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Free radical degradation of guar gum

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Abstract

Thermal as well as microwave mediated free radical degradation of Guar gum in to lower molecular weight fragments was studied. Swollen suspensions of guar flour, containing either potassium persulphate or hydrogen peroxide, in aqueous isopropyl alcohol were heated to effect depolymerisation. From the intrinsic viscosity of the resulting products, molecular weight was calculated using the Mark-Houwink equation. It was shown that both hydrogen peroxide and potassium persulphate degrade guar gum in a concentration dependent manner and persulphate appeared to reduce molecular weight more effectively than hydrogen peroxide. Microwave heating also promoted the degradation of guar gum and was much faster than conventional thermal reactions. Thus prepared lower molecular weight guars are also shown to have better film forming properties.

Keywords: Guar gum; Degradation; Microwave radiation; Free radical

1. Introduction

Guar gum is a polygalactomannan obtained from the seeds of a leguminaceae plant, *Cyamopsis tetragonalobus*, grown mainly in north western India and Pakistan. It is a water soluble polysaccharide and because of its low cost and excellent viscosifying properties, it and its derivatives are extensively used in industrial applications including food [1], oil recovery [2], personal care [3], etc. Structurally it has a back bone of β-1,4-linked mannose units with α-1,6-linked galactose units attached as side chains to almost every alternate mannose unit (Fig. 1).

One of the main uses of guar gum is in food industry where its bulking, stabilizing and water binding properties are exploited [4]. It is also used in dietary supplements as an indigestible sugar in obesity treatment. Another very important industrial use of guar gum is as a hydraulic fracturing fluid in oil and gas recovery [5,6]. In these and other applications guar gum needs to be degraded in a controlled manner in to lower molecular weight fractions.

Depolymerisation of polysaccharides has been widely studied [7]. Though acid [8] and enzymatic hydrolysis [9,10] are most common, other methods such as γ-irradiation, extrusion [11,12], ultrasonication [13] and free radical degradation [14,15] are also reported. Acid and enzymatic degradation of guar gum itself was investigated [16]. In practice it is often difficult to make large quantities of depolymerised macromolecules with controlled degradation. In this study we report thermal and microwave mediated free radical degradation of guar gum.

2. Experimental

Guar gum used was of commercial grade (S.D. Finechem, Mumbai, India). Potassium persulphate (KPS), Hydrogen peroxide, methanol and isopropanol (all S.D. Finechem, Mumbai, India) were used as received. Peroxy content of hydrogen peroxide was determined to be 55%.

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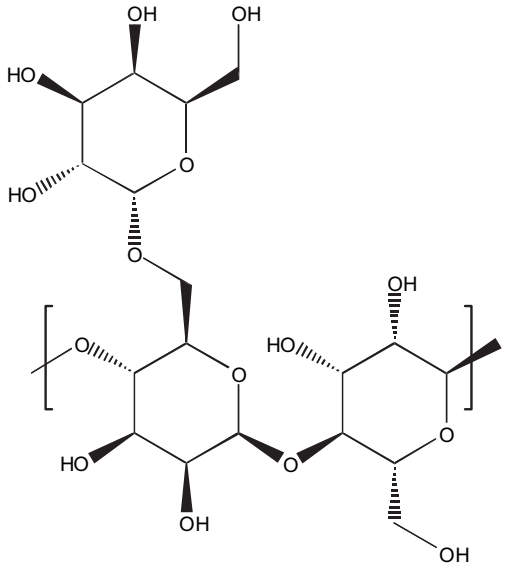

Fig. 1. Chemical structure of guar gum.

2.1. Thermal degradation of guar gum

In a typical experiment 20 g of purified guar gum was dispersed in 200 ml of isopropanol in a 500 ml round bottomed flask. While stirring the suspension with a magnetic bead, 40 ml of distilled water containing required amount of either potassium persulphate or hydrogen peroxide was added slowly. This freely stirring suspension was heated to 100 °C and kept at that temperature for different times. The reaction mixture was then allowed to cool to room temperature and filtered. The filtrate was washed successively with 30% aq. Methanol, methanol and dried in an air-circulating oven at 60 °C until constant weight.

2.2. Microwave degradation

A total of 100 g of guar gum was added to 200 ml distilled water containing 1 g of potassium persulphate initiator and kneaded well. It was then ground in a kitchen mixer cum grinder in to a fluffy, soft sponge like material. Roughly 10 g of this material was then taken in a cylindrical vial made of Teflon and subjected to microwave radiation in Ethos-1600 machine at 100 °C. Power settings and time were the variables experimented to control the degradation. The products were washed successively with 30% methanol and methanol. Dried in an air-circulating oven at 60 °C until constant weight.

2.3. Molecular weight determination

Molecular weights of various depolymerised guar gum compounds were determined from their intrinsic viscosity values and its relation to molecular weight via Mark Houwink equation as reported earlier [17]. Briefly, using a Ubbelohde capillary viscometer the relative viscosity (η_r) was measured ($\eta_r \cong T/T_0$, where T is the solution flow time and T_0 is solvent flow time). From this the specific viscosity was calculated ($\eta_{sp}=\eta_r-1$). Intrinsic viscosity (η) is normally determined by measuring reduced viscosity η_{red} ($=\eta_{sp}/C$) at various concentrations in dilute solution and extrapolating to concentration $C=0$. The concentration dependence is often expressed in terms of the following relationship.

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C$$

where K is known as Huggins constant. For flexible polymer molecules in good solvents K is often near to 0.35, although somewhat higher values occur in poor solvents. In the present work, a value of 0.35 was adopted in the above equation to calculate intrinsic viscosity by measuring specific viscosity in dilute solutions

$$[\eta] = [(1+1.4\eta_{sp})^{1/2} - 1]/0.7C$$

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

$$[\eta] = k\, M_v^{\alpha}$$

with $\alpha=0.732$ and $k=3.8\times10^{-4}$ [18].

2.4. Tensile strength

Tensile strength and elongation at break of native and depolymerised guar gum, using 0.5, 1, 2, 3% KPS, were studied from dried rectangular films (0.08 mm × 1 cm × 5 cm) using Universal Testing Machine (Shimadzu, Japan, AGS-10 KNG).

3. Results and discussion

Guar gum is a high molecular weight seed gum. It forms colloidal solutions, even in cold water, and imparts very high viscosities. Because of this and its water binding capacity, it is used in such wide ranging applications such as food, textile, medicine and oil exploration. In certain applications where bulking is needed it is necessary to depolymerise guar gum. One emerging area of application for polysaccharides is their use as solvent soluble polyols in coatings applications. For this purpose we needed a simple method to degrade guar gum in to smaller fragments so that they can be further modified to achieve solvent solubility. Herein we present results of our work on free radical mediated degradation of guar gum.

Table 1
Thermal degradation of guar gum

S.No	Reagent	Reagent concentration (%)	Time (h)	η_{sp}	$[\eta]$	Molecular weight $\times 10^{-6}$
	–	Native guar	–	1.29	13.77	1.70
1	H_2O_2	1	1	0.95	10.75	1.21
2	H_2O_2	1	2	0.92	10.43	1.16
3	H_2O_2	1	3	0.90	10.32	1.14
4	H_2O_2	2	1	0.86	9.87	1.07
5	H_2O_2	2	2	0.83	9.61	1.03
6	H_2O_2	2	3	0.79	9.20	0.97
7	H_2O_2	3	1	0.78	9.06	0.96
8	H_2O_2	3	2	0.75	8.83	0.92
9	H_2O_2	3	3	0.67	7.95	0.80
10	KPS	0.5	1	0.63	7.58	0.75
11	KPS	0.5	2	0.59	7.15	0.69
12	KPS	0.5	3	0.56	6.85	0.65
13	KPS	1	1	0.39	5.01	0.42
14	KPS	1	2	0.38	4.86	0.41
15	KPS	1	3	0.37	4.72	0.39
16	KPS	2	1	0.20	2.71	0.18
17	KPS	2	2	0.19	2.59	0.17
18	KPS	2	3	0.18	2.46	0.16
19	KPS	3	1	0.10	1.31	0.07
20	KPS	3	2	0.09	1.28	0.07
21	KPS	3	3	0.08	1.16	0.06

3.1. Thermal degradation of guar gum

Guar gum was subjected to free radical degradation using potassium persulfate and hydrogen peroxide. The effect of these reagents, their stoichiometry, time of reaction on specific and intrinsic viscosity of guar gum is presented in Table 1. As can be seen, both the reagents smoothly degraded guar gum in a concentration dependent manner. Potassium persulphate appeared to degrade guar better than hydrogen peroxide as evidenced by fall in η_{sp}. The extent of degradation depended more on the concentration of the radical generator rather than time. Viscosity average molecular weight of different guar macromers prepared was calculated using Mark Houwink equation and results are plotted in Fig. 2. As is evident it was possible to prepare a wide M_v range of guar gum using potassium persulphate and hydrogen peroxide.

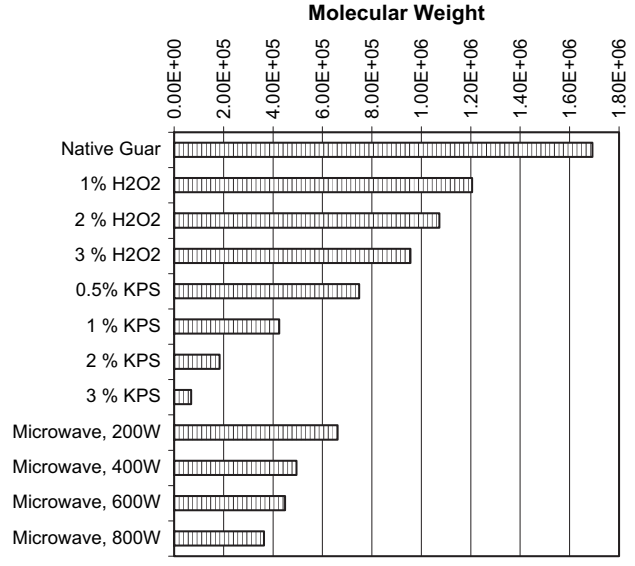

Fig. 2. Effect of reagent and its concentration on the molecular weight of guar gum. Microwave reactions were run for 5 min with 1% KPS and others for 1 h at 100 °C.

Table 2
Effect of microwave heating on guar gum

S.No	Power level (W)	Time (min)	2% solution viscosity (cps)	η_{sp}	$[\eta]$	Molecular weight $\times 10^{-6}$
	Native guar	–	>25,000[a]	1.29	13.77	1.69
1	200	5	3750	0.57	6.92	0.66
2	200	10	1100	0.36	4.67	0.39
3	200	15	950	0.34	4.35	0.35
4	400	5	2000	0.45	5.60	0.50
5	400	10	900	0.36	4.58	0.38
6	400	15	900	0.36	4.19	0.33
7	600	5	1450	0.41	5.22	0.45
8	600	10	1000	0.39	5.00	0.42
9	600	15	900	0.36	4.67	0.39
10	800	5	900	0.35	4.48	0.36
11	800	10	900	0.33	4.32	0.35
12	800	15	850	0.32	4.20	0.33

All reactions were done using 1% KPS at 100 °C.
[a] With 2 h hydration.

3.2. Microwave degradation

Microwave heating is the first new heating technique since the discovery of fire [19]. This heating is based on the ability of some materials to convert electromagnetic energy in to heat and it has revolutionised cooking and chemistry [20,21]. The main advantages of using microwaves for heating in chemistry are better yields, shorter reaction times, reduction of by-products and thermal decomposition. In polymer chemistry several papers describing polycondensation [22], resin curing [23,24], graft copolymerisation [25] have appeared. We investigated the microwave heating for the free radical degradation of guar and the results are presented in Table 2.

As can be seen, microwave heating also degraded guar gum and it did so at a very rapid pace. Thus it was

Table 3
Tensile strength and % elongation at break of guar gum and thermally degraded guar gum

Sample	Maximum stress (N/mm^2)	Elongation at break (%) EB
Guar	20	0.66
0.5% KPS	36	1.44
1% KPS	39	1.39
2% KPS	40	1.52
3% KPS	46	1.84

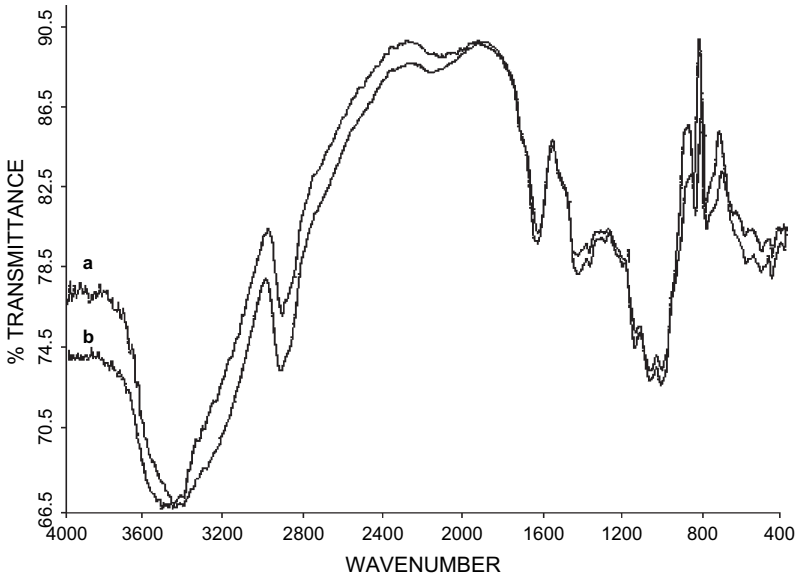

Fig. 3. FTIR spectra of: (a) native guar; and (b) degraded guar (Table 1 entry 17).

shown that guar gum can be degraded with free radical generators like potassium persulphate and hydrogen peroxide in a concentration dependent manner by both thermal as well as microwave heating.

3.3. Tensile strength

Guar, because of it's very high molecular weight, forms colloidal solutions. Hence films obtained from its solutions are brittle [26]. For certain applications like coatings it is desirable to have true solutions and better film forming properties. Tensile strength and elongation at break (%) EB of the films prepared from aqueous solutions of pure guar and depolymerised guar are shown in Table 3. It can be seen that degradation improved the tensile strength as well as elongation at break values. Thus depolymerised guar gum, with high water solubility, low viscosity and better film forming properties, should be useful in surface coating formulations.

3.4. IR spectral analysis

To compare the chemical structural identities of guar and degraded guar, we have recorded Infrared spectra.

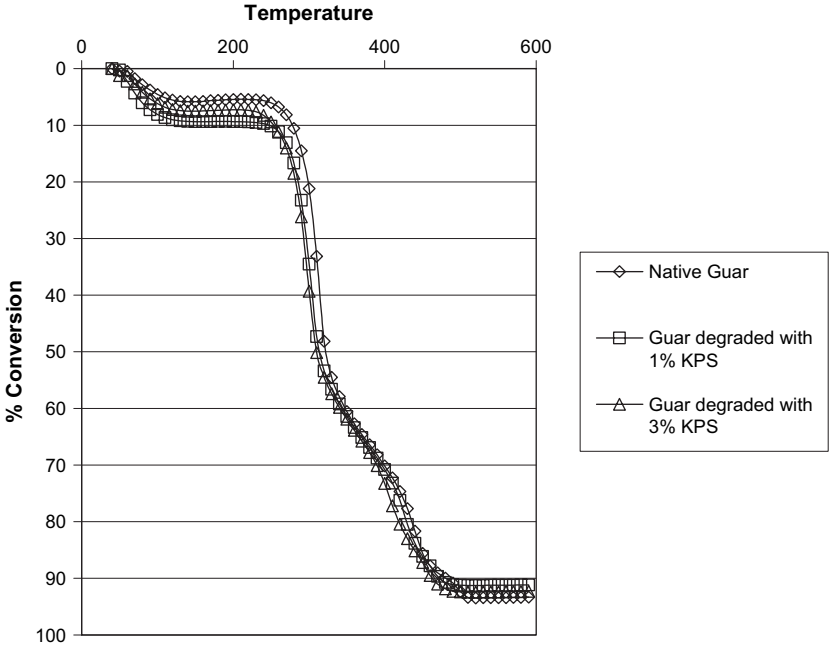

Fig. 4. TGA of guar gum and thermally degraded guar gums.

As can be seen from Fig. 3, the degraded guar has a spectrum superimposable over that of native guar. This suggests that there are no major functional group transformations during this reaction and only random free radical chain scission might have taken place during these transformations.

3.5. Thermogravimetric analysis

Thermogravimetric analyses, in air, of native and thermally degraded guar gum, using 1 and 2% potassium persulphate, are depicted in Fig. 4. The % conversion vs. temperature curves of all these polymers are almost identical. This also suggests that there is no major change in chemical structure of these polymers and during free radical depolymerisation no crosslinking has taken place.

4. Conclusions

It was shown that guar gum can be degraded in to lower molecular weight fragments using free radical generators like potassium persulphate and hydrogen peroxide. Though both thermal energy and microwaves could effect depolymerisation, the latter did so at a more rapid rate than the former.

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