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KINETIC STUDY OF THERMAL DEGRADATION OF GUAR GUM ESTERS

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ABSTRACT

The guar gum esters were synthesized by reacting guar gum with various anhydrides. The degree of substitution of guar gum esters was estimated. The thermal degradation of guar gum and its esters in the presence of air was examined by thermogravimetry to ascertain their relative thermal stabilities on the basis of various temperature parameters. The experiments were carried out at a heating rate of 10 °C min^{-1} in the range 25–550 °C.

INTRODUCTION

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are promising techniques for the study of the thermal behavior of polysaccharides [1–3]. Daugviliene et al. [4] carried out a comparative study of the thermal decomposition of structural modification of polysaccharides. The effect of the nature of the substituent groups on the stability and mode of decomposition of the polysaccharide derivatives has been studied by DTA and TGA [5]. The free energies of activation for the thermal degradation of the polysaccharide and its derivatives are reported to be equal [6].

In recent years, anionic, cationic and non-ionic derivatives of guar gum have become an important part of total guar gum consumption. These derivatives are not approved for food use at present, although some may be in the future. The development of the derivatives has followed the pattern for industrial grade products.

In the present work, some guar gum esters are synthesized by the reaction of guar gum with cyclic or aliphatic acid anhydrides and the thermal properties of these polymers are studied to correlate structure–property relations.

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EXPERIMENTAL

Ester synthesis

The dry guar gum (0.01 mol) was allowed to react with anhydride (0.09 mol) in acetic acid (25 ml) containing 4 ml of pyridine. The reaction was refluxed at 120 °C for 4 h. After completion of the reaction, the mixture was discharged in chloroform–ethyl acetate mixture (125 ml, 50/50 v/v) with high speed agitation. After removing the solvent mixture by decantation, the solid residue of the guar gum ester was re-slurried once in the solvent mixture and was then recovered by centrifugation and dried in vacuum at room temperature. Following a similar method, a number of guar gum esters were synthesized and the degree of substitution of the esters (Table 1) was determined using the general method detailed in ref. 7.

To prepare guar gum acetate–butyrate containing various compositions of the acetate and butyrate moieties, the proportions of acetic anhydride and butyric anhydride were varied during the reaction. The proportions (in %) are shown in parentheses in Table 1. The maleates of the guar gum esters (i.e. guar gum acetate, guar gum propionate and guar gum butyrate) were prepared by reaction of guar gum esters with maleic anhydride under specified experimental conditions.

Infrared analysis

Infrared (IR) analysis of guar gum and guar gum esters was carried out on a Perkin Elmer IR 983 spectrophotometer. A broad band extending from 3600–3200 cm^{-1} was observed in the IR spectra of guar gum and its esters.

TABLE 1

Preliminary characteristics of guar gum esters

Ester	Color	Degree of substitution
Guar gum (GG)	White	–
GG acetate (AC)	White	4.35
GG propionate (Pr)	White	1.80
GG butyrate (Bu)	White	1.21
GG AC–Bu (80/20)	White	3.13
GG AC–Bu (70/30)	White	3.00
GG AC–Bu (60/40)	White	2.79
GG AC–Bu (50/50)	White	2.53
GG succinate	White	6.14
GG maleate	Yellow	5.78
Maleate of GG AC	Yellow	4.85
Maleate of GG Pr	Yellow	5.01
Maleate of GG Bu	Yellow	5.45

This is the characteristic stretching vibration of the hydroxyl group [8]. The appearance of the band in the IR spectra of the guar esters may be due to the free -OH groups which remain unreacted during esterification. The bands at 1150 and 1110 cm^{-1} may be assigned to the bridge -C-O-C stretching modes. The weak bands at 935 cm^{-1} may be due to 1 : 4 and 1 : 6 linkages present in the guar gum moiety and the band at 810 cm^{-1} may be due to the presence of ring breathing (β) [9].

The presence of the ester–carbonyl group is indicated by a strong band at 1750 cm^{-1} in the IR spectra of guar esters; however a small shift in the ester–carbonyl group is observed as the length of chain increases [10]. In the spectra of maleate esters, the ester–carbonyl band appears at 1700 cm^{-1} because conjugation lowers the ester–carbonyl frequency. On the lower frequency side of the ester–carbonyl band, a slight inflexion is observed. This may be attributed to the carbonyl group of the end carboxyl group of the polymer chain. In the spectra of guar gum succinate, guar gum maleate and the maleates of the guar gum esters, this type of inflexion is observed at 1690 cm^{-1}. In the IR spectra of guar gum esters, containing an end carboxyl group the band at 1315 ± 5 cm^{-1} arises from a C–O vibration coupled with an OH in-plane deformation vibration.

Thermogravimetric analysis

Weight loss experiments of guar gum and guar gum esters were performed using a Du Pont 951 thermogravimetric analyzer in air. The polymer sample was powdered to the same average mesh size and dried carefully. The amount of polymer sample was approximately 50 mg. Thermogravimetric experiments were carried out at a heating rate of 10 °C min^{-1}

RESULTS AND DISCUSSION

On comparing the degree of substitution of guar gum esters (Table 1) prepared under the same reaction conditions, it was found that in aliphatic acid anhydride esters of guar gum, the degree of substitution decreases as the chain length increases. This indicates that as the chain length of acid anhydrides increases, the reactivity towards esterification decreases. It was also observed that the esters prepared from dicarboxylic acid anhydrides have a higher degree of substitution than those prepared from aliphatic acid anhydrides. This indicates that cyclic anhydrides are more reactive than aliphatic acid anhydrides. In the case of esters containing both acetate and butyrate moieties, the degree of substitution decreases as the percentage of acetate content decreases. Maleate ester derivatives of guar gum have a yellow color due to the presence of conjugation in the maleate group which is absent in other ester derivatives.

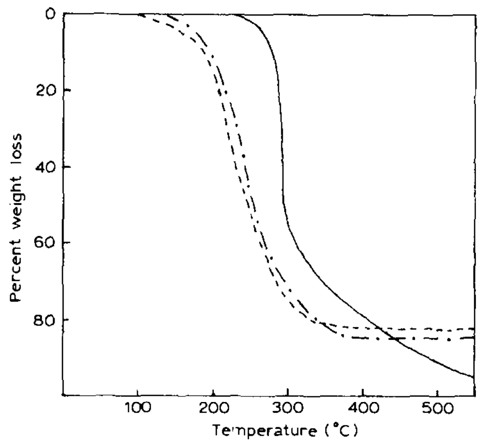

Fig. 1. Thermogravimetry of guar gum esters: guar gum (———); guar succinate (- - - - -); guar maleate (·—·—·).

All the guar esters were found to be insoluble in common organic solvents and did not melt before decomposition.

Thermogravimetric analysis

Thermogravimetric curves are plotted in Figs. 1–4. Each figure shows the weight loss of the sample in air as a function of temperature. The aliphatic acid anhydride esters of guar gum are stable up to 240 °C and the dicarboxylic acid anhydride esters of guar gum are stable up to 100 °C. However, the rate of degradation of the aliphatic acid anhydride esters of guar gum is

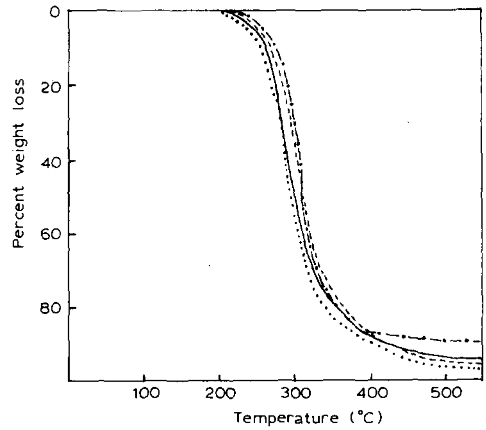

Fig. 2. Thermogravimetry of guar gum esters: guar AC–Bu (50/50) (———); guar AC–Bu (60/40) (· · · · · ·); guar AC–Bu (70/80) (- - - - -); guar AC–Bu (80/20) (·—·—·).

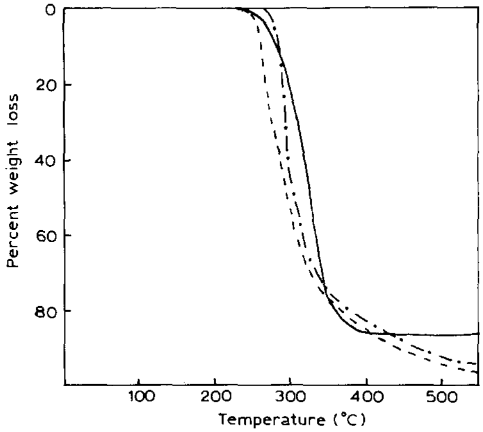

Fig. 3. Thermogravimetry of guar gum esters: guar acetate (———); guar propionate (- - - - -); guar butyrate (·—·—·).

very high. The maleates of the guar gum esters (guar gum acetate, guar gum propionate and guar gum butyrate) are degraded in two steps.

In order to estimate the kinetic parameters it was assumed that the reaction obeys first-order kinetics and eqn. (1) was used

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kC \tag{1}$$

where C is the concentration of the reactant, t is the time and k is the rate constant.

The van't Hoff equation for the temperature coefficient of the equilibrium constant (K_c) of a reaction is

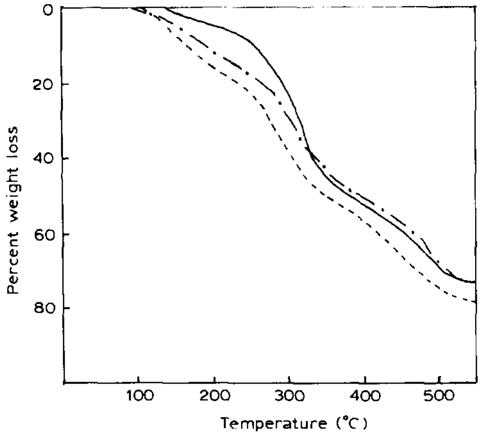

Fig. 4. Thermogravimetry of guar gum esters: maleate of guar acetate (———); maleate of guar propionate (- - - - -); maleate of guar butyrate (·—·—·).

TABLE 2

Temperature characteristics of guar gum esters

Ester	T_0 (K)	T_{10} (K)	T_{max} (K)	T_s (K)	IPDT (K)	Percent residue at 550 ° C	E_1 (kJ mol^{-1})	E_2 (kJ mol^{-1})
Guar gum	508	548.0	563	598.0	617	94.0	218.6	–
GG acetate	496	555.5	603	590.5	615	86.0	92.4	–
GG propionate	515	538.0	558	588.0	611	97.0	82.4	–
GG butyrate	539	558.0	568	573.0	596	94.0	50.2	–
GG AC–Bu (80/20)	477	548.0	588	578.0	606	87.0	142.9	–
G AC–Bu (70/30)	477	543.0	583	573.0	599	94.5	99.9	–
GG AC–Bu (60/40)	477	528.0	553	570.5	594	96.0	94.0	–
GG AC–Bu (50/50)	481	535.5	563	565.5	588	93.0	60.2	–
GG succinate	379	458.0	503	523.0	556	82.0	54.7	–
GG maleate	413	465.5	528	528.0	561	85.0	67.7	–
Maleate of GG AC	403	525.5	593, 748	668.0	657	73.0	38.0	56.0
Maleate of GG Pr	378	440.5	568, 713	653.0	649	78.5	28.8	48.1
Maleate of GG Bu	358	463.0	588, 763	623.0	623.0	73.0	23.4	48.9

$d \log K_c/dT = \Delta E/RT^2$

The law of chemical equilibrium relates the equilibrium constant to a ratio of rate constants [i.e. $K_c = (K$ (forward reaction)$/K$ (backward reaction))]. Thus, Arrhenius [11] suggested that a reasonable equation for the variation of the rate constant with the temperature is given by

$d \log K/dT = E_a/RT^2$

and by integration

$\ln K = -E_a/RT + \ln A$

Thus a plot of log K against the reciprocal of the temperature is a straight line of slope equal to $-E_a/2.303R$, where E_a is the activation energy and R is the gas constant. Table 2 indicates the activation energy values of the experimental samples. It is clear that the activation energy E_a for the degradation of guar gum is highest, i.e. 218.6 kJ mol^{-1}. Substitution of guar gum decreases the values of E_a. This means that the degradation rates of guar gum esters are faster than guar gum. It is also observed that an increase in the chain length of substitution decreases the value of E_a, i.e. the degradation rate becomes faster as the chain length of substitution increases. The degradation rate of the esters having an end carboxyl group is high in the case of succinate and maleate. However the maleates of the guar gum esters (acetate, butyrate and propionate) degrade in two steps having an initial rapid degradation step followed by a slower one.

In order to compare the TGA data of various polymer samples of related structure (or polymers related in some other way) certain temperature parameters are evaluated from TGA data. The temperature parameters such as T_0 (initial decomposition temperature), T_{10} (temperature for 10% weight loss), T_{max} (temperature for maximum rate of decomposition) were determined and are given in Table 2.

T_0, T_{10} and T_{max} are single features and therefore, to get a quantitative picture of the relative stability of guar gum and its esters, the half volatization point (T_s) and the integral procedure decomposition temperature (IPDT) were calculated [12] and are listed in Table 2. IPDT represents the overall nature of the TGA curve for the temperature range 25–550 °C. T_s is the temperature at which half of the ultimate weight loss has occurred. The ultimate weight loss was measured at 550 °C, beyond which the thermograms were observed to level out, indicating completion of the degradation. It was observed that T_s and IPDT values are highest for the maleates of the guar gum esters, suggesting their high thermal stability. Esterification of guar gum in the presence of aliphatic acid anhydride or in the presence of dicarboxylic acid anhydride decreases the thermal stability of guar gum. Thus, the nature of the substituent groups in guar gum esters has an important influence on the stability of the esters and the following order of stability has been noted: maleate of guar gum acetate > maleate of guar gum propionate > maleate of guar gum butyrate > guar gum acetate > guar gum propionate > guar gum acetate–butyrate (80/20) > guar gum acetate–butyrate (70/30) > guar gum acetate–butyrate (60/40) > guar gum acetate–butyrate (50/50) > guar maleate > guar succinate. This observation suggests that no general relationship exists between the stability of the ester and the size of the substituent group attached to the guar gum chains. This may be due to the irregular trend in the degree of substitution of guar gum esters.

CONCLUSIONS

In the esterification of guar gum, the nature and the length of the substituent plays on important role. The reactivity of dicarboxylic acid anhydrides towards esterification is greater than the reactivity of aliphatic acid anhydrides. In the case of aliphatic acid anhydrides, the reactivity towards esterification decreases as the chain length of the substituent increases. Thermogravimetric analysis shows that esterification of guar gum increases its degradation rate and decreases its thermal stability, with the exception of the maleates of the guar esters.

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