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The effects of methylparaben on the gelatinization and thermal decomposition of corn starch

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This paper was written to honor Dr. David Dollimore on the occasion of his 70th birthday.

Abstract

The effects of methylparaben, frequently used preservative, on the gelatinization and solid state decomposition of corn starch were determined. It was observed that methylparaben causes a decrease in the gelatinization temperature of the starch by up to 14.8°C. The starch was shown to degrade in two consecutive reactions, an initial dehydration, followed by the formation of a carbonaceous residue. The decomposition was altered by the methylparaben, as suggested by an increase in the temperature of the dehydration reaction, indicating that a higher temperature was required to drive off the bound water. The activation energy for the major decomposition was also higher when the preservative was present. The methylparaben was shown to evaporate via a zero-order kinetic process, with an increasing activation energy in the presence of corn starch. The melting point was unaffected. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Starch is frequently used by the food and pharmaceutical industries in a gelatinized form. Gelled starch is more digestible and has a more pleasing taste than raw starch. It effects the texture of foods by absorbing water and increasing the viscosity of the solution. It provides a matrix in which drugs can be dispersed. The extent of gelatinization and the gelatinization temperature can be affected by many factors, including fat content, amylose content and granule size. The use of food additives, especially preservatives, are very common in the food industry. The effects of a commonly used preservative, methylparaben, on the gelatinization and degradation of corn starch are examined in this study, using thermal analysis with a rising temperature program. This information could be of use in applications to starch containing foods.

Starch granules are composed of two main components, amylose and amylopectin. Amylose is a linear polymer of glucose molecules, connected by $\alpha(1 \rightarrow 4)$ linkages in a left handed helix. Amylopectin has extensive branching, via $\alpha(1 \rightarrow 6)$ linkages, in addition to the $\alpha(1 \rightarrow 4)$ linkages. Some amylose molecules may also branch. The ratio of amylose and amylopectin is important to the gelling and pasting properties of starch. Most of the gelling properties are due to amylose, which precipitates in aqueous solution to initiate gelatinization when heated. Due to branching, amylopectin is much more stable than amylose, so

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gelatinization occurs at a slower rate and a higher concentration is required. Gelatinization usually occurs over a range of 5–10°. The gelatinization temperature of corn starch is usually in the range of 62–72°C [1].

Solid state reactions include phase transitions such as melting, evaporation and sublimation, as well as decomposition reactions, resulting in the production of different compounds [2]. Thermal analysis can be used to monitor these reactions by determining the rate of mass loss as the substance undergoes the process, using simultaneous TGA–DTA with a rising temperature program. The specific rate constants and the kinetic mechanism are determined with experimental data obtained from the TGA plot of percentage mass loss versus time or temperature and the Differential thermal analysis (DTG) plot of rate of mass loss ($\mathrm{d}m/\mathrm{d}t$) versus time or temperature [3]. The specific rate constants are determined by Eq. (1):

$$k = \frac{\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\beta\right]}{\mathrm{f}(\alpha)}, \qquad (1)$$

where α is equal to the fraction reacted and β is equal to the heating rate, in degrees per second [4]. The term $\mathrm{f}(\alpha)$ can be obtained from tables of different mechanisms. For first order mechanisms, it is equal to $(1-\alpha)$ [3]. For zero order reactions, the specific rate constants are calculated by dividing $\mathrm{d}m/\mathrm{d}t$ by the cross sectional area of the sample crucible. The Arrhenius equation is used to calculate the activation energy:

$$k = A\,\exp\left(\frac{-E_\mathrm{a}}{RT}\right), \qquad (2)$$

or

$$\ln k = \ln A - \frac{E_\mathrm{a}}{RT}, \qquad (3)$$

where k the specific rate constant, E_a the activation energy, R the gas constant, A the pre-exponential term and T the Kelvin temperature [4]. A plot of $\ln k$ versus $1/T$ is linear, with a slope equal to E_a/R and an intercept equal to A. DTA can be used to determine the temperature range at which a reaction, such as gelatinization or melting, takes place. It also characterizes the reaction as endothermic or exothermic.

In this study, simultaneous TGA–DTA is used to determine the effects of methylparaben on a food and pharmaceutical grade native corn starch, Pure-Dent® B700. The gelatinization and decomposition temperatures of the preserved samples and untreated samples are compared. The kinetic mechanisms of decomposition are determined. The Arrhenius constants are calculated for methylparaben with and without corn starch.

2. Experimental

2.1. Reagents

The Pure-Dent® B700 corn starch [$H(C_6H_{10}O_5)_nOH$] was a gift from the Grain Processing Corporation. It is a food and pharmaceutical grade starch with a moisture content of 9.0–12.5%, as stated on the product data sheet provided by the manufacturer. The methylparaben ($HOC_6H_4CO_2CH_3$) was obtained from Aldrich Chemical, 99% purity.

2.2. Thermal analysis

The thermal analysis equipment consisted of a simultaneous TGA–DTA unit, TA Instruments Model Number 2960, with Thermal Analyst 2000 software, TGA–DTA-1.0, V1.0B. The samples were analyzed in a platinum crucible. An empty platinum crucible served as a reference. A heating rate of 10°C/min was used during all experiments. The samples were analyzed in dry nitrogen at 100 ml/min. The gas flow rate was monitored with an electronic flowmeter.

2.3. Procedure

Three runs were completed with either the pure methylparaben or corn starch, to serve as control samples. Preserved samples were made by mixing 2 g of corn starch and varying amounts of methylparaben, with sufficient distilled water to form a damp paste. The percentage of methylparaben used was larger than used in practice in order to obtain optimal resolution on the available thermal analysis equipment. The samples were thoroughly mixed and allowed to dry at ambient temperature for one week. The dried samples were ground to a fine powder. Each sample was analyzed three times to assure consistent result. Table 1 contains the composition of each sample.

Table 1
Composition of corn starch and methylparaben pastes

Sample	Corn starch (g)	Methylparaben (g)
1	2.0058	0.5045
2	2.0041	1.0043
3	2.0088	2.0075

3. Results and discussion

3.1. Methylparaben

Pure methylparaben was analyzed to obtain baseline data. The sample size varied from 10.0647 to 10.7369 mg. The DTA plot exhibited two endotherms that corresponded to melting and evaporation. The experimental data is summarized in Table 2. A very small mass loss was observed at the melting point, which probably is the result of the loss of air or water from the crystal lattice [5]. There was complete mass loss after the melting point, as the sample evaporated. The DTG plot contained one very small peak, which was the result of the mass loss at the melting point. A large, sharp peak, which abruptly returned to the zero baseline, was also observed. This peak is characteristic of the zero order kinetic process of evaporation. The maximum rate of mass loss was determined and the results can be found in Table 2. Fig. 1a and b contains a representative TGA, DTG and DTA plots of methylparaben, heated 10°C/min in dry nitrogen.

The specific rate constants of evaporation were calculated by dividing d*m*/d*t* by the cross sectional area of the sample crucible (0.2951 cm^2). The plot of ln k versus $1/T$ was linear. The activation energy and the pre-exponential term were calculated from the slope and the intercept, respectively. The results are summarized in Table 3. A representative plot of ln k versus $1/T$ can be found in Fig. 2.

3.2. Pure-dent® B700 corn starch

The corn starch was analyzed at 10°C/min to 500°C. The sample size varied from 6.1597 to 6.6774 mg. The TGA curve in Fig. 3a contained three distinct regions. The mass decreased approximately 11% in the temperature range from about 50 to 125°C. This is indicative of the loss of adsorbed water from the gel structure. The mass then remained stable until 281°C, when it rapidly decreased as the starch decomposed to a carbonaceous residue. The mass loss then stabilized after about 350°C was reached. At 500°C, 10–15% of the original mass remained, in the form of a black residue. The DTG curve in Fig. 3a contained a small peak, which corresponded to a small mass loss at 281°C. A large, relatively symmetrical peak was observed immediately following the first peak, representing the rapid degradation of the starch.

Table 2
Experimental TGA–DTA data for methylparaben in N_2

Run	Melt endotherm[a] (°C)	Evaporation endotherm[a] (°C)	Maximum d*m*/d*t* ($mg\ min^{-1}$)
1	127.9	227.9	3.028
2	127.9	228.9	3.164
3	127.9	228.9	3.201
Mean	127.9	228.5	3.131

[a] Temperatures noted are peak temperatures.

Table 3
Arrhenius constants of methylparaben

Run	Equation	R^2	E_a ($kJ\ mol^{-1}$)	A ($mg\ min^{-1}\ cm^{-2}$)
1	$y = -8369.8x + 19.186$	0.9989	69.59	2.2×10^8
2	$y = -8324.1x + 19.103$	0.9987	69.21	2.0×10^8
3	$y = -8384.6x + 19.239$	0.9988	69.71	2.3×10^8
Mean	–	–	69.50	2.2×10^8

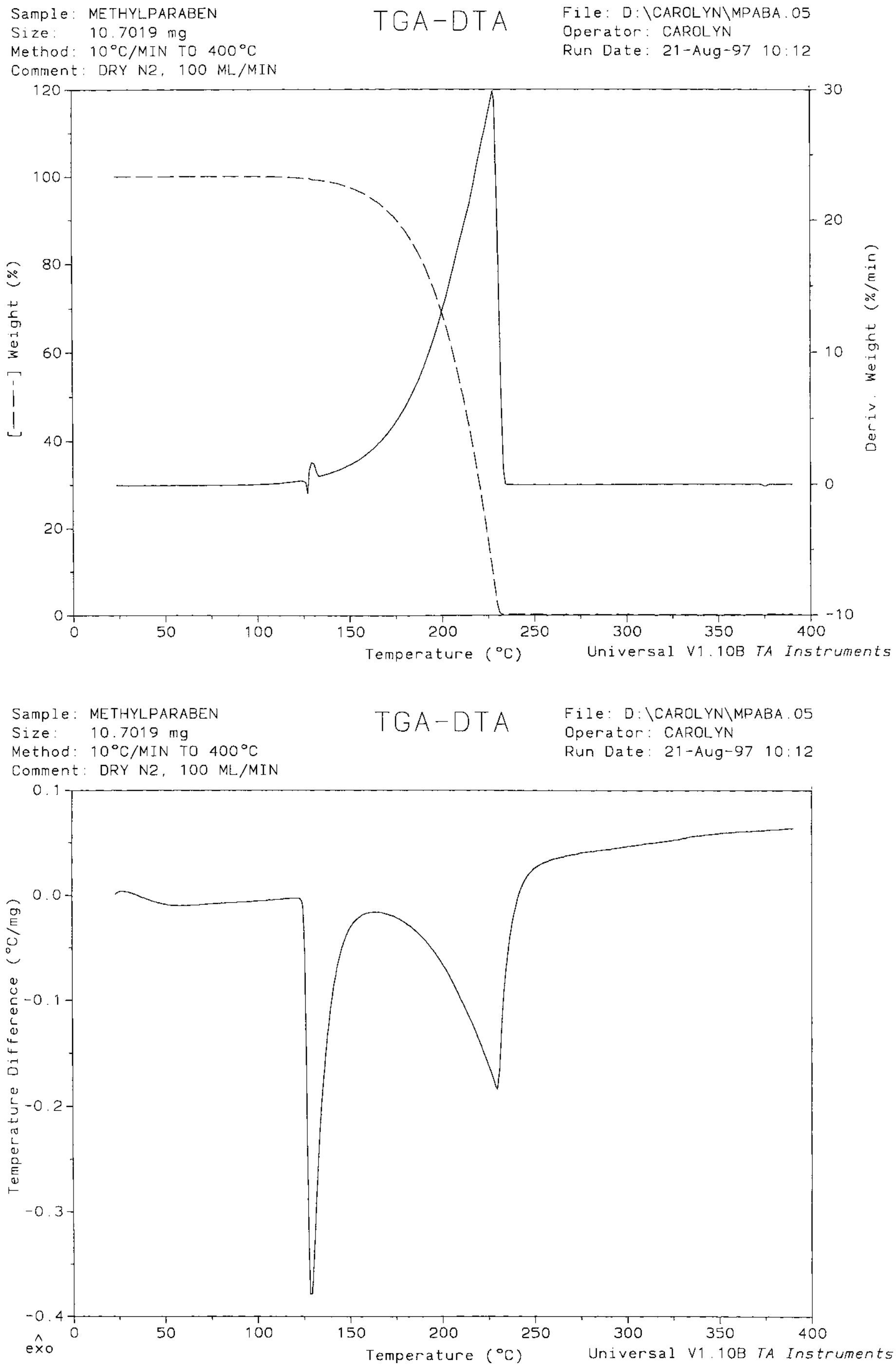


Fig. 1. (a) Representative TGA, DTG plots of methylparaben. (b) Representative DTA plot of methylparaben.

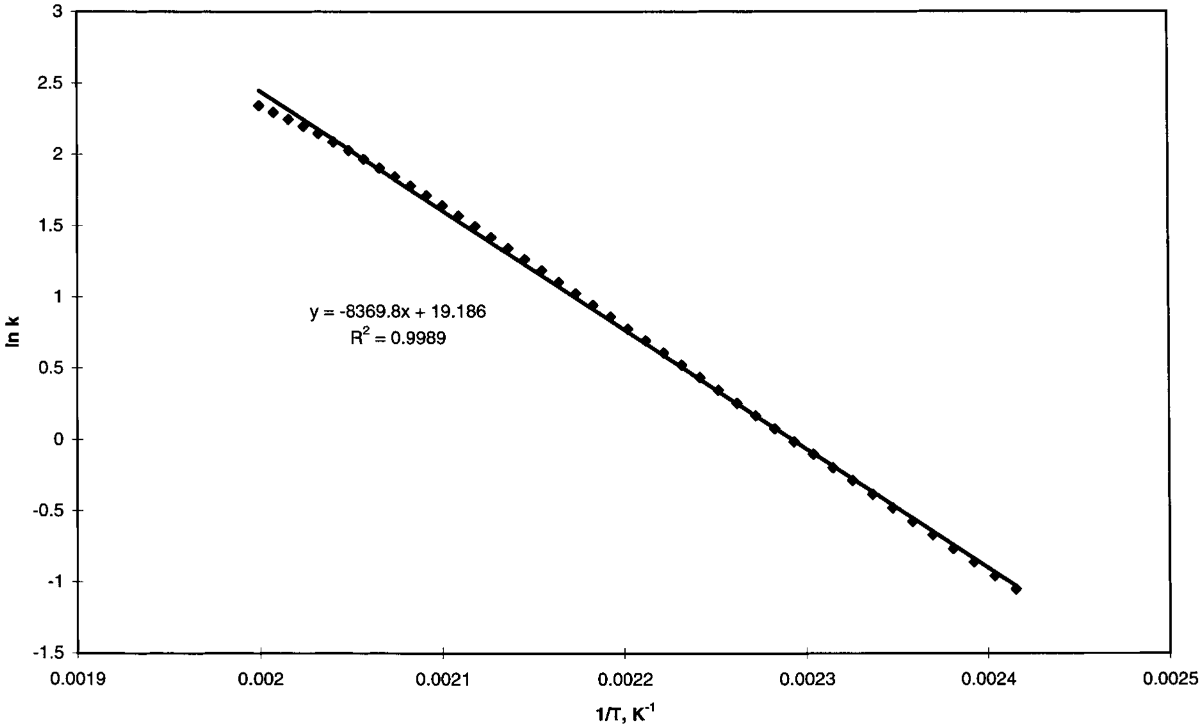


Fig. 2. Kinetic plot of ln k versus $1/T$ for methylparaben.

The DTA curve in Fig. 3b consisted of three peaks. The first peak was observed at 61°C and corresponds to the loss of free water and possible gelatinization of the starch. A small peak was observed at 281°C, the temperature at which mass loss was initiated. A large peak was observed at 310°C, when d*m*/d*t* was the greatest. The presence of the two endotherms and two DTG peaks (one very minor) indicates that two consecutive reactions occur. Bound or structural water is initially lost, followed by the formation of a carbonaceous residue. The experimental data is summarized in Table 4. In order to select the appropriate kinetic expression, the shape of the TGA plot was considered, using the method of Dollimore et al. [4,6–9]. The initial reaction temperature (T_i) and the final reaction temperature (T_f) were observed to be diffuse, narrowing down the mechanism to first order. The specific rate constants were calculated for the major decomposition reaction using the appropriate expression and plots of ln k versus $1/T$ were constructed. To confirm that the mechanism was first order, the geometrical and diffusion expressions were also utilized. The first order mechanism gave the most linear response, with the regression coefficient closest to unity. The degra-

Table 4
Experimental TGA–DTA data for pure-dent B700 corn starch in N_2

Run	Endotherm 1[a] (°C)	Endotherm 2[a] (°C)	Endotherm 3[a] (°C)	Maximum d*m*/d*t* (mg min^{-1})
1	61.3	281.3	316.1	1.587
2	61.3	281.3	316.1	1.718
3	61.3	281.3	316.1	1.630
Mean	61.3	281.3	316.1	1.645

[a] Temperatures noted are peak temperatures.

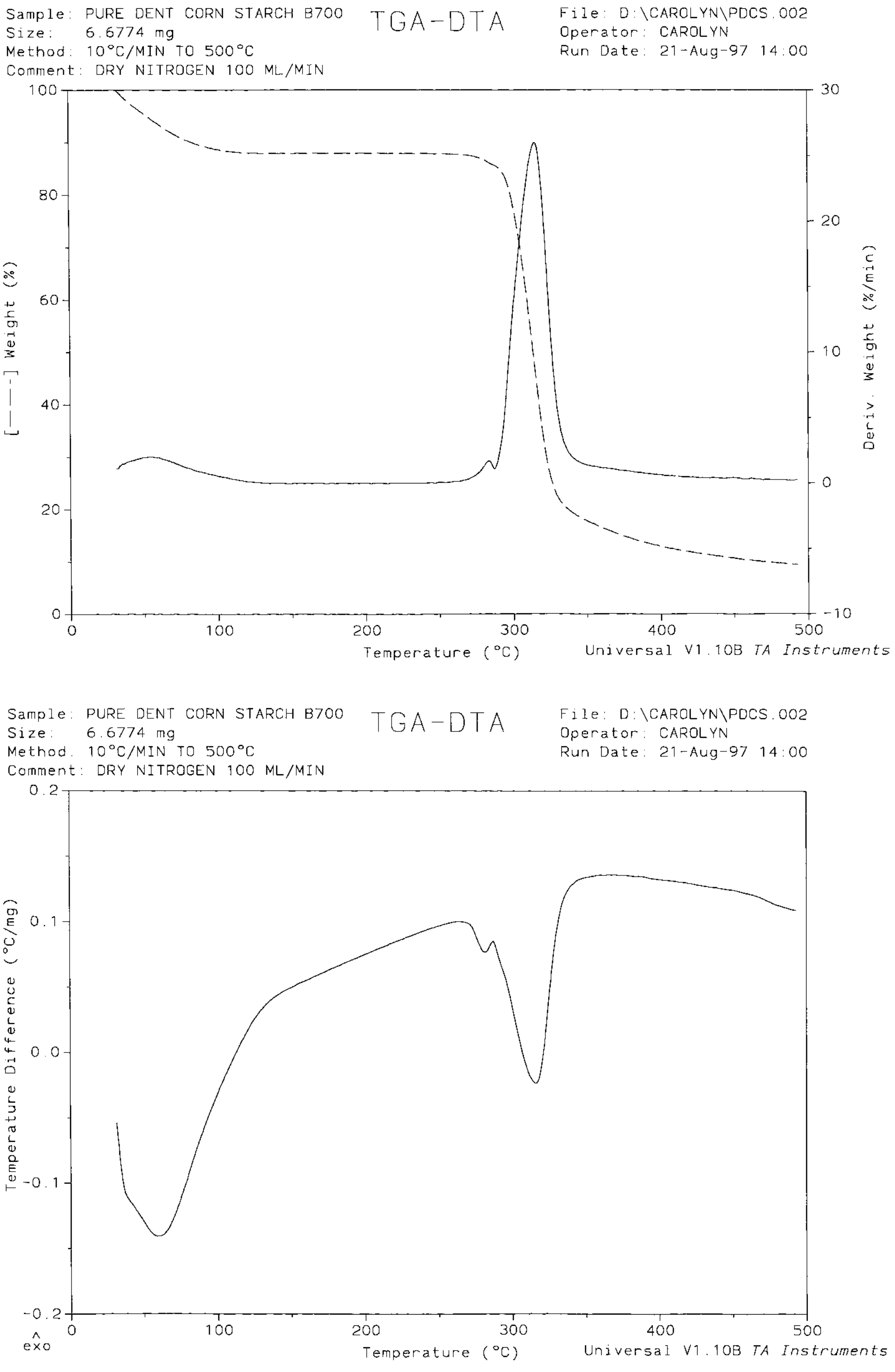


Fig. 3. (a) Representative TGA, DTG plots of corn starch. (b) Representative DTA plot of corn starch.

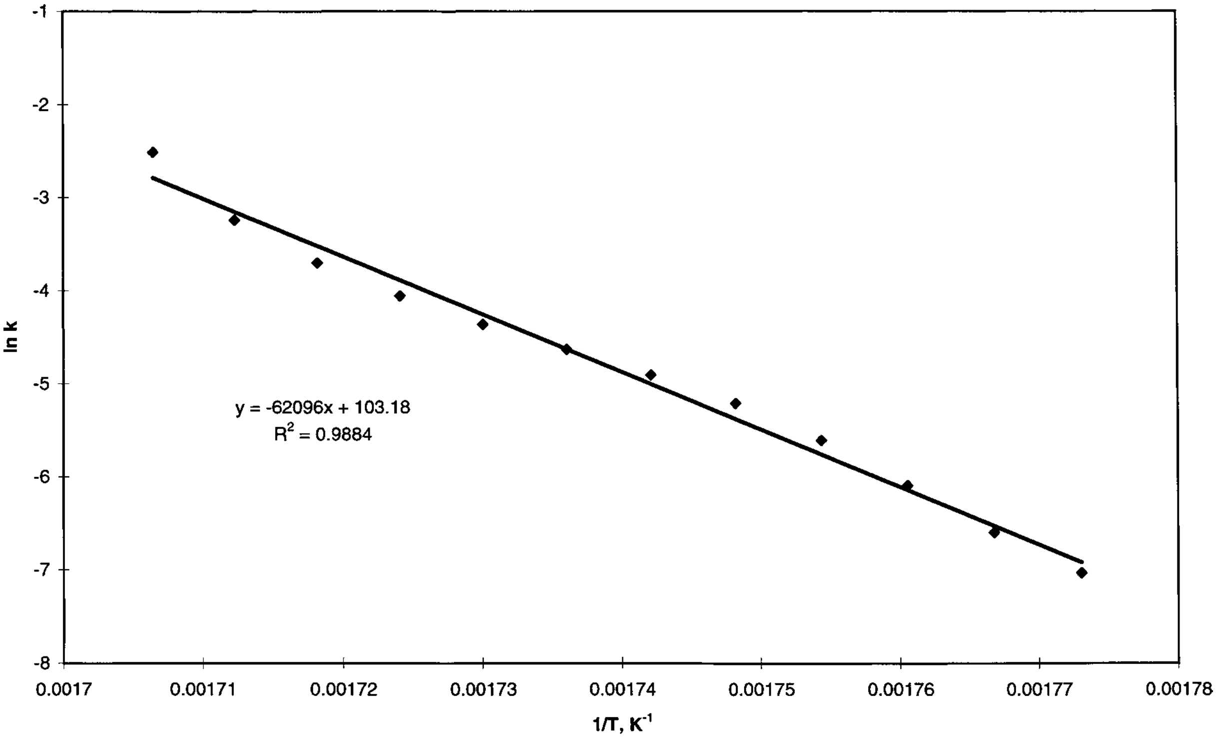


Fig. 4. Kinetic plot of ln k versus $1/T$ for corn starch.

dation of starch was also designated as a first order process by others workers, using different methods [10]. A sample kinetic plot can be found in Fig. 4.

3.3. Corn starch and methylparaben mixture

The methylparaben and corn starch mixtures were analyzed in dry nitrogen at 100 ml/min, using a heating rate of 10°C/min. Three runs were completed with the sample containing 0.5045 g of methylparaben. The sample size varied from 7.5983 mg to 8.2389 mg. The experimental data is summarized in Table 5. Representative TGA, DTG and DTA plots can be found in Fig. 5a and b. The DTA plot of temperature difference versus temperature contained five endotherms in all three runs. The first endotherm corresponds to starch

Table 5
Experimental TGA–DTA data for starch and methylparaben mixtures in N_2

Run[a]	Endotherm 1[b] (°C)	Endotherm 2[b] (°C)	Endotherm 3[b] (°C)	Endotherm 4[b] (°C)	Endotherm 5[b] (°C)
1	52.9	127.4	183.9	283.7	316.1
2	52.9	127.4	185.1	282.5	316.1
3	57.7	127.4	188.7	282.5	316.1
4	60.1	127.4	194.7	283.5	316.1
5	55.3	127.4	191.1	283.7	316.1
6	45.7	127.4	191.1	283.7	316.1
7	44.5	127.4	199.5	289.1	313.7
8	46.9	127.4	200.3	293.3	314.9
9	48.0	127.4	201.9	291.3	313.7

[a] Runs 1–3 = 0.5 g methylparaben; Runs 4–6 = 1 g methylparaben; Runs 7–9 = 2 g methylparaben.

[b] Temperatures noted are peak temperatures.

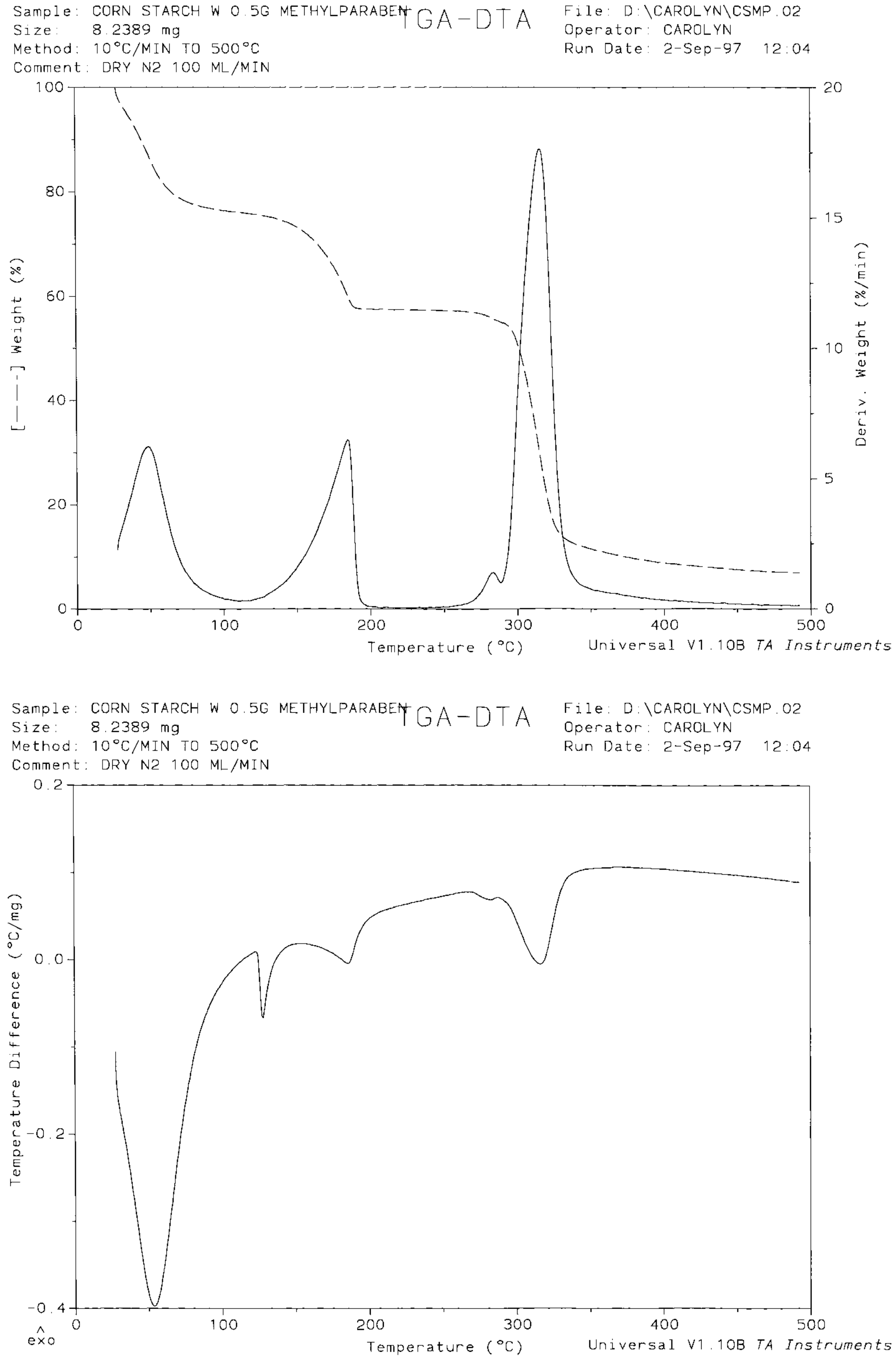


Fig. 5. (a) Representative TGA, DTG plots of methylparaben, 0.5 g with corn starch. (b) Representative DTA plot of methylparaben, 0.5 g with corn starch.

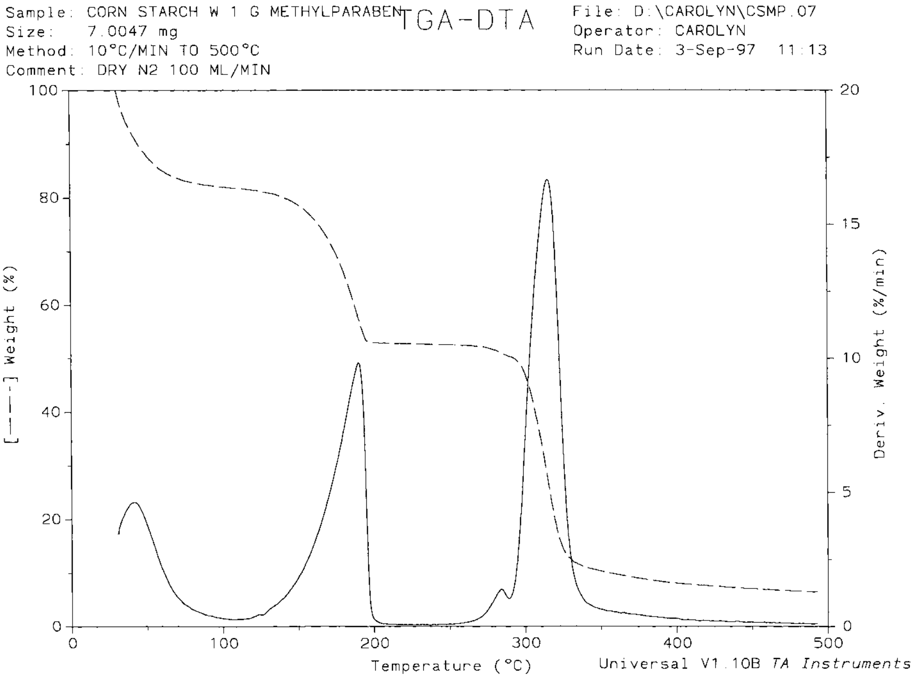
gelatinization and loss of adsorbed water. The second endotherm represents the melting point of the methylparaben. The consistent temperature of the melting point suggests that methylparaben remains in a solid state, when added to a starch and water slurry, rather than dissolving. The third endotherm corresponds to the evaporation of the liquid methylparaben from the corn starch gel. The fourth and fifth endotherms represent the loss of structural water and the degradation of the starch to a carbonaceous residue, respectively.

The curve of weight percentage versus temperature contained three distinct plateaus. The first plateau represented a 12–25% mass loss in the temperature range of 100–150°C, as the result of water loss from the mixture. This mass loss could be avoided by drying the samples in an oven, but the starch will gelatinize at temperature higher than 60°C, so important experimental data will be lost. The second plateau, occurring in the temperature range of 190–280°C, represented about a 19% mass loss as the methylparaben evaporated. The final plateau occurred after about 350°C, as the corn starch degraded. At 500°C, 6.7–7.6% of the initial mass remained as a black residue. The DTG plots contained three large peaks and one small peak, representative of the mass losses discussed previously.

Three runs were also completed with the mixture containing 1.0043 g of methylparaben, using the same experimental conditions. The sample size varied from 6.7037 mg to 8.1027 mg. Representative TGA, DTG and DTA plots can be found in Fig. 6a and b. Endotherms were observed at about the same temperatures, as in the previous runs. The experimental data is summarized in Table 5. The second and third endotherms have increased areas, confirming that they are the result of the melting and evaporation of the methylparaben. The TGA plot contained plateaus in the same temperature range, as observed in the previous runs. The mass loss from the evaporation of the methylparaben was 53–57% of the initial mass, as expected. At 500°C, 7–9% of the initial mass was present as a carbonaceous residue.

The final set of samples contained 2.0075 g of methylparaben. The same conditions were used and the sample size varied from 6.8132 mg to 6.9820 mg. A representative TGA, DTG and DTA plots can be found in Fig. 7a and b. Similar endothermic behavior was observed on the DTA plot, with the following exceptions. The methylparaben peaks had greater areas than in the previous set of samples, as expected. The small, initial endotherm that corresponds to the dehydration of corn starch (Endotherm 4) was barely detectable in all three runs. The TGA plot contains plateaus in the same temperature ranges. On the DTG plots for these samples, the maximum rate of mass loss is much greater for the methylparaben than the starch. In the other samples, the opposite occurs. This was expected since the ratio of methylparaben to corn starch is equal. The volatile component was expected to easily evaporate, resulting in the greater mass loss.

When the experimental data is compared, it can be observed that the temperatures of Endotherm 4 (loss of bound water) increased as the amount of methylparaben increased. It was at the lowest temperature when no methylparaben was added. When 2 g of methylparaben was added, a difference of 10°C was observed. The area of the peak also decreased as the amount of preservative was increased. This suggests that methylparaben, specifically in high concentrations, affects the degradation of corn starch by increasing the temperature required to drive off the bound water. The large peak, corresponding to the degradation of the corn starch (Endotherm 5), remained constant, until the highest concentration of methylparaben was added. It decreased from 316.1 to 314.1°C. The endotherm that corresponded to desorption (Endotherm 1) was observed at lower temperatures when the methylparaben was present. It occurred consistently at 61.3°C in the control samples. When the preservative was added the temperature steadily decreased. This suggested that adsorbed water was more readily lost, indicating a competition between the water and the methylparaben to adsorb on the granular surface. This is significant in applications where desorption and gelatinization is crucial such as dough making or thickening. The melting point of methylparaben was unaffected by the presence of the corn starch. This was unexpected since the non-volatile starch might be thought to depress the melting point of the methylparaben in a simple colligative process. For starch and preservative mixtures, the temperature of the evaporation endotherm (Endotherm 3) increased as the amount of methylparaben increased, suggesting that the presence of the starch inhibits the evaporation of the methylparaben,



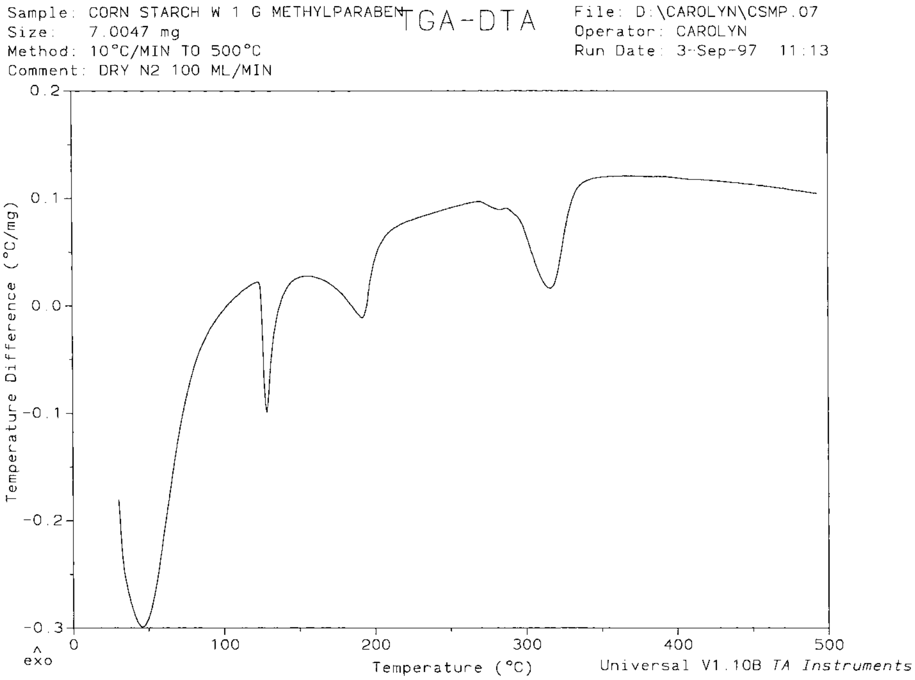
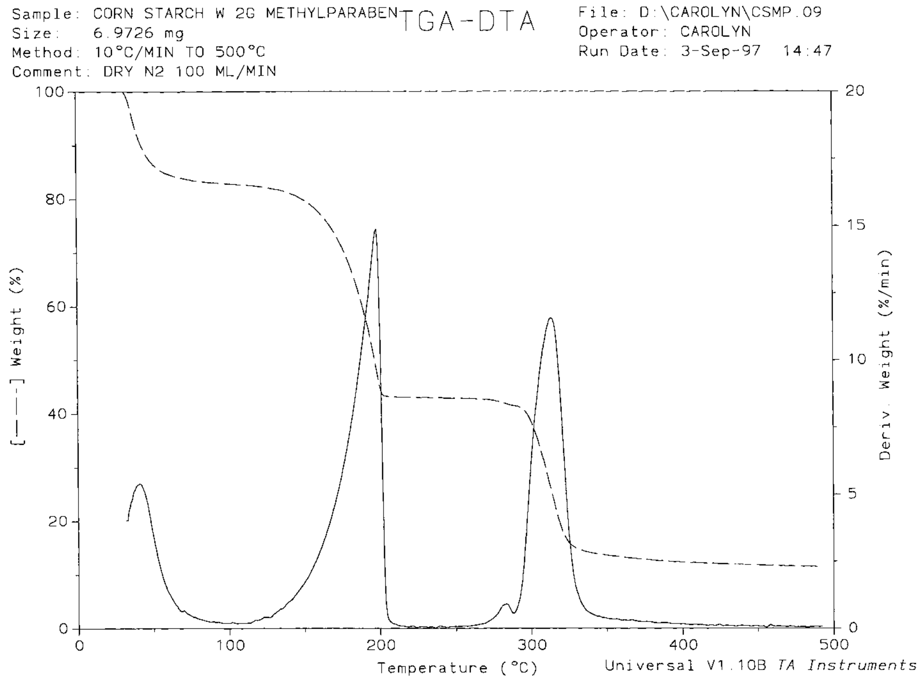


Fig. 6. (a) Representative TGA, DTG plots of methylparaben, 1.0 g with corn starch. (b) Representative DTA plot of methylparaben, 1.0 g with corn starch.



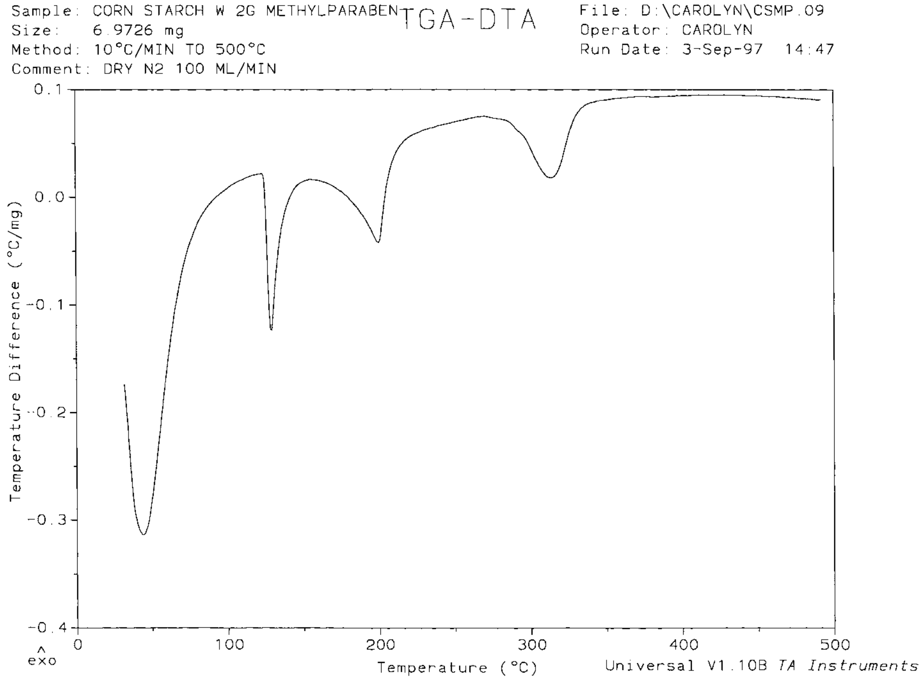


Fig. 7. (a) Representative TGA, DTG plots of methylparaben, 2.0 g with corn starch. (b) Representative DTA plot of methylparaben, 2.0 g with corn starch.

since the available surface area is decreased by the presence of the starch granules.

The activation energies of evaporation were calculated for the mixtures, using data obtained from the second peaks of the DTG plots and the method described previously. Comparing the activation energies for the evaporation of methylparaben, it can be observed that the samples mixed with the starch had higher activation energies than the control samples. This supports the theory that the starch inhibits evaporation, because more energy is required to evaporate a smaller amount of material. The activation energy increased as the amount of methylparaben was increased. This results from the loss of available surface area for the zero order process.

The activation energies for the first order decomposition of the starch in the mixtures were also calculated, using data obtained from the fifth peaks of the DTG plots and the method described previously. The activation energies were 514.56, 534.83 and 546.34 kJ mol^{-1}, for the 0.5, 1.0 and 2.0 g methylparaben samples, respectively. As the amount of preservative increased, the activation energy increased, suggesting that the material alters the kinetic process in some manner, either by inhibition through an alteration in the reaction interface or by changing the process, during all or part of the degradation.

4. Conclusions

The effect of food additives should be considered before using them in cooked or baked products. The thermal behavior is easily studied using simultaneous TGA–DTA with a rising temperature program. It was observed in this study that the desorption, gelatinization and degradation of corn starch were effected by the presence of methylparaben, in the following manners. The desorption and gelatinization temperature of the starch was decreased by 14.8°C. The performance of the starch as a thickener and texturizer may be altered if methylparaben was used in relatively high concentrations. The corn starch degraded via a first order process, which was preceded by the loss of bound water. The dehydration occurred at a higher temperature, when the methylparaben was present. The dehydration endotherm had a smaller area, indicating that the extent of the reaction decreased. The activation energy of starch decomposition was higher when the preservative was added. The methylparaben evaporated via a zero order kinetic mechanism. The activation energy of evaporation was increased by the presence of the starch, because there was less available surface area for evaporation, due to the presence of the starch granules. However, the melting point was unaffected.

References

[1] D.R. Lineback, Bakers digest 58 (1984) 16.
[2] M.E. Brown, D. Dollimore, A.K. Galwey, in: C.H. Bamford, C.F. Tipper (Eds.), Comprehensive Chemical Kinetics, Reactions in the Solid State, vol. 22, Elsevier, Amsterdam, 1980, pp. 1–9, 12–15, 115–117.
[3] M.E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London, 1988, pp. 127–134.
[4] D. Dollimore, P. Tong, K.S. Alexander, Thermochimica Acta 282/283 (1996) 13–27.
[5] D. Dollimore, C. O'Connell, Thermochimica Acta 324 (1998) 33–48.
[6] D. Dollimore, T.A. Evans, F.A. Wilburn, Thermochimica Acta 188 (1991) 77–85.
[7] D. Dollimore, T.A. Evans, Y.F. Lee, F.A. Wilburn, Thermochimica Acta 196 (1992) 255–265.
[8] D. Dollimore, T.A. Evans, Y.F. Lee, F.A. Wilburn, Thermochimica Acta 198 (1992) 249–257.
[9] D. Dollimore, J. Thermal Analysis 38 (1992) 111–130.
[10] A.A.A. Soliman, N.A. El-Shinnawy, F. Mobarak, Thermochimica Acta 296 (1997) 149–153.