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EFFECT OF POLY(ETHYLENE GLYCOL) 4000 AND POLY(ETHYLENE GLYCOL) 4000 DISTEARATE ADDITIVES ON THE THERMAL DECOMPOSITION OF TAPIOCA STARCH

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ABSTRACT

Incorporation of poly(ethylene glycol) 4000 and poly(ethylene glycol) 4000 distearate into tapioca starch influences the pattern of its thermal degradation. Involvement of free radicals generated by poly(ethylene glycol) decomposition is suggested as a plausible mechanism for the enhancement of the rate of thermal degradation of the starch.

INTRODUCTION

Thermal treatment of starch at moderate temperatures ($< 200\,^{\circ}$C) in acidic, alkaline or neutral conditions is an important industrial process leading to the manufacture of different grades of pyrodextrins [1–10]. Pyrodextrins exhibit a wide range of physical and chemical properties including white dextrins, yellow dextrins and British gums. The chemical changes occurring during the thermal treatment of starch have been the subject of thorough investigations over a long period of time. As a result, the degradation products of pyrolysis of starch at different temperatures and the effect of many inorganic salts as additives on the thermal degradation of starch are known, although the chemical changes occurring during dextrinization of starch are still not fully understood.

Water, carbon dioxide and carbon monoxide constitute the major decomposition products of starch on pyrolysis, whereas furan, 2-methylfuran, 2-furaldehyde, formaldehyde, formic acid, acetaldehyde, acetone, etc. are among the minor decomposition products. Incorporation of certain inorganic salts was found to lower the threshold temperature for the decomposition of starch, and the decomposition products were found to contain increased amounts of carbon dioxide and carbon monoxide. Bryce and Greenwood [11–13] have investigated the kinetics of decomposition of amylomaize starch in the presence of two series of inorganic salts: salts having (i) a common cation, and (ii) a common anion. An apparent

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reduction in activation energy of the order of 10–13 kcal mol^{-1} is reported for the decomposition of these mixtures as compared with that of starch.

The influence of organic additives on the thermal decomposition of starch has not been widely investigated. A recent paper on the thermal degradation patterns of starch grafted with polyacrylonitrile pendent groups [14] reported that the presence of polyacrylonitrile chains appears to have a significant influence on the thermal decomposition of starch. Given the commercial importance of thermally treated starches, the influence of additives on thermochemical changes in starch merits further investigation, and in this paper we report on the effect of poly(ethylene glycol) 4000 (PEG 4000) and poly(ethylene glycol) 4000 distearate (PEGDS 4000) on the thermal decomposition of tapioca starch.

EXPERIMENTAL

Materials

PEG 4000 (LR grade), stearic acid (AR grade), sulphuric acid (AR grade), toluene (LR grade), hexane (LR grade).

Methods

Synthesis of poly(ethylene glycol) distearate

200 g (0.05 mol) of PEG 4000, 56 g (0.2 mol) of stearic acid, 5 ml of concentrated sulphuric acid and 750 ml of toluene were mixed in a 2 l RB flask fitted with a Dean–Stark apparatus. The mixture was refluxed and the water formed was separated continuously. The reaction was continued for 12 h and the volume of toluene reduced to 400 ml by distilling off the excess solvent. The product was precipitated in hexane (2 l), and redissolved in 300 ml toluene, and the mineral acid was neutralized with sodium bicarbonate and further precipitated in hexane (2 l). The solid mass was dried under vacuum at 60 °C to constant weight.

Modification of gelatinized tapioca starch

Tapioca starch (16 g) was suspended in 500 ml of distilled water in a 1 l beaker and heated with constant stirring at 90 °C for 1 h to ensure complete gelatinization. The gelatinized sample was weighed (the volume reduced to ≃ 300 ml owing to evaporation of water) and divided into eight equal parts (each containing 2 g of starch, dry weight). The volumes were made up to 50 ml and the additives PEGDS (100, 200, 400, 600 and 800 mg: samples I–V respectively) and PEG (100 and 800 mg: samples VI and VII respectively) were incorporated in a minimum amount of water. Sample VIII, with no additive, was retained as a control gelatinized product. The samples were stirred for a further 10 min and the water evaporated off to dryness in an oven at 100 °C. Samples I–V contained 5, 10, 20, 30 and 40% PEGDS and samples VI and VII 5 and 40% PEG, respectively, based on dry weight of starch.

Physical mixtures of tapioca starch and modifiers

Mixtures of gelatinized tapioca starch and PEG/PEGDS were prepared by dispersing 2 g quantities of the dry gelatinized starch sample (sample VIII) in solutions of PEGDS (100 and 400 mg: samples IX and X respectively) and PEG (100 and 400 mg: samples XI and XII respectively) in 20 ml of acetone, and evaporating off the solvent to dryness with constant stirring.

Thermogravimetry

Thermogravimetric (TG) analysis was performed using a Du Pont thermal analyser, Model 990. Approximately 12 mg of sample was heated at the rate of 10 °C min^{-1} in a nitrogen atmosphere. The expected weight loss at each temperature for the PEG/PEGDS modified starches was computed from the percentage PEG/PEGDS content in the sample and the individual weight loss, independently, for starch and PEG/PEGDS at that particular temperature, e.g. [Expected weight loss for 20% PEGDS modified tapioca starch at 350 °C] = [Weight loss at 350 °C in TG of tapioca starch] × 0.8 + [Weight loss of 350 °C in TG of PEGDS] × 0.2.

RESULTS AND DISCUSSION

TG curves for the thermal decomposition of gelatinized tapioca starch, PEG 4000 and PEGDS 4000 in nitrogen atmosphere are shown in Fig. 1. Weight losses owing to decomposition at different temperatures are given in Table 1. The initial stage of weight loss for the starch sample (up to 150 °C) is attributed to loss of moisture in the sample, and the weight percentage of moisture was not considered in calculating the weight loss values for the starch samples. The major decomposition weight loss occurs between 300 and 350 °C for starch and between 375 and 450 °C for PEG and PEGDS. The effect of the PEG and PEGDS additives on the thermal decomposition of tapioca starch is indicated by the TG curves for samples I–VII, containing respectively 5, 10, 20, 30 and 40% PEGDS and 5 and 20% PEG by weight with respect to starch in the modified sample. These thermograms are given in Figs. 2 and 3.

A physical mixture of starch and PEGDS or PEG decomposed under pyrolytic conditions through mutually non-interfering mechanisms should give rise to a weight loss pattern that could be computed from the percentage composition of the individual components of the mixture and the weight loss at each temperature on thermal treatment for starch and the

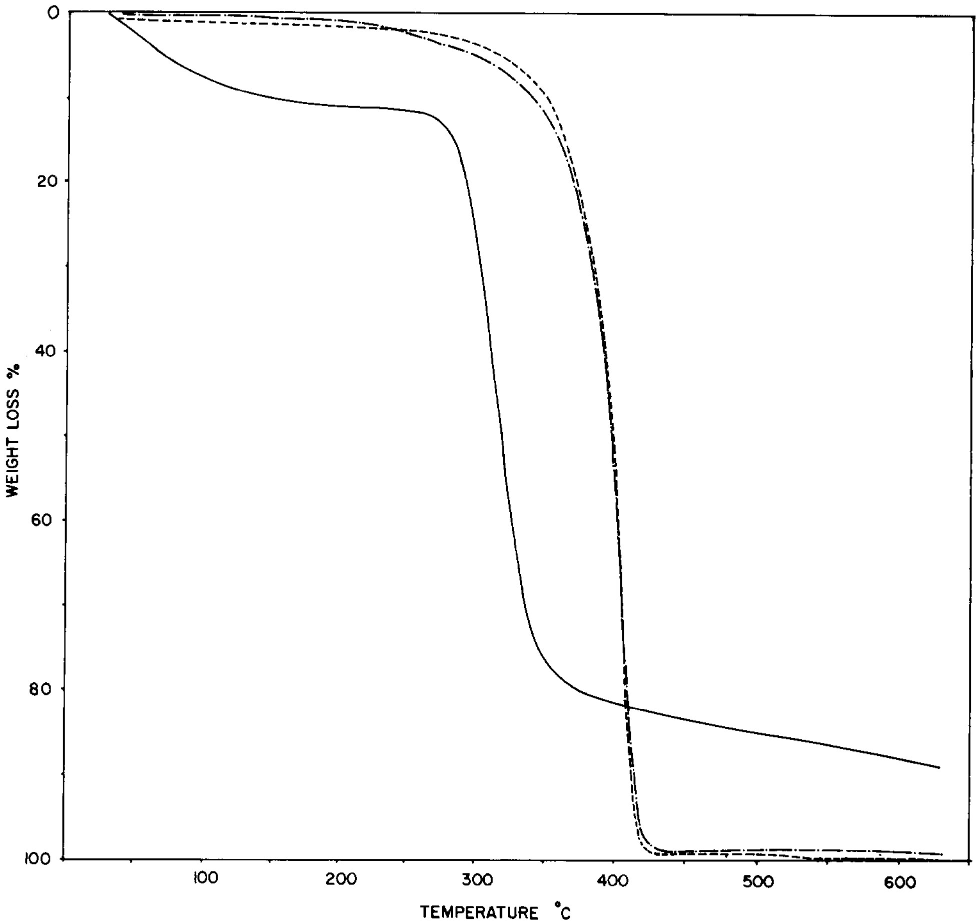


Fig. 1. TG curves for gelatinized tapioca starch (———), PEGDS (·–·–·) and PEG (— — —).

additive ingredients independently. Table 2 compares the weight losses observed for the variously modified starches with the computed values for each composition assuming mutually non-interfering mechanisms for the

TABLE 1

Percentage weight loss during thermal degradation of gelatinized tapioca starch, PEG 4000 and PEGDS 4000

Sample	Temperature (° C)					
	200	250	300	350	400	450
Gelatinized tapioca starch	0	0	11	70	76	79
PEG 4000	0	0.8	2.4	9.3	56.7	98.4
PEGDS 4000	1.2	2.8	6	12.4	64	98

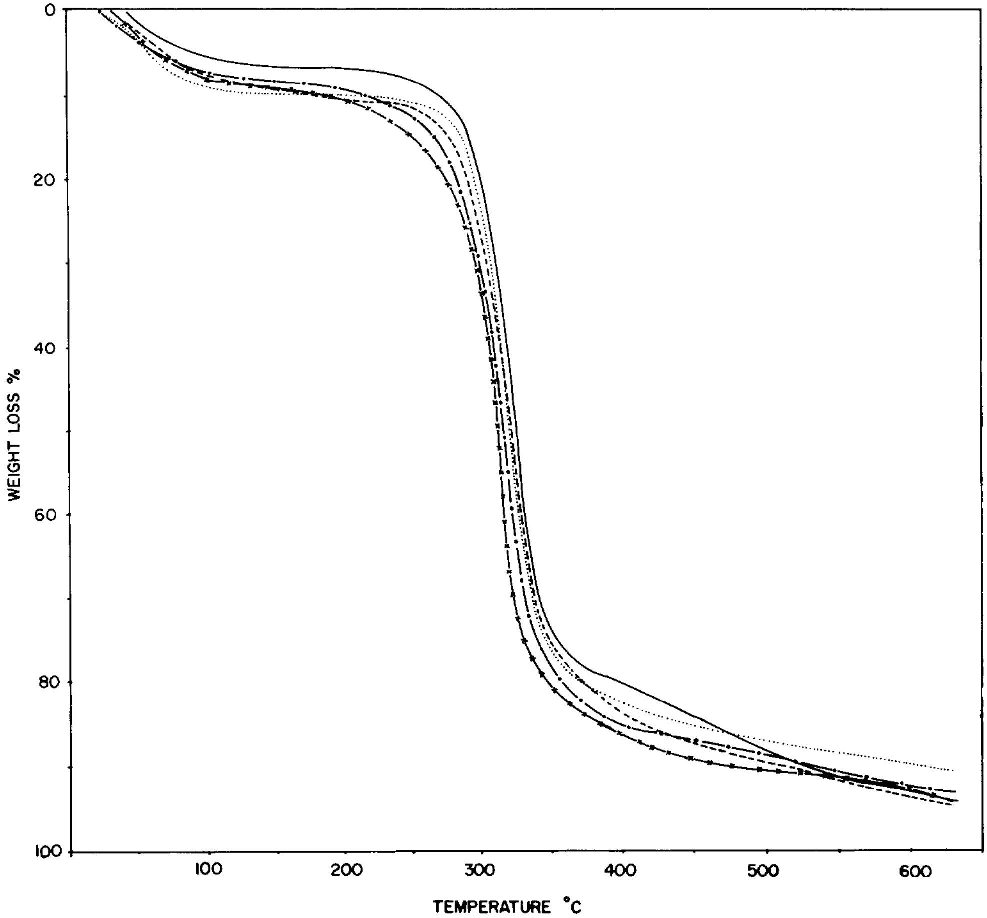


Fig. 2. TG curves for 5 (······), 10 (———), 20 (— — —), 30 (·—·—·) and 40% (×——×) PEGDS modified tapioca starches.

thermal decomposition of the individual components. The degradation of the modified starches can be seen to be faster than expected. The change in the decomposition pattern is most pronounced in the temperature range 250–400 °C. The increase in weight loss increases with the amount of additive, as is indicated by the increase in weight loss at 350 °C (6.2, 13.3, 16.4, 18.5 and 24.2% increase for PEGDS modified starches containing 5, 10, 20, 30 and 40% PEGDS, respectively). Similarly, increases of 4.6 and 23.2% weight loss are observed for the PEG modified starches containing 5 and 40% PEG, respectively. The magnitude of the influence on thermal decomposition appears to be same for PEGDS and PEG, which suggests that the effect may be due to participation of the polyethylene glycol chain segment common to both the sample types in the degradation mechanism.

Figures 4, 5 and 6 give the Coats–Redfern [15] plots for gelatinized tapioca starch, PEG and PEGDS and the various modified starches. Good

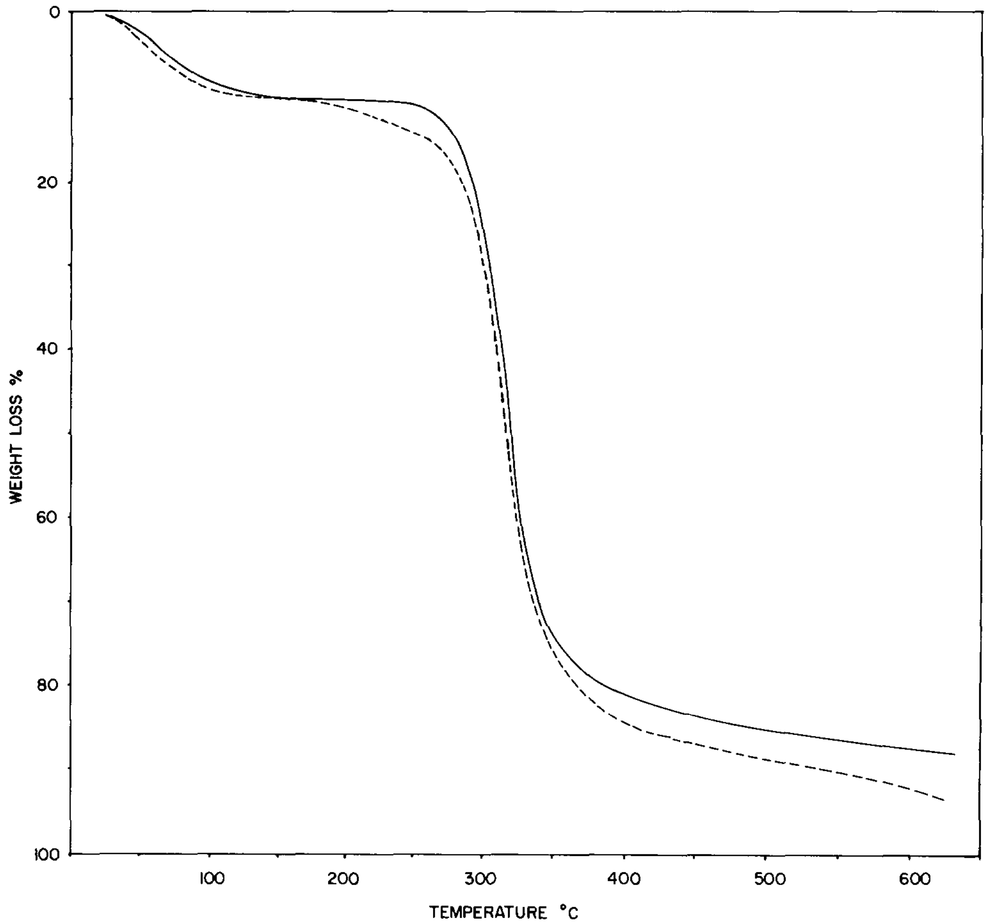


Fig. 3. TG curves for 5% (———) and 40% (— — —) PEG modified tapioca starches.

fits are obtained for the reaction order parameters, $n = 1$. The major decomposition between 200 and 400 °C appears to involve only one stage. The activation energies for the decomposition of the various samples, deduced from the slopes of the Coats–Redfern plots, are given in Table 3. The values obtained indicate a decrease in weight loss with increasing PEGDS or PEG content. This lowering of the activation energy for decomposition explains the increased decomposition at a particular temperature up to 400 °C with increased amounts of additive. The activation energies for the PEG and PEGDS modified starches for the same percentage modification are also observed to be of the same order. Figure 7 gives the plot of weight loss at 250, 300, 350 and 400 °C vs. percentage of PEGDS content for the modified starches. The plots show a linear trend for the various modified starch samples, whereas the unmodified samples (0 and 100% PEGDS) give rise to distinctly discontinuous points in the plots. This

TABLE 2

Percentage weight loss (observed and expected) during thermal decomposition of PEGDS and PEG modified tapioca starch

Sample		Temperature (°C)					
		200	250	300	350	400	450
5% PEGDS	Observed	0	1.1	14.2	73.3	80.4	82.7
	Expected	0.1	0.1	10.8	67.1	75.4	80.0
	Δwt. loss	0.1	1.0	3.4	6.2	5.0	2.7
10% PEGDS	Observed	0.4	2.1	17.2	77.5	83.9	86.5
	Expected	0.1	0.3	10.5	64.2	74.8	80.9
	Δwt. loss	0.3	1.8	6.7	13.3	9.1	5.6
20% PEGDS	Observed	1.3	3.4	20.0	74.9	84.3	86.8
	Expected	0.2	0.6	10.0	58.5	73.6	82.8
	Δwt. loss	1.1	2.8	10.0	16.4	10.7	4.0
30% PEGDS	Observed	0.9	3.5	17.3	71.2	80.1	83.1
	Expected	0.4	0.8	9.5	52.7	72.4	84.7
	Δwt. loss	0.5	2.7	7.8	18.5	7.7	−1.6
40% PEGDS	Observed	0.8	10	30.6	71.2	84.8	–
	Expected	0.5	1	9.0	47.0	71.2	86.6
	Δwt. loss	0.3	9	21.6	24.2	13.6	–
5% PEG	Observed	0	0.9	17.8	71.6	78.7	81.3
	Expected	0	0.04	10.6	67	75	80
	Δwt. loss	0	0.86	7.2	4.6	3.7	1.3
40% PEG	Observed	0.9	4.4	20.4	68.9	81.8	84.9
	Expected	0	0.3	7.7	45.7	68.3	86.8
	Δwt. loss	0.9	4.1	12.8	23.2	13.5	−1.9

TABLE 3

Activation energies for the thermal decomposition of starch and modified starch samples

Sample	Activation energy (kcal mol^{-1})
Gelatinized tapioca starch	45.3
PEG	49.6
PEGDS	47.7
5% PEGDS	40.4
10% PEGDS	34.0
20% PEGDS	33.5
30% PEGDS	27.8
40% PEGDS	25.61
5% PEG	35.8
40% PEG	28.3

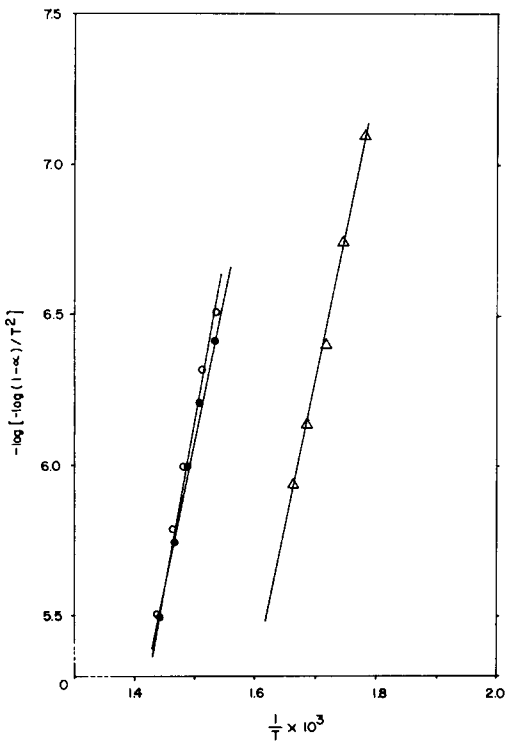


Fig. 4. Coats–Redfern plots for thermal decomposition of gelatinized tapioca starch (△), PEG (○) and PEGDS (●): $-\log[-\log(1-\alpha)/T^2]$ is plotted vs. $1/T \times 10^3$, where α is the extent of decomposition calculated from the thermograms and T is the temperature.

TABLE 4

Percentage weight loss (observed and expected) during thermal decomposition of gelatinized starch + PEG/PEGDS physical mixtures

Sample		Temperature (°C)					
		200	250	300	350	400	450
5% PEGDS	Observed	0	0.7	11.5	69.6	77.6	80.2
	Expected	0	0.15	10.8	67.1	75.4	80.0
	Δwt. loss	0	0.55	0.7	2.5	2.2	−0.2
20% PEGDS	Observed	0.8	2.9	16.25	65.4	73.3	76.3
	Expected	0.2	0.6	10.0	58.5	73.6	82.8
	Δwt. loss	0.6	2.3	6.25	6.9	−0.3	−6.5
5% PEG	Observed	0	0.9	16.2	65.4	71.1	74.1
	Expected	0	0.04	10.6	67	75	80
	Δwt. loss	0	0.86	5.6	−1.6	−3.9	−5.9
20% PEG	Observed	0	1.8	16.4	67.1	74.7	77.8
	Expected	0	0.2	9.3	57.9	72.1	82.9
	Δwt. loss	0	1.4	7.1	9.2	2.6	−5.1

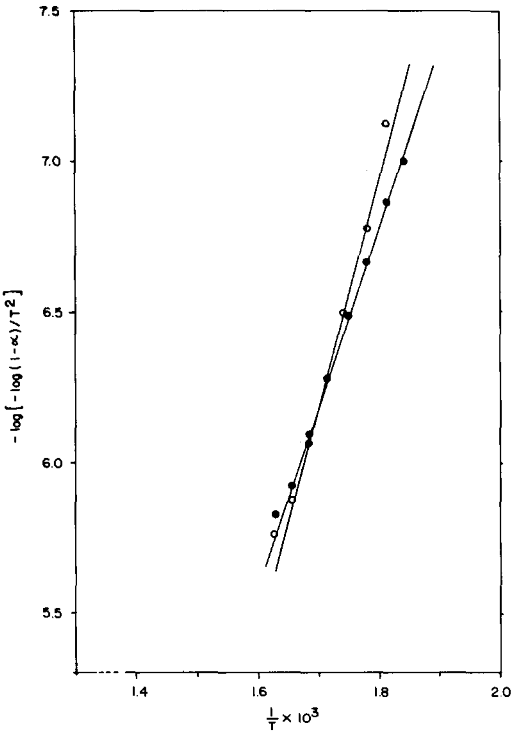
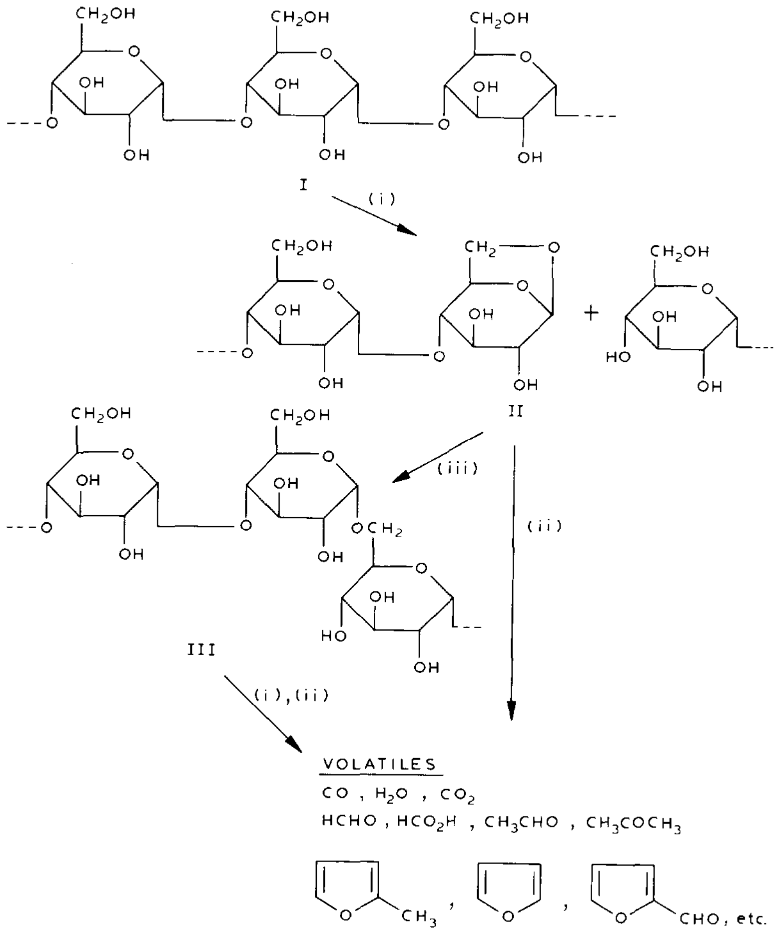


Fig. 5. Coats–Redfern plots for thermal decomposition of 5 (○) and 40% (●) PEG modified starches: $-\log[-\log(1-\alpha)/T^2]$ is plotted vs. $1/T \times 10^3$, where α is the extent of decomposition calculated from the thermograms and T is the temperature.

suggests that the mechanisms involved in thermal decomposition when the polymers are mixed together are different from their individual degradation mechanisms.

Amylose and amylopectin molecules are strongly associated in the unmodified starch samples in dry conditions, and we would expect maximum molecular interaction to take place between starch in the gelatinized form and PEG and PEGDS, since the associations between the molecules are weakened on heat treatment in water. The effects of modification should be minimal when the two ingredients are mixed with starch in the dry solid form. Physical mixtures of PEG and PEGDS (5 and 20% each) with starch were therefore prepared, as described in the Experimental section. TG curves for these samples indicated only marginal change in the thermal degradation as compared with the degradation expected (Table 4). This suggests that molecular level interactions between the additive and starch are important in bringing about the changes in thermal degradation.

The major reactions involved in the pyrolysis of starch are represented in the following scheme



It is postulated that pyrolytic treatment of starch (**I**) involves rupture of α-D-(1,4)-glucopyranose chains (step (i)), leading to the formation of shorter chains with 1,6-anhydroglucopyranose end groups (**II**) [16]. At higher temperatures the 1,6-anhydroglucopyranose end groups could become detached leading, on subsequent rearrangement and cleavage, to the mixture of volatile products (step (ii)). On the other hand, the end group of product **II** could react intermolecularly with hydroxyl groups (mainly at C6) to give product **III** with (1,6)-α or β-D-branch points [17,18]. Product **III** could then in turn lead to the formation of volatile products, through steps (i) and (ii).

However, inhibition of the formation of product **III** (step (iii)) would essentially result in a faster rate of formation of volatiles from product **II**. Thermolytic conversion of **II** to **III** would involve the formation of free radicals, and subsequent intermolecular attack of the radicals on the hydroxyl groups. Radicals generated by the thermal degradation of polyethylene glycol chain segments of PEG and PEGDS in modified starch samples

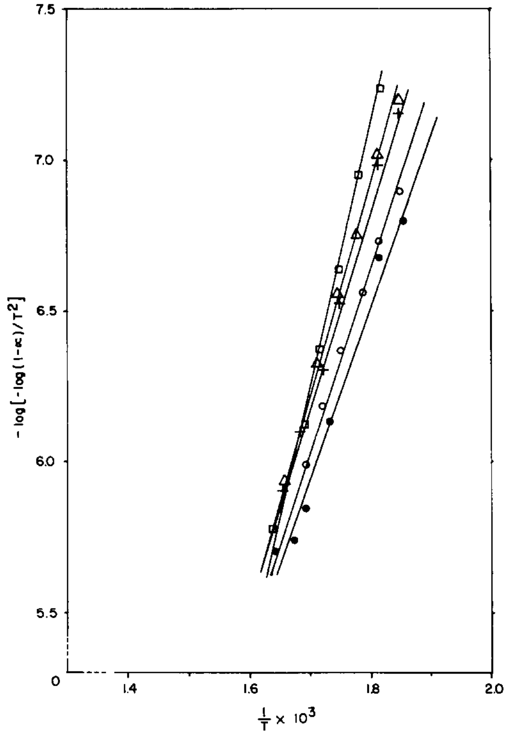


Fig. 6. Coats–Redfern plots for the thermal decomposition of 5 (□), 10 (△), 20 (×), 30 (○) and 40% (●) PEGDS modified starches: $-\log[-\log(1-\alpha)/T^2]$ is plotted vs. $1/T \times 10^3$, where α is the extent of decomposition calculated from the thermograms and T is the temperature.

could inhibit the steps of the mechanism involving intermolecular radical reactions, in the conversion of **II** to **III**, by functioning as a radical sink. Thus, inhibition of the formation of product **III** during thermal treatment, through the presence of polyethylene glycol in the modified starch samples, could essentially result in increased production of 1,6-anhydroglucopyranose end groups and thereby of volatile products (hence a higher weight loss in the TG curve as compared with unmodified starch). There have been many reports of mutual influence on thermal degradation of two polymers in thermal treatment when the molecules are placed in juxtaposition [19–21]. The influence of polymethyl methacrylate on the thermal decomposition of polyurethane, polystyrene, castor oil polyurethane, etc. can be explained by invoking involvement of free radicals generated by decomposition of one of the polymers interacting with the intermediate products of decomposition of the other.

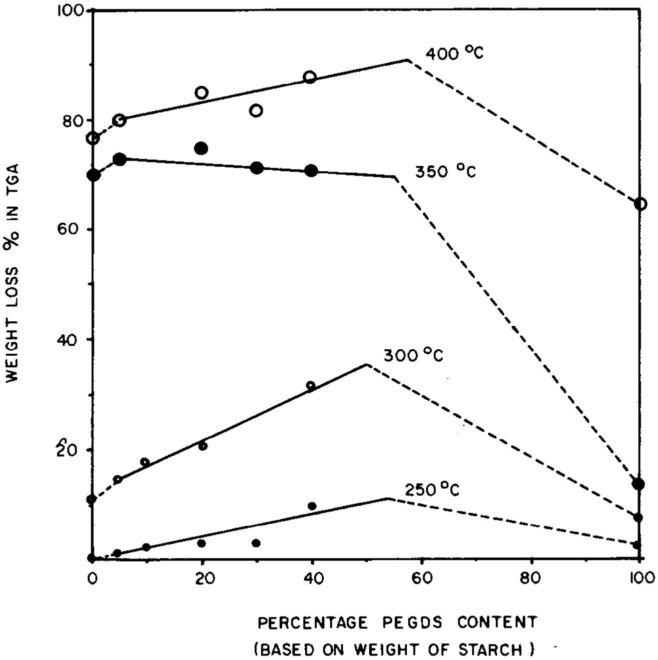


Fig. 7. Plot of percentage weight loss at 250 (•) 300 (o), 350 (●) and 400 °C (O) vs. percentage PEGDS content in modified tapioca starch.

CONCLUSIONS

Polyethylene glycol and polyethylene glycol distearate modification enhances the rate of thermal degradation of tapioca starch, and the change in weight loss pattern resulting from PEG/PEGDS modification depends on the extent of the modification (weight loss increases with increasing additive level). Correspondingly, the activation energy for thermal degradation decreases with increasing PEG or PEGDS additive level.

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