1965), the viscosity of such polymers is related to molecular entanglements and entanglement junctions. In the

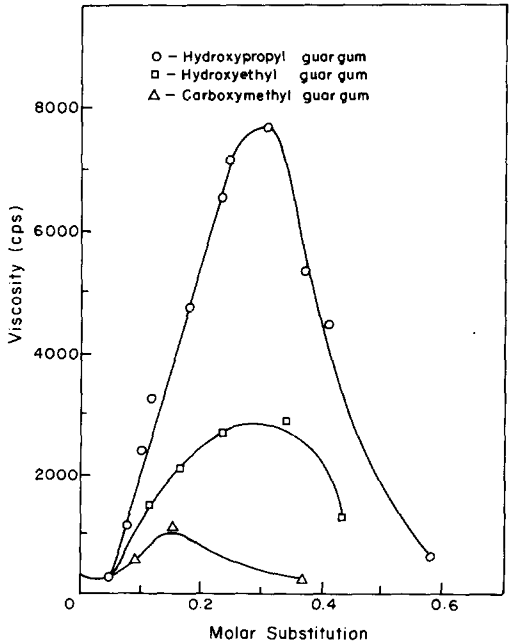

Fig. 4. Effect of molar substitution on the viscosity of guar gum derivatives.

case of hydroxyalkyl derivatives of guar gum it can be visualised that, by the introduction of substituent groups, the galactomannan polymer which was already branched would become further branched resulting in more entanglements and therefore higher viscosity. This situation will hold good till a certain degree of MS is reached, beyond which further branching will inhibit intermolecular attraction, entanglements and water cluster formation resulting in reduced viscosity. Because of longer chain length of the HPG group, as compared to the HEG group, these effects will be more pronounced in the case of HPG gum. Carboxymethyl derivatives showed low viscosity at all DS levels, when compared to HEG and HPG derivatives. This is due to polymer degradation because of the use of high concentrations of alkali in their preparation.

Figure 5 shows the concentration–viscosity data for various derivatives. It is found that gums having lower MS do not show much increase in viscosity as compared to gums having higher MS. At moderately high MS and higher concentration, it is expected that there would be more molecular entanglements (Beuche, 1962; Graessley, 1965). Such gums have shown higher viscosities with increasing concentration.

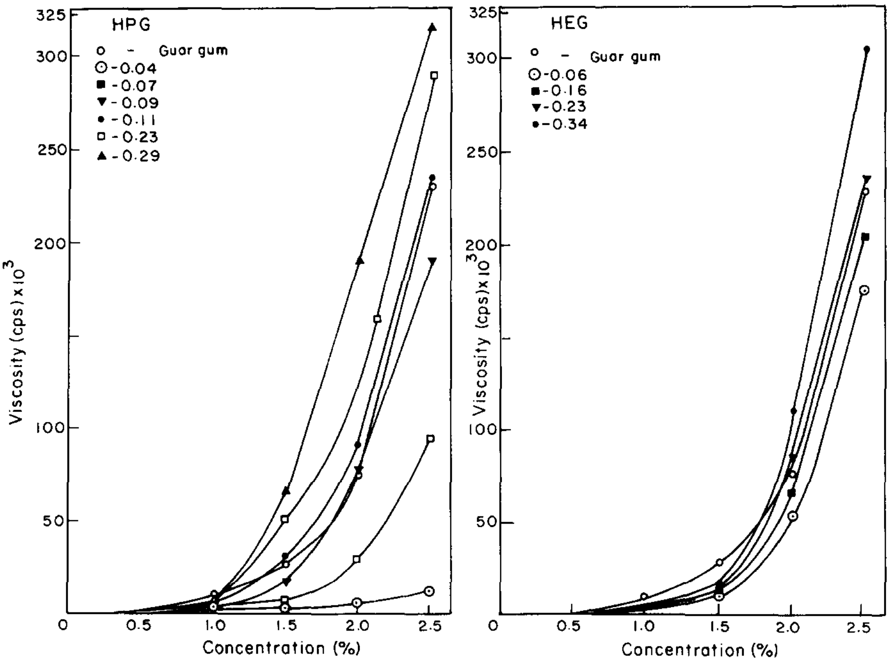

Fig. 5. Effect of concentration on the viscosity of hydroxyalkyl guar gums.

Rheology

Introduction of substituent groups in the guar galactomannan is found to change the rheological properties of the derivatives only to a small extent. Figure 6 shows that the slope of viscosity reduction of 1% guar gum solution, under varying shearing rates, is more than that of the derivatives. Similar observations were made at different concentrations also. This indicates that, in modified gums, the substituent groups get in the way of each other under the shearing action and cause more hindrance in the orientation of molecular chains in the laminar flow compared to the guaran molecule.

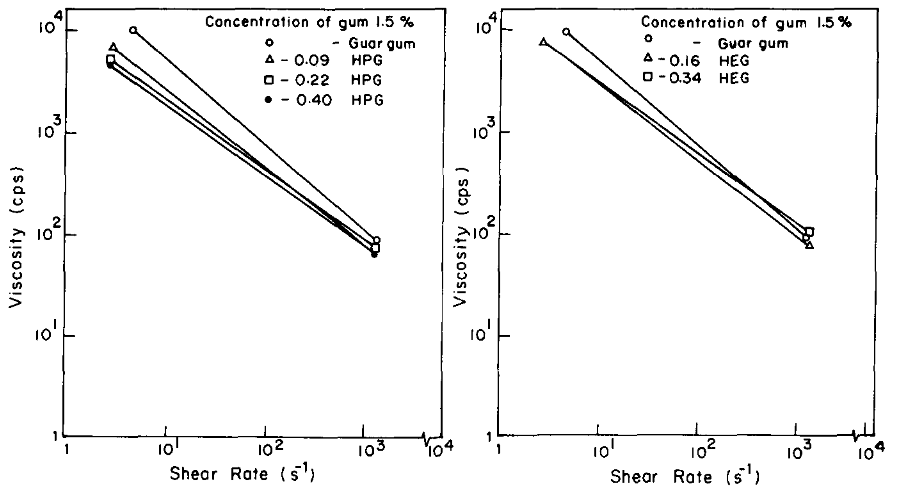

Fig. 6. Rheology of hydroxyalkyl guar gums.

Solubility

Polysaccharides are hydrocolloids and hence their solutions scatter light. The intensity of scattered light is a measure of insolubles in the polysaccharide solution, i.e. the higher the insolubles greater will be the intensity of scattered light. Figure 7 shows the intensities of scattered light when 0·25% gum solutions of different derivatives were placed in a Nephalo Turbidity Meter. The values are expressed at NTU. The data show that the solubility of gums increases with increasing MS and that at higher MS the gum solutions are as clear as water. Higher solubility of derivatised gums is due to greater accessibility of hydroxyl groups for

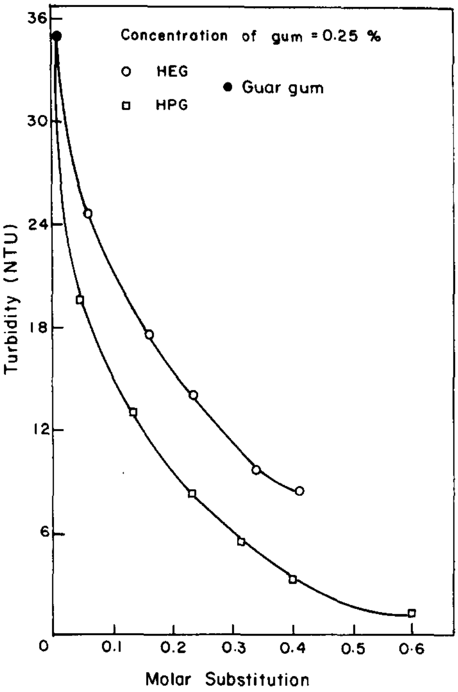

Fig. 7. Effect of molar substitution on the solubility of hydroxyalkyl guar gums.

solvation and some depolymerisation due to alkaline degradation. If, at some points in the polymer molecule, polyalkoxy groups are formed during the derivatisation, they will also contribute to solubility of the derivatives by increasing the intermolecular chain distances and making available more hydroxyl groups for solvation. However, the probability of formation of polyalkoxy condensates at low MS levels is rather remote.

Figure 8 shows the relationship of concentration of derivatives with turbidity. The data indicate that at higher MS values the gums give higher solubility and improved clarity which decreases with increasing concentration. This could be due to a combination of factors such as higher paste viscosity, change in refractive index and particle aggregation at higher gum concentrations. Between HPG and HEG gums, the former showed higher solubility at high MS levels.

Moisture regain and hydration

Figures 9 and 10 show the effect of chemical modification of guar gum on the moisture regain and hydration rates of derivatives. The results are

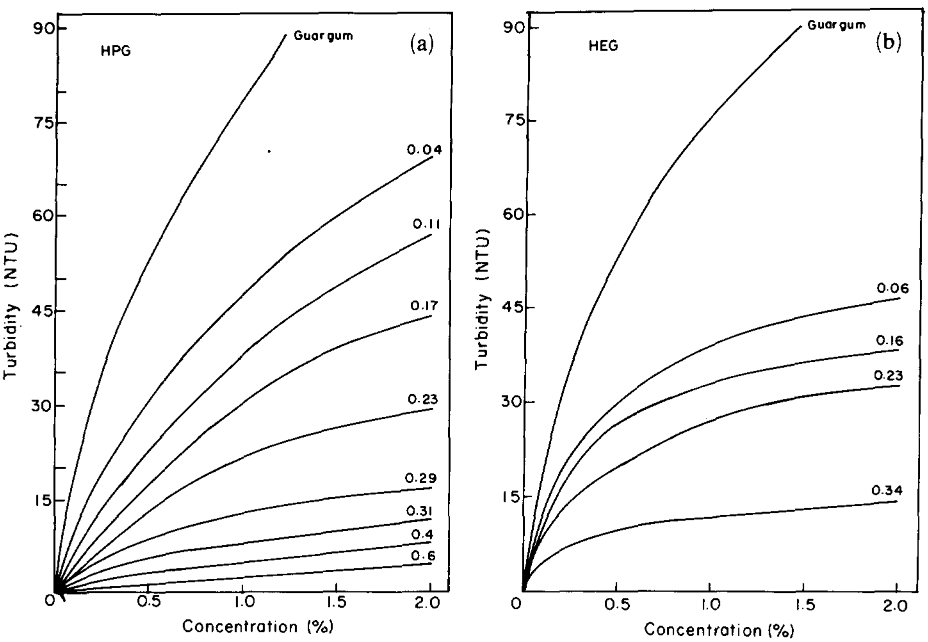

Fig. 8. (a) Effect of solution concentration on the turbidity of hydroxypropyl guar gums. (b) Effect of solution concentration on the turbidity of hydroxyethyl guar gums.

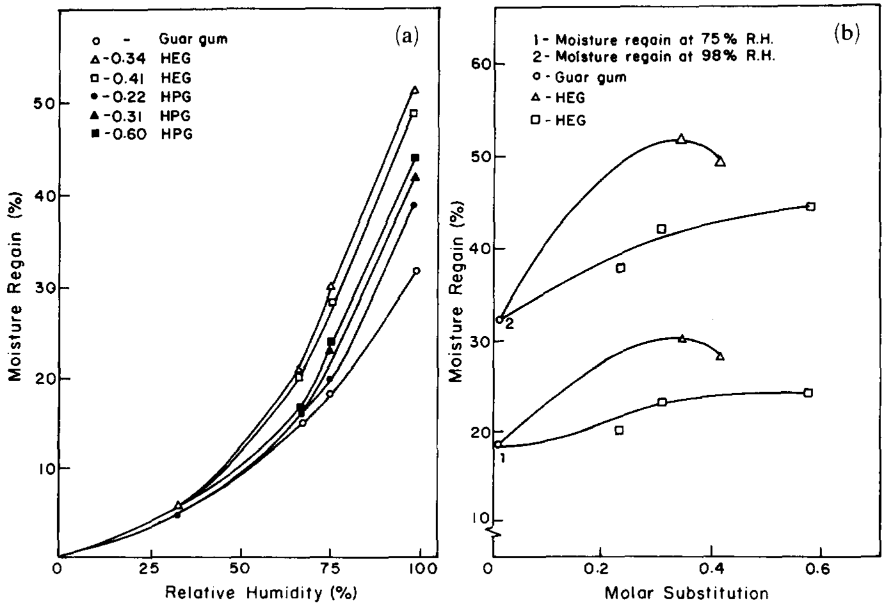

Fig. 9. (a) Moisture regain by hydroxyalkyl guar gums. (b) Effect of molar substitution on moisture regain of hydroxyalkyl guar gums.

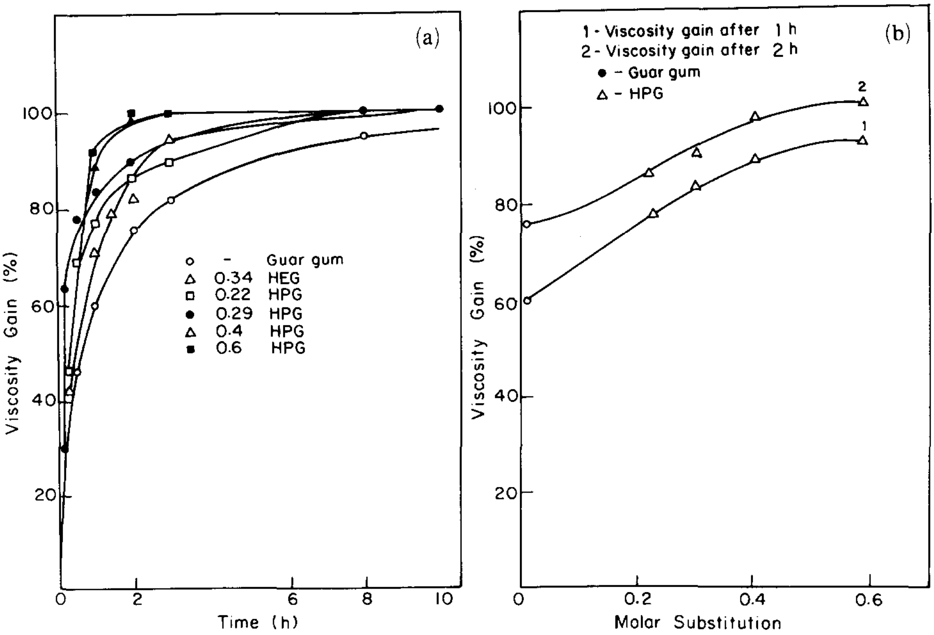

Fig. 10. (a) Viscosity gain due to hydration of hydroxyalkyl guar gums as a function of time. (b) Effect of molar substitution on viscosity gain due to hydration.

in conformity with the explanations given for the properties explained earlier. Thus at higher substitution levels, the gum structure is opened up for easy access by water molecules, as a result of which both moisture regain and hydration rates increase with increasing MS.

Hydration rates, measured as percent of total achievable viscosity attained at different intervals of time, indicates that HPG gums are hydrated faster than HEG gums at all MS levels. However, the moisture regain by HE gums at different humidities is more than HPG gums. This is most probably due to hydrophobic character of methyl group adjacent to a secondary hydroxyl group of HPG group, which hinders the moisture regain. However, in solution, the hydration is more influenced by the availability of hydroxyl groups for solvation and cluster formation.

CONCLUSIONS

A study of the solution properties of *O*-(2-hydroxyethyl), *O*-(2-hydroxypropyl) and *O*-carboxymethyl derivatives at various degrees/moles of substitution has revealed that the properties are dependent on two factors: (1) the extent of modification; and (2) alkaline degradation during the derivatisation reaction.

ACKNOWLEDGEMENTS

The authors thank the Director of ATIRA for permission to publish this paper. One of us (HP) thanks the Council of Scientific & Industrial Research, New Delhi, for the grant of a fellowship.

REFERENCES

Ahmed, F. & Whistler, R. L. (1950). *J. Amer. Chem. Soc.*, **72**, 2524–5.
BeMiller, J. N. (1965). In *Starch Chemistry and Technology*, Vol. 1, ed. R. L. Whistler & E. F. Paschall. Academic Press, New York, pp. 521–32.
Bueche, F. (1952). *J. Chem. Phys.*, **20**, 1959–64.
Deodhar, S. & Luner, P. (1980). In *Water in Polymers* (ACS Symposium Series No. 27), ed. S. P. Rowland, pp. 273–86.
Evans, W. L. (1942). *Chem. Rev.*, **31**, 537–60.
Graessley, W. W. (1965). *J. Chem. Phys.*, **43**, 2696–703.
Grasdalen, H. & Painter, T. J. (1980). *Carbohydr. Res.*, **81**, 59–66.
Hui, P. A. & Neukom, H. (1964). *Tappi*, **47** (1), 39–42.
Lindberg, B. (1956). *Svensk Papperstidning*, **59**, 531–4.
Lortz, H. Z. (1956). *Anal. Chem.*, **28**, 892–5.
Machell, G. & Richards, G. N. (1957). *J. Chem. Soc.*, 4500–6.
Machell, G. & Richards, G. N. (1958). *J. Chem. Soc.*, 1199–204.
Morton, W. E. & Hearle, J. W. S. (1962). *Physical Properties of Textile Fibres*. Butterworths, London.
Painter, T. J., Lindberg, B. & Hoffman, J. (1975). *Acta Chem. Scand., B*, **29** (1), 137.
Painter, T. J., Gonzalez, J. J. & Hemmer, P. C. (1979). *Carbohydr. Res.*, **69**, 217–26.
Rafique, C. M. & Smith, S. (1950). *J. Amer. Chem. Soc.*, **72**, 4634–7.
Richards, G. N. & Sephton, H. H. (1957). *J. Chem. Soc.*, 4492.
Rowland, S. P. (1977). In *Textile and Paper Chemistry and Technology*, ed. J. C. Arthur, ACS Symposium Series No. 49, pp. 20–45.
Sowden, J. C. (1957). In *Advances in Carbohydrate Chemistry*, Vol. 12, ed. M. L. Wolfrom. Academic Press, New York, pp. 35–79.
Urquhart, A. R. (1960). In *Moisture in Textiles*, ed. J. W. S. Hearle & R. H. Peters. Butterworth Scientific Publications, Manchester, pp. 23–25.
Whistler, R. L. (1971). In *Carbohydrates in Solution* (ACS Symposium Series No. 117), ed. R. F. Gould. Washington, pp. 242–55.
Whistler, R. L. (1973). In *Industrial Gums*, ed. R. L. Whistler & J. N. BeMiller. Academic Press, New York, pp. 10–15.
Whistler, R. L. & BeMiller, J. N. (1958). In *Advances in Carbohydrate Chemistry*, Vol. 13, ed. M. L. Wolfrom. Academic Press, New York, pp. 289–328.
Whistler, R. L. & BeMiller, J. N. (1961). *J. Org. Chem.*, **26**, 2887–92.