

INVESTIGATION OF PYROLYSIS KINETICS OF CARBOXYMETHYL HYDROXYPROPYL SESBANIA GUM

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Abstract

The thermal pyrolysis of carboxymethyl hydroxypropyl sesbania gum and hydroxypropyl sesbania gum in air and nitrogen atmospheres were studied in order to establish the thermal stability of carboxymethyl hydroxypropyl sesbania gum. The results indicate that the stability of carboxymethyl hydroxypropyl sesbania gum against pyrolysis is higher than that of hydroxypropyl sesbania gum. The main state of carboxymethyl hydroxypropyl sesbania gum and hydroxypropyl sesbania gum can be assigned as random noncrystalline.

Keywords: polysaccharide, pyrolysis, thermal stability

Introduction

Sesbania gum (SG) is a natural galactomannan extracted by milling from the seeds of sesbania, a plant of the bean family. The main structure involves $\beta(1\rightarrow4)$ -linked mannanose connected by a branch chain to $\alpha(1\rightarrow6)$ -linked galactose [1]. The molecular weight is about 230 000 [2].

SG has been extensively used in industrial applications, but its relative instability has led to its being replaced by hydroxypropyl SG (HPSG), particularly for use in the oil and gas industry. A more recent development is carboxymethyl HPSG (CMHPSG).

The goal of this research was to investigate the stability and kinetics of HPSG and CMHPSG by means of thermal analysis. The results will be utilized in industrial applications.

Experimental

Preparation of the samples

HPSG (MS, 0.45) was prepared as in [1], while CMHPSG (MS, 0.42; DS, 0.3) was prepared from SG by reaction with chloroacetic acid and epoxypropane.

Pyrolysis experiments

Experiments were carried out on a Perkin-Elmer TGS-2 instrument at a heating rate of $5^{\circ}\text{C min}^{-1}$ under flowing air or nitrogen; or on a DSC-2C differential scanning calorimeter; data were processed with a TADS-3600.

Discussion and conclusion

Stability of HPSG and CMHPSG against pyrolysis

Analysis of TG curves

The temperatures of initial mass loss (T_o) and of completion of mass loss (T_e) were evaluated on the basis of the Coats-Redfern method. Pyrolysis parameters (T_o and T_e) for HPSG and CMHPSG at $5^{\circ}\text{C min}^{-1}$ in flowing air or nitrogen are listed in Table 1.

Table 1 Major pyrolysis temperatures of the samples at different temperatures

Sample		$T_o/^{\circ}\text{C}$	$T_e/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_d/^{\circ}\text{C}$
HPSG	air	209.6	308.2	275.1	237.5
	N_2	208.2	309.1	274.8	235.8
CMHPSG	air	215.8	308.9	274.0	237.8
	N_2	214.0	310.9	274.0	237.8

T_o – temperature of initial mass loss

T_e – temperature of completion of mass loss

T_p – temperature of highest rate of mass loss

T_d – calculated starting pyrolysis temperature.

T_o and T_e for CMHPSG are seen to be higher than those for HPSG. This indicates that the carboxymethyl group improves the heat-resistant properties. The values of T_o and T_e were virtually identical in flowing air and in nitrogen.

Figures 1 and 2 indicate two mass loss stages for HPSG and CMHPSG in flowing air and in nitrogen. The first decomposition stage in the TG curves of CMHPSG is steeper than that for HPSG. The results also indicate that the molecular weight distribution of CMHPSG is narrower than that of HPSG, the intrinsic molecular weight distribution being affected by the chemical modification.

Analysis of the TG curves shows that the first stage involves the thermal decomposition of the substituted branched chain group and the sugar cycle. The second stage involves the carbonization pyrolysis of the primary chain.

In Fig. 3, the peak height of CMHPSG is higher than that of HPSG at a heating rate of $10^{\circ}\text{C min}^{-1}$ in air or in nitrogen. Figure 3 also indicates that the thermal stability of CMHPSG is higher than that of HPSG. The TG curves do not exhibit an absorption peak for crystalline melting or a viscosity-flow temperature. This indicates that CMHPSG and HPSG have a non-crystalline structure of random distribution, and do not pass through the molten state in the pyrolysis process of decomposition into solids and gases of small molecular weight.

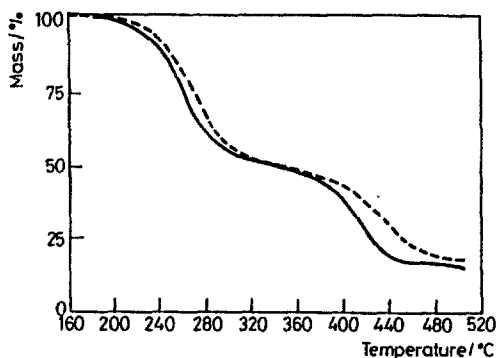


Fig. 1 TG curves of different samples in air; ---- CMHPSG, — HPSG

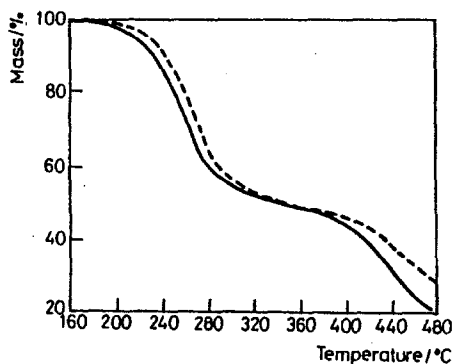


Fig. 2 TG curves of different samples in nitrogen; ---- CMHPSG, — HPSG

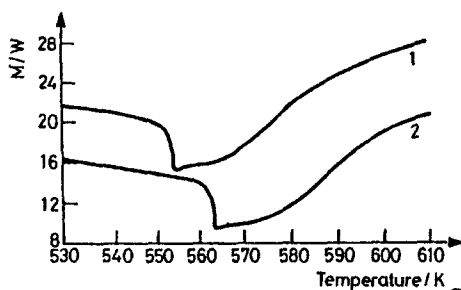


Fig. 3 DSC curves of different samples; 1) HPSG, 2) CMHPSG

Analysis of thermal decomposition kinetics

Processing of the TG data by the Coats-Redfern method [3] leads to the reaction order (n), apparent activation energy (E) and pre-exponential constant (A) values listed in Table 2.

Table 2 Parameters E , n and A in different atmospheres

Sample		n	$E/\text{kJ mol}^{-1}$	A/s^{-1}
HPSG	air	1.6	125.2	$2.54 \cdot 10^{13}$
	N_2	1.1	163.0	$1.32 \cdot 10^{14}$
CMHPSG	air	1.9	156.5	$5.23 \cdot 10^{13}$
	N_2	1.6	184.8	$5.01 \cdot 10^{14}$

Table 2 reveals that, both in flowing air and in nitrogen, the activation energy of CMHPSG is higher than that of HPSG, demonstrating that CMHPSG has the higher thermal stability.

The activation energy in flowing air is lower than that in nitrogen. This relates to the possibility of oxidative reactions of the samples in the process of pyrolysis.

To summarize, this investigation has established that CMHPSG has better heat-resistant properties than HPSG, which in turn is more thermally stable than the original, chemically unmodified SG [4].

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We express our thanks to Dr. Yaxiong Xie for his help in this work.

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