

STUDY OF HYDRATION KINETICS AND RHEOLOGICAL BEHAVIOUR OF GUAR GUM

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ABSTRACT

BACKGROUND

Guar galactomannan is a plant polysaccharide with extensive applications in food, paper, textile and petroleum industries. The main advantages for using guar are its low cost, easy availability and capacity to form viscous solutions and gels at low concentration. Additionally, chain architecture of guar galactomannan can be selectively modified to tailor properties of guar formulations and open up new opportunities for guar usage. The parameters such as hydration of guar, intrinsic viscosity measurements for determining the molecular weight of guar, rheological properties of guar were studied.

RESULTS

Experimental data have been correlated with the different models: flow curves with the Cross, Carreau and Meter-Bird model. The volume mean size of guar gum was 53.7 μ m and the molecular weight of guar near neutral pH was 967000 g/mol which were determined by intrinsic viscosity measurements. Hydration kinetics followed the logarithmic model. The behaviour of guar was interpreted in terms of Carreau model.

CONCLUSION

In this investigation the parameters such as hydration of guar, intrinsic viscosity measurements for determining the molecular weight of guar, rheological properties of guar were studied which would be very useful in modifying chain architecture of galactomannan to alter its properties which would open new opportunities for the use of guar.

Keywords: Guar gum, Hydration, Rheology, Dissolution Kinetics.

INTRODUCTION

Gums are polymeric substances which, in an appropriate solvent or swelling agent, form highly viscous dispersions or gels at low, dry substance content. All gums are polysaccharides composed of sugars other than glucose. (1,2) Guar gum is a hydrocolloid obtained from the endosperm of the *Cyanmopsis tetragonolobus* belonging to the family Leguminosae. The structure of guar gum consists of a linear backbone of β (1,4)-linked D-mannose units with various amounts of α (1,6)-linked D-galactose side chains. The ratio of mannose to galactose is 2:1. Guar gum is an economical thickener and stabilizer. It easily hydrates in cold water to give highly viscous solution. The very high viscosity attained at low concentrations makes guar gum an excellent thickener in the food industry, such as in

soups, desserts, pie fillings. The molecular weight of guar gum is between 220,000 and 300,000. However molecular weight as high as 0.1-2.8 million have also been reported. (3,4) Guar gum and its derivatives are major ingredients in drilling muds and fingering fluids in oil industry and in the textile industry guar solutions help to improve the printing quality. (3,5,6)

A number of factors are known to influence the hydration or dissolution process including the molecular weight and concentration of the galactomannan in the guar powder and also the environmental conditions such as temperature and pH and the presence of co solutes such as sucrose and salts. The major determinant of hydration kinetics is particle size, which reflects the change in surface area exposed to water. The rate and degree of hydration of guar gum are critical variables in influencing its biological activity. (3,5,6)

Rheology is defined as the science involved in the study of flow and deformation of materials. It is a powerful tool that can be used to characterize a wide range of materials ranging from solutions, melts, and gels, particulate systems among others (2,7).

Guar has now assumed a larger role among the domesticated plants due to its unique functional and rheological properties. Its ability to suspend solids, bind water by hydrogen bonding, control the viscosity of aqueous solutions and form strong tough films, have accounted for its rapid growth and use in various industries. Industrial grade guar gum is used in paper, textile processing, explosives, detergents, drilling fluids, ceramics, paints and many other industries. The purified grade is used in the pharmaceuticals, dielectric, cosmetic and food Industries. (2)

The hydration property of guar gum and other water soluble non-starch polysaccharides (s-NSP) is an important characteristic in many applications where solutions of these polymers often need to be prepared. Guar gum can significantly modify metabolism and gut function of experimental animals and humans. These metabolic effects are considered to be of clinical value in the dietary management of diabetes mellitus.

In view of the extensive applications of guar gum in various processes, biological environments and keeping in view that it is a low cost polysaccharide, easily available, nontoxic and biodegradable, the purpose of this work was

- To prepare and characterize guar sols
- To measure the intrinsic viscosity and to determine the effect of molecular weight in acidic, near neutral and alkaline media, which find applications in food and dietary fields.
- To develop a method of measuring the hydration rate of guar gum and the selection of a suitable empirical model for determining hydration kinetics as well as hydration index which is a main criteria in biological process especially in drug delivery systems.
- To determine the effect of shear rate and pH on the viscosity of guar sols that find application in many industries like cosmetics, fermentation, explosives, and mining industries and in polymer processing.
- Generation of flow curves at different pH media.

MATERIALS

Guar gum, Borax, Sodium chloride, Hydrochloric acid, Sodium hydroxide (of LR grade) was obtained from National Chemicals Limited, Vadodara.

EXPERIMENTAL METHODOLOGY

The guar gum dispersions were prepared by weighing a definite amount of guar and sprinkling into a rapidly swirling vortex of 100 ml deionised water in a glass beaker at 30±1°C. A magnetic stirrer was used to create the vortex in the deionised water. Guar gum samples were gently tapped manually on the sides of the beaker thoroughly. This encouraged a rapid and even dispersion of the sample into the water vortex created by magnetic stirrer, thus minimizing the aggregation of particles and producing a homogeneous polymer solution.

The time taken to add the guar sample was 60-90 s. Post dispersion was carried out by reducing the speed of agitated mass. Guar samples dispersed in water for 30 minutes were allowed to rest in refrigerator undisturbed for a period of 24 hours. The viscosity at the end of 24 hours was considered to be the ultimate viscosity. Care was taken that there was no loss of volume.

Viscosity of the sols was determined using the Brookfield cone and plate Rheometer at shear rates of 0.25-150 s⁻¹. The solutions of guar with varying pH in the range of 2-13.4 were also prepared. The lower pH value was controlled by adding sulphuric acid while alkaline pH was maintained by adding sodium hydroxide. The intrinsic viscosity measurements were performed using an Ostwald glass viscometer by measuring the efflux time of guar sols of concentration ranging from 0.05-0.3 g (w/v).

RESULTS AND DISCUSSION

4.1 CHARACTERISATION OF GUAR

4.1.1 PARTICLE SIZE DISTRIBUTION

Determination of particle size is very important as it influences the hydration and viscosity of the guar. The major determinant of hydration kinetics is the particle size, which reflects the changes in surface area exposed to water. There is an inverse relationship between the dissolution rate and particle size. (6)

In view of this, guar gum was characterized on the basis of particle size. The guar gum flour was screened through a 200 mesh Taylor sieve screen where all the particles passed through it suggesting that the sizes to be less than 74µ. The guar was further analyzed for particle size distribution using a Sympatec Helos (H1004) Laser Particle Size Analyzer with pressure at 3 bars and duration of 5 seconds. The volume mean diameter was found to be 53.7µm. The size distribution and volume mean diameter are reported in Figure 4.1

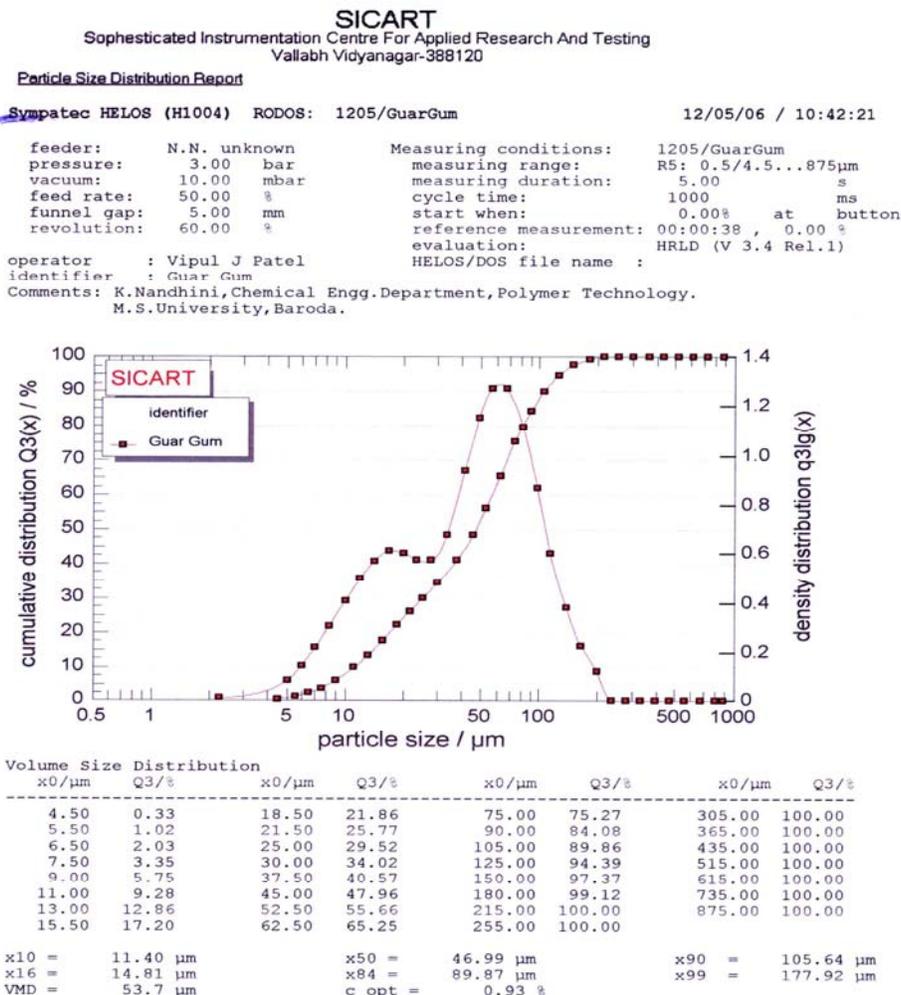


Figure. 4.1. Particle size distribution of guar gum.

The mean particle size of food grade guar as reported by various investigators including Wang et al (3,5,6,8) also happens to be in the range of 54-500µm

4.1.2 INTRINSIC VISCOSITY MEASUREMENTS

Intrinsic viscosity measurements were performed using Ostwald viscometer for guar sols in the concentration ranging from (0.05-0.3% w/v) of guar at various pH conditions ranging from 2-13.4 covering acidic, near neutral and basic environments.

The intrinsic viscosity a measure of the size of the isolated molecules was determined using equation 4.1 as

$$\text{Intrinsic viscosity} = \eta = \left(\frac{\eta_{sp}}{c}\right)_{c=0} = \left(\frac{\ln \eta_r}{c}\right)_{c=0} \dots \dots \dots (4.1)$$

The intrinsic viscosity was determined by taking specific viscosity at various concentrations and extrapolating the concentration to c = 0. The concentration dependence is also expressed by Huggins equation (4.2) as

$$\frac{\eta_{sp}}{c} = \eta + k\eta^2 c \dots\dots\dots (4.2)$$

Where k =Huggins constant

From the intrinsic viscosity, viscosity average molecular weight M_v was estimated using Mark-Houwink's equation (4.3)

$$\eta = KM^a \dots\dots\dots (4.3)$$

Where η = Intrinsic viscosity obtained from the graph.

K = Proportionality constant

M = Molecular weight of the polymer

a = Shape factor

K and a are also called as Mark-Houwink constants and their values are obtained from the literature (8,9,10) as $K = 3.8 \cdot 10^{-4}$ and $a = 0.732$.

The molecular weight at different pH of guar gum were tabulated in Table 4.1.

Table 4.1: Molecular weight at different pH of Guar

pH	Intrinsic viscosity (dl/g)	Huggins constant	Molecular weight (g/mol)
2	5.5259	2.641	485000
3	6.5257	2.182	609000
4	5.9664	2.152	539000
6.4	9.1495	0.655	967000
8	5.9868	3.27	542000
10	6.2132	2.03	570000
13.4	1.4974	9.842	81600

At pH 6.4 (the pH of deionised water) the intrinsic viscosity value was determined to be 9.149 dl/g which is in close agreement to reported values of guar galactomannan of 10-12.6 dl/g.(11). On moving away from neutral pH there is a decline in the values of intrinsic viscosity. This could be attributed to partial hydrolysis of polysaccharides by acid/alkali and also due to the variation in the dielectric constant of solvents resulting in a decrease in the molecular weight. Wang et al (12) also reported the viscosity of guar gum to be slightly lower in acidic pH than neutral pH. They suggested the degradation of guar galactomannan under acidic conditions was random with respect to chain cleavage and $\text{pH} > 2$ does not very much effect the molecular weight of galactomannan.

A decrease in intrinsic viscosity noted can also be attributed to the change in water structure affecting the interaction between water/galactomannan and galactomannan/galactomannan molecules. The weak protonation of the hydroxyl groups in galactomannan and water molecules caused by high H^+ may reduce the inter and intra molecular hydrogen bonding. It is possible that galactomannan molecules are less expanded in acidic media and the hydrogen bonding between water and galactomannan is less prevalent. The value of Huggins constant for pH 6.4 is 0.655 which is in

the specified range of 0.35-0.9 as quoted in the literature (12). However it was observed that the Huggins constant was much greater in acidic and alkaline media indicating the poor incompatibility of solvent with solute.

4.2 HYDRATION OF GUAR

The hydration kinetics of different concentrations of guar gum powder (0.6-1.2 %) (w/v) was studied using viscosity development as an index of hydration rate. The hydration studies were carried out and the viscosity of the different guar sols (0.5-1.2 %) at 0.5 to 100 s⁻¹ shear rates was measured

First order kinetics and Logarithmic model were used to fit the hydration kinetics. In view of the first order model not fitting the experimental data satisfactorily, the logarithmic model was used to fit the data and showed that the model fitted the experimental data reasonably well with > 0.95 correlation coefficient.

The model is given by,

$$\ln\left(1 - \frac{\eta_t}{\eta_\infty}\right) = b + k \ln t \dots\dots\dots (4.4)$$

η_t = Zero shear viscosity at time t

η_∞ = Ultimate viscosity

k and b = Hydration constants.

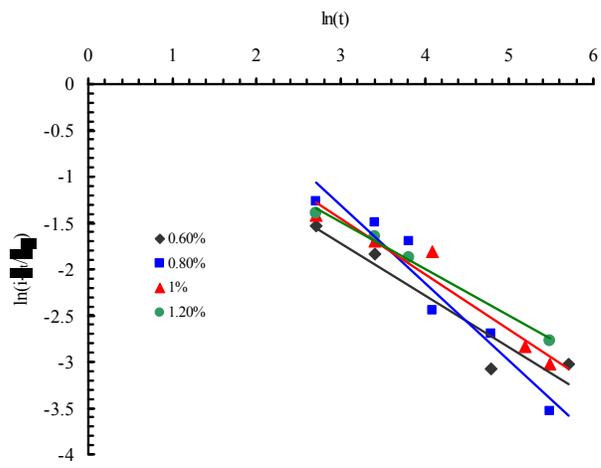


Figure. 4.2. Hydration curves at different guar concentrations

From Figure 4.2 it can be seen that the slope k and intercept b increase in the concentration range 0.6 to 1.2%. From the results obtained it is helpful to generate the relationship between the hydration rate and the concentration. Zero shear viscosity was taken at 0.5 s⁻¹ as it was not possible to measure viscosity at shear rates lower than 0.5 s⁻¹. This value also corresponds to the first Newtonian plateau

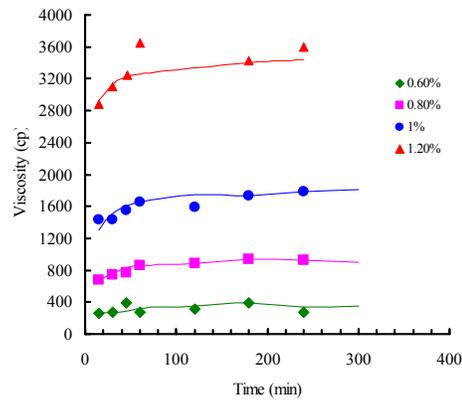


Figure 4.3. Viscosity developments at shear rate of 0.5 s⁻¹

Figure 4.3 shows a plot of η vs. t at different concentration of guar gum sols. It can be seen that the plateau in the curve was attained at lower times when almost > 90% of viscosities was developed at 60 minutes.

The reason for choosing $t_{0.9}$ time period rather than $t_{0.5}$, was that it covered the main period of hydration process during which most of the viscosity had developed and also that the viscosity was approaching the plateau value or ultimate viscosity.

Thus the Equation 4.4 can thus be rearranged as

$$t = \left[\left(1 - \frac{\eta_t}{\eta_\infty} \right) / e^b \right]^{1/k} \dots\dots\dots (4.5)$$

Substituting $\eta_{0.9} = 0.9\eta_\infty$ in the above Equation gives

$$t_{0.9} = \left(\frac{0.1}{e^b} \right)^{1/k} \dots\dots\dots (4.6)$$

Table 4.2 reports the $t_{0.9}$ values for concentration ranges 0.6 to 1.2%.

Table 4.2: Hydration index at different guar concentration

Concentration (g/dl)	$t_{0.9}$ (min)
0.6	56.48
0.8	65.58
1	82.85
1.2	99.65

It is assumed that the particle hydrates in a uniform manner and does not fragment during the dissolution/hydration process. Slight higher shear rates employed in this experiment could have resulted in fragmentation and accelerated the overall hydration process and the solution tend to get hydrated rapidly due to enhanced surface area leading to an enhancement of viscosity.

4.3 RHEOLOGICAL STUDIES OF GUAR GUM DISPERSIONS

The flow curves of guar sols in the concentration range of 0.8-1.2% (w/v) over a pH range of 3-9 were generated over a shear range of 0.1-300 s⁻¹. The data were tabulated in Table 4.3 and flow curves were plotted.

Table 4.3: Viscosity at different pH

Shear rate(s ⁻¹)	pH=3 Viscosity (cp)			pH=6.4 Viscosity (cp)			pH=9 Viscosity (cp)		
	0.8%	1%	1.2%	0.8%	1%	1.2%	0.8%	1%	1.2%
0.12	-			-	2459	5419	619.9	1400	4539
0.5	-			737.1	1892	4681	737.1	1990	4570
1	939.8	2009	3888	700	1880	3833	681.8	1732	3851
2	746.3	1686	3169	552.8	1649	3087	543.6	1474	3068
5	604.4	1246	2189	445.9	1209	2156	449.6	1069	2130
10	460.7	919.5	1524	361.2	884.5	1518	359.3	785	1502
20	346.4	642.2	-	274.6	619.2	-	276.4	550.1	-
40	242.3	428.9	-	-	-	-	-	-	-
50	-	-	-	176.2	359	-	176.9	318.4	-
100	142.3	-	-	118.1	-	-	121.4	-	-
150	110.6	-	-	92.51	-	-	95.45	-	-

As it is apparent the flow curve resemble to that for typical polymer sols, they show the first Newtonian plateau at low shear rates, a transition from Newtonian to pseudoplastic behaviour in low shear range depending on the concentration of the sols used was observed. This transition shifts to higher shear rate as the concentration is decreased.

This transition is expected according to Grassley entanglement theory, the decrease in viscosity with increasing shear rate is caused by shear induced change in the network entanglements. The behaviour of flow curves were interpreted using established rheological models.

Higher parameter models were necessary to represent the rheological behaviour. The models used to fit the experimental data were Carreau model, Cross model and Meter-Bird model. Power law model was used to fit the behaviour in the pseudoplastic region.

These models were used to fit the flow curves covering the whole shear range as shown in the Figure 4.4.

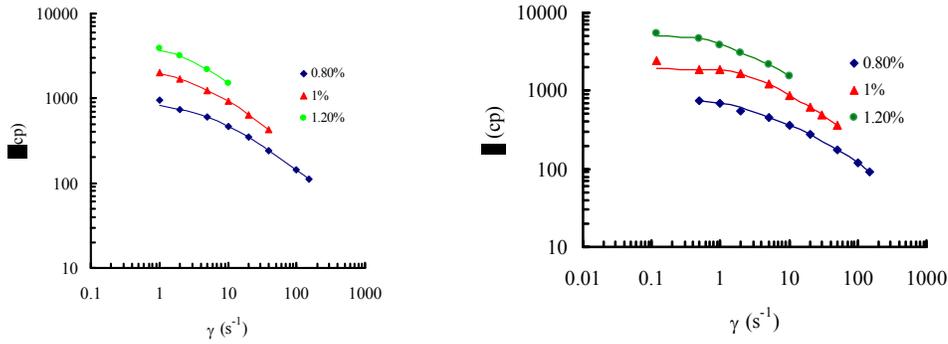


Figure 4.4. Flow curves at pH 3, 6.4.

Power law model was used to fit the experimental data in the pseudoplastic regime. Attempts were made to fit the experimental data generated in this work and are detailed below.

The full Carreau Model (13,14) is expressed by the following equation

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = [1 + (\lambda\gamma)^2]^{\frac{n-1}{2}} \dots\dots\dots (4.9)$$

The Carreau model parameters were given in Table 4.4.

Table 4.4: Carreau model parameters

C(g/dl)	pH=3			pH=6.24			pH=9		
	λ (s ⁻¹)	n	η_0 (cp)	λ (s ⁻¹)	N	η_0 (cp)	λ (s ⁻¹)	n	η_0 (cp)
0.8	0.2739	0.462	939.8	0.1818	0.3655	790	0.2173	0.4278	619
1	0.3921	0.4594	2009	0.666	0.4285	2459	0.3703	0.4059	1990
1.2	0.5128	0.444	3888	1.02	0.5874	5419	0.5555	0.4743	4570

The parameter (n) value calculated from the models closely related to the value of (n) calculated from the power law model (fitting in pseudoplastic range). This can be seen from Figure 4.5

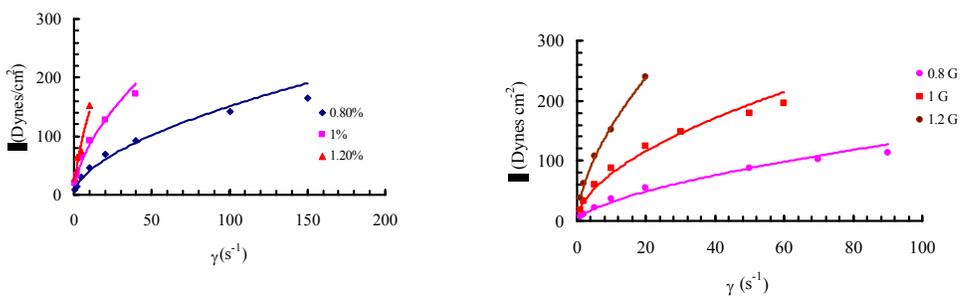


Figure 4.5. Power law model at pH 3, 6.4

The comparison of values of (n) were tabulated in Table 4.5.

Table 4.5. Comparison of flow index (n)

C(g/dl)	pH=3		pH=6.24		pH=9	
	Carreau model	Power law	Carreau model	Power law	Carreau model	Power law
0.8	0.462	0.5724	0.5874	0.6326	0.4278	0.7148
1	0.4594	0.5823	0.4285	0.5574	0.4059	0.5601
1.2	0.444	0.649	0.3655	0.6005	0.4743	0.7483

The carreau model fitted the data best and the experimental and calculated viscosities are reported in Table 4.8(a), (b) and (c). Meter-Bird model also fits the data but the percentage deviation was too large.

At 1 and 1.2 (w/v) %, the zero shear viscosity was found to increase on increasing the pH from 3 to 6.4 and decreased at pH 9. The characteristic time constant too followed the same trend. At concentration 0.8 (w/v) % zero shear viscosity decreased on increasing the pH. The characteristic time constant and flow index decreased on increasing the pH from 3 to 6.4 and then increased at pH 9 as per the Table 4.6.

Table 4.6. Carreau model fitting at pH 6.4

Shear rate (s ⁻¹)	0.8%			1%			1.2%		
	η_{exp} cp	η_{cal} cp	ABS(1- η_{cal}/η_{exp}) *100	η_{exp} cp	η_{cal} cp	ABS(1- η_{cal}/η_{exp}) *100	η_{exp} cp	η_{cal} cp	ABS(1- η_{cal}/η_{exp}) *100
0.12	-	-	-	2459	2454.53	0.18	5419	5402.4	0.31
0.5	737.1	787.9	6.9	1892	2386.2	26.12	4681	5166.6	10.37
1	700	781.8	11.7	1880	2214.1	17.77	3833	4677.6	22.04
2	552.8	759.4	37.39	1649	1837.0	11.41	3087	3862.5	25.12
5	445.9	652.5	46.35	1209	1206.3	0.22	2156	2745.3	27.33
10	361.2	497.1	37.64	884.5	826.7	6.53	1518	2074.5	36.66
20	274.6	340.3	23.93	619.2	558.9	9.72	-	-	-
30	-	-	-	492.9	443.7	9.99	-	-	-
50	176.2	193.9	10.09	359	331.5	7.64	-	-	-
100	118.1	125.3	6.11	-	-	-	-	-	-
150	92.51	96.9	4.79	-	-	-	-	-	-
		<i>SUM</i>	1.849		<i>SUM</i>	89.56		<i>SUM</i>	121.83
		<i>APD</i>	20.543		<i>APD</i>	9.9515		<i>APD</i>	20.3

CONCLUSIONS

Guar galactomannan is a plant polysaccharide with extensive applications in food, paper, textile and petroleum industries. The main advantages for using guar are its low cost, easy availability and capacity to form viscous solutions and gels at low concentration. Additionally, chain architecture of guar galactomannan can be selectively modified to tailor properties of guar formulations and open up new opportunities for guar usage. For example, reducing the galactose (side chain) content of guar can be utilized to form synergistic gels with biopolymers such as xanthan and carrageenan in various food applications. In the oil and gas industry, cross-linked guar gels are used to transport sand (proppant) into artificially created fractures oil bearing rock in order to enhance petroleum productivity.

In this investigation the parameters such as hydration of guar, intrinsic viscosity measurements for determining the molecular weight of guar, rheological properties of guar were studied. The volume mean size of guar gum was 53.7 μ m and the molecular weight of guar near neutral pH was 967000 g/mol which were determined by intrinsic viscosity measurements. Hydration kinetics followed the logarithmic model.

This work can be extended to find the effect of salts and solvents on viscosity of guar sols and characterization of guar gel. Further studies on loss and storage modulus of guar as well as gels needs to be investigated using dynamic measurements. Influence of particle size on hydration needs to be investigated in detail. Ageing and biodegradation of guar need to be identified. Detail mechanisms of gelling of guar with borax and focus on thermal degradation of guar gels and resilience to thermal decomposition need to be determined.

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