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Thermal behavior of galactomannan guar gum and its periodate oxidation products

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Oxidation of polysaccharides leading to the cleavage of the C_2–C_3 bond of the monosaccharide building blocks and formation of dialdehyde groups are difficult products to characterize by infrared (IR) and NMR spectral analysis, due to the formation of hemialdal and hemiacetal structures. A study of the thermal behavior (TGA, DTA and DTG) of a galactomannan (guar gum) and a series of its periodate oxidized products (1.2, 3.1, 13, 26.7 and 54.9% oxidation, based on periodate consumption) shows that thermal analysis is a sensitive tool for differentiating periodate oxidized products which have very similar IR spectra. The TG, DTG and DTA data showed that the samples belonged to three categories: those having low (~3%) levels of oxidation; intermediate levels of oxidation (13–26%); and high levels of oxidation (26–54%), and each category had a characteristic profile. © 1997 Elsevier Science Ltd

INTRODUCTION

Natural polysaccharides are biopolymers generally considered to be biocompatible and environment friendly materials. Derivatizations of such polysaccharides leads to a variety of speciality polymers. Structural studies, reactions and applications of polysaccharides and their oxidation products has been the object of some of our research in recent years due to their scientific as well as their industrial significance (Desai *et al.*, 1978; Morita, 1965; Patel *et al.*, 1988; Perkins & Mitchell, 1957; Scott, 1939; Varma & Chavan, 1995a, b, c). Periodate oxidation of polysaccharides leads to the cleavage of the *cis*-α-diol (C_2–C_3 or C_3–C_4) bond of the monosaccharide building blocks and the formation of dialdehyde groups. These dialdehydes are difficult products to characterize by IR and NMR spectral analysis due to the formation of hemialdal, hemiacetal and cross-linked structures. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of some polysaccharides, and their derivatives, have been reported and found to be promising and sensitive techniques for characterizing structural modifications of these natural polymers (Varma, 1984; Varma & Jamdade, 1985; Varma & Chavan, 1994) which were oxidized to varying extents using sodium metaperiodate in an aqueous medium. These thermal studies provide a sensitive method for characterizing such materials.

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EXPERIMENTAL

Materials

Low molecular weight guar gum (Edicol ULV/50) was obtained from Indian Gum Industries, Bombay, India. Sodium metaperiodate was obtained from Loba Chemie, Bombay, India.

Preparation of dialdehyde galactomannans

Low mol. wt guar gum (5.5g) was dispersed in 350ml distilled water and allowed to swell for 4h. Now 0·5g sodium metaperiodate, dissolved in 5ml water, was slowly added to the guar gum dispersion. The contents of the flask were covered with aluminum foil and heated at 55°C for 7h. The reaction mixture was cooled and slowly poured into three volumes of methanol to precipitate out the dialdehyde galactomannan. The latter was filtered, dried, redissolved in water and again precipitated in methanol to purify it. Unreacted metaperiodate was analyzed by titrimetry (Varma, 1984). This afforded a product where 0·6% of the total number of mono-

saccharide building blocks were oxidized to give the C_2–C_3 dialdehyde galactomannan. Infrared spectra in KBr pellet did not yield any useful clues, since the aldehyde groups are in the hemiacetal and hemialdal forms (Zhbankov, 1966). However, the changes in the thermal behavior and the consumption of metaperiodate in the reaction suggest that the dialdehyde galactomannan has been formed.

The synthesis and characterization of the other periodate oxidized guar gum products were carried out in a similar manner. The exact reaction conditions are shown in Table 1.

Thermal analysis

Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) were carried out using a Seiko Instruments TG/DTA 32 instrument equipped with a SSC 5100 Disk Station and SP-530 Plotter. The studies were carried out in an air and nitrogen atmosphere at a heating rate of 10°C, in the range 25–600°C.

Results and discussion

A study of the synthesis procedure for periodate oxidation of guar gum (Table 1) shows that the reaction is relatively slow as compared to some other polysaccharides such as cellulose (Nevell, 1963; Varma *et al.*, 1985) and requires about 30h for completion at 70°C.

Tables 2 and 3 show thermal analysis data for a series of periodate oxidized guar gum (1·2–54·9% oxidized monomer units) under nitrogen and air atmosphere, respectively. From the two tables it is seen that the onset degradation temperature in nitrogen and air does not vary significantly, but the final degradation temperature is much lower in air.

The final degradation temperature under the air atmosphere is in the region of 500°C, while under nitrogen it is >600°C. Also, the % weight loss, under the air atmosphere at all temperatures, is much greater (86·9–98·8% range at 500°C) than under the nitrogen atmosphere (62.8–98.8% range at 500°C). Even at lower temperatures (220 and 320°C), the % weight losses under the air atmosphere are much greater than under the nitrogen atmosphere. Similar observations have also been made for other polysaccharides, such as cellulose (Ouensanga & Picard, 1988).

The differential thermogravimetry (DTG) curves studied under nitrogen atmosphere show, in all cases, a major peak (indicating weight loss) below 313°C (Table 2). However, under air atmosphere there is a major peak around 300°C for samples which are not oxidized or those having a low degree of oxidation (3·1% oxidized guar gum), with minor peaks at high temperatures (446 and 506°C, respectively). However, for 13% oxidized guar gum, the peak at 291°C is a minor peak, while the peak at 447°C is a major peak; for 26·7% oxidized guar gum there are two major peaks at 285 and 470°C, respectively, and for 54·9% oxidized guar gum there are two major peaks at 298 and 465°C, respectively. Thus, there are major differences in the DTG curves, studied under air and nitrogen atmospheres, showing that major weight losses occur below 300°C under nitrogen for samples of all degrees of oxidation studied, while under air, major weight losses occur around 300°C for samples of low degrees of oxidation (~3%), and around 470°C for samples having intermediate oxidation levels (about 13%) (see Tables 2 and 3). For samples having high oxidation levels (between 26·7 and 54·9% in this study), major weight losses occur around 290 and 470°C, respectively.

Data for the differential thermal analysis (DTA) curves under air atmosphere (Table 3) shows that for low degrees of oxidation of guar gum (around 3%), major exothermic oxidation peaks are observed from a temperature of 300°C onwards, right up to 500°C, but at higher degrees of oxidation (13–26·7%), the exothermic peak is around 450°C. At still higher levels of oxidation (54.9% oxidized sample), the exothermic oxidation peak around 300 and 450°C are both prominent. In the nitrogen atmosphere also, for low degrees of oxidation (around 3%), the exothermic oxidation peaks are observed in the 270–450°C region, while for 13% oxidized guar gum the major oxidation reactions took place above 500°C. For the 26·7% oxidized sample, the exothermic oxidations took place at the lower temperature of 288°C, as well as at 552°C, while

Table 1. Reaction conditions for sodium metaperiodate oxidation of guar gum in water

% oxidation	Wt of guar gum taken (g)	Wt of periodate taken (g)	mL Water per g guar taken	Reaction temp (°C)	Reaction time (h)	Wt of periodate reacted (g)	% yield of methanol precipitated product
0.6	5.5	0.5	355	55	7	0.0455	83.6
1.2	22	4	1240	55	7	0.3585	88.2
3.1	22	4	1240	55	30	0.8754	82.3
13.0	22	4	1240	70	30	3.7698	63.6
26.7	22	8	1280	70*	30	7.7454	15.9
54.9	22	16	1360	70	30	15.9369	9.3

*When this reaction was carried out at 60°C for 30h, the oxidation achieved was only 14.7% having a yield of 20.9%.

Table 2. Thermal analysis data of periodate oxidized galactomanan (guar gum) in nitrogen

% Oxidation	TG		% weight loss at			DTG	DTA
	Onset degrad. temp. °C	Final degrad. temp. °C	220°C	320°C	500°C		
0	235	Not distinct*	13	63	88	Only one peak at 306°C	Broad (exothermic) oxidation peaks in the 300–500°C range
1.2	222	529	13.7	58.3	91.3	Major peak at 295°C, minor peak at 493°C	Broad (exothermic) oxidation peaks in the 270–450°C and another sharp oxidation peak at 494°C
3.1	230	Not distinct*	11.6	66.5	78.6	One major peak at 293°C	Broad (exothermic) oxidation peaks in the 283–450°C range, and a small broad oxidation peak at 583°C
13.0	223	Not distinct*	11.8	57.0	76.9	One major peak at 291°C	Small (exothermic) oxidation peak at 298°C and major oxidation peaks at 497°C and 534°C
26.7	200	-do-	10.3	45.2	62.8	Major peak at 283°C, minor peak at 318°C	(Exothermic) oxidation peaks at 288 and 552°C
54.9	190	-do-	7.4	38.9	64.0	Major broad peak at 313°C	Broad oxidation peak at 335°C (range 300–500°C)

*Continuous downward tapering of TG curve up to 600°C.

Table 3. Thermal analysis data of periodate oxidised galactomannans (guar gum) in air

% Oxidation	TG		% weight loss at			DTG	DTA
	Onset degrad. temp. °C	Final degrad. temp. °C	220°C	320°C	500°C		
0	231	505	10.9	61.4	98.8	Major peak at 302°C, minor peak at 446°C	Broad (exothermic) oxidation peaks in the 300–350°C range. Sharp oxidation peaks at 446 and 489°C
3.1	222	515	12.7	59.8	90.9	Major peak at 293°C, minor peak at 506°C	Exothermic oxidation peaks at 304, 346 and 506°C
13.0	216	465	15.5	56.1	94.3	Minor peak at 291°C, major peak at 447°C	Very small (exothermic) oxidation peak at 300°C, strong sharp oxidation peak at 447°C
26.7	212	497	15.0	47.4	94.7	Two major peaks at 285 and 470°C	Small (exothermic) oxidation peak at 286°C and strong sharp oxidation peak at 470°C
54.9	202	480	8.8	44.4	86.9	Two major peaks at 298 and 465°C	Strong broad (exothermic) oxidation peak at 318°C and a strong sharp oxidation peak at 466°C

the 54·9% oxidized sample underwent exothermic reactions continuously from 300°C onwards up to 500°C. Thus, in DTA studies, as in DTG studies, we observe that the samples belonged to their categories, those having low degrees of oxidation intermediate levels of oxidation and high levels of oxidation, and each had a characteristic oxidative degradation pattern as described above.

Thus, a thermal study of an homologous series of oxidized guar gum samples shows that TG, DTG and

DTA are all highly characteristic for different levels of oxidation, and can be conveniently used not only to characterize the sample (as to its degree of oxidation), but also to yield important information pertaining to the relation between molecular composition and oxidative stability. We are investigating different types of oxidized polysaccharides and shall be throwing further light on their thermal and other spectral characteristics in subsequent publications.

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