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The combustion of starch, cellulose and cationically modified products of these compounds investigated using thermal analysis

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Abstract

The combustion of cellulosic material and of related starch, starch components is followed using a simultaneous TG–DTA unit. The materials were characterized using solid-state NMR. It was found that the combustion proceeded via gaseous combustion. A study of the degradation in nitrogen on the thermal analysis equipment shows that the glowing combustion originated from carbonaceous residues of the degradation of the material during the gaseous combustion step. The α_r–α_s method of following the degradation in nitrogen was used to show the reactivity pattern on a comparative basis. This method was also used to study the reactivity pattern in the overlapping combustion reaction in air. In both the cases, the cationic material appeared to have higher reactivity than the unmodified native material. © 1997 Elsevier Science B.V.

Keywords: Cellulose; Starch; TG; Thermal analysis

1. Introduction

The combustion of cellulose is known to comprise two stages – gaseous combustion in which the gaseous degradation products catch fire, and then glowing combustion in which the carbonaceous residue pyrolyzes with the evolution of CO, CO_2 and water [1–4]. Both these processes are exothermic but basically the degradation of the cellulose in the gaseous combustion stage is endothermic. It is only that the exothermic character of the combustion of the gases produced overwhelms the endothermic character of the basic reaction that produces the exotherm observed in DTA plots in this region. It does mean, however, that much useful information can be gleaned about this portion of the combustion process by examining the gases released in studies involving an inert atmosphere as found by Price and Horrocks [5,6] in their mass spectroscopic studies. In the experiments reported previously [7–9], the influence of inorganic additives on the cellulose was shown to be important as suitable additives could increase the carbonaceous residues and alter the combustion-temperature ranges associated with the gaseous and the glowing combustion. These studies have a relation to similar projects on starch and related materials. Recent research has produced cationically modified starches used as additives in the paper, cosmetic and related industries [10,11]. It seemed prudent to carry out a parallel investigation on such substances.

Starch is a carbohydrate polymer, consisting of two polymers, amylose and amylopectin [12]. In the

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present study starch was modified cationically using the procedure previously outlined. In order to make a comparative analysis of the modified starch, amylose and amylopectin were also treated to the same conditions. Microcrystalline cellulose (MCC), which is structurally similar to starch was also cationically modified. A comparison was then attempted between the modified and the unmodified material using the α_r–α_s method of comparison [13].

2. Materials and methods

The cationically modified materials were synthesized following the procedure of Carr et al. [14] using 3-chloro-2-hydroxypropyltrimethylammonium chloride. It was obtained from Fluka. Corn starch, amylose, amylopectin and MCC were all treated in a similar fashion. The thermogravimetry experiments were conducted using a simultaneous TG–DTA unit from TA instruments, model # 2960. The atmosphere around the samples was maintained constant using a gas flow rate of 100 ml min^{-1}. Platinum crucibles were used to hold the samples, with an empty crucible used as reference. The structure of the product formed was analyzed using solid-state NMR. A 50 MHz spectrophotometer, using cross polarization, magic angle spinning was used at 1 ms contact time and a 4 s pulse delay sequence. Corn starch, amylose and amylopectin, both from corn starch, were provided by Sigma. MCC, known as Avicel, was from FMC. It is a purified, partially depolymerized α-cellulose derived from fibrous plants.

3. Results and discussion

The unmodified and the modified material were structurally analyzed using the solid-state NMR [15]. Both starch and cellulose are polymers of anhydroglucose units. Starch is composed of amylose and amylopectin units. Amylose is linear, whereas amylopectin is branched. Cellulose, on the other hand, consists of only β(1,4)-linkages. As can be seen from the plot (Fig. 1) for corn starch, the peak at 62 ppm is due to the pendant methylene carbon, at 100 ppm it is due to the anomeric methine carbon and from 82 to 72 ppm due to the remaining carbon atoms present in the basic starch backbone. The cationic material (Fig. 2) shows an additional peak at 56 ppm due to the CH_3 group in the substituted cationic group. From this data the degree of substitution (DS) in each case was determined by integration of the peaks.

$$\mathrm{DS} = \frac{A_{56}}{A_{100} + A_{70} + A_{82} + A_{62} + A_{56}}$$

where A_x corresponds to the integrated area of peak x. The values for DS for all the modifications varied between 0.03 to 0.04, indicating that every 3 to 4 units per 100 were modified. Native corn starch has been previously analyzed by solid-state NMR [16,17]. Similar results were also obtained from the NMR structures of the modifications on amylose, amylopectin and MMC.

Having established that the materials were successfully modified, they were examined using thermal analysis. As previously mentioned, cationically modified carbohydrates are used in the paper industry as additives. Here, we wanted to study the effect of this modification on the reactivity of the starch and cellulose under the given conditions and compare it with the unmodified materials in order to examine what effect this has on the flammability, and this was achieved by thermal analysis, using TG. The basic degradation shows an endothermic conversion to a carbonaceous residue. The TG–DTG plots for MCC and corn starch serve as typical examples of the four unmodified and modified materials studied (Figs. 3 and 4). The difference between the cellulose and corn starch is seen from the DTG plot, which shows an initial peak overwhelmed by the main degradation process for the corn starch as contrasted with the cellulose degradation which exhibits a single degradation peak. With regard to the height of this initial peak, for corn starch it can be argued that it is due to modifications of the surface leading to surface components which are more reactive. This initial peak is also seen for amylose and amylopectin. The yield of carbonaceous residue in each case presents different values. Both the height of the first peak relative to the second peak on the DTG, and the percentages of carbonaceous residue are recorded in Table 1. In the cationically modified materials the initial peak is enhanced due, it is believed, to much more extensive surface modification for all samples including cellulose. Typical plots of TG–DTG for cationic cellulose

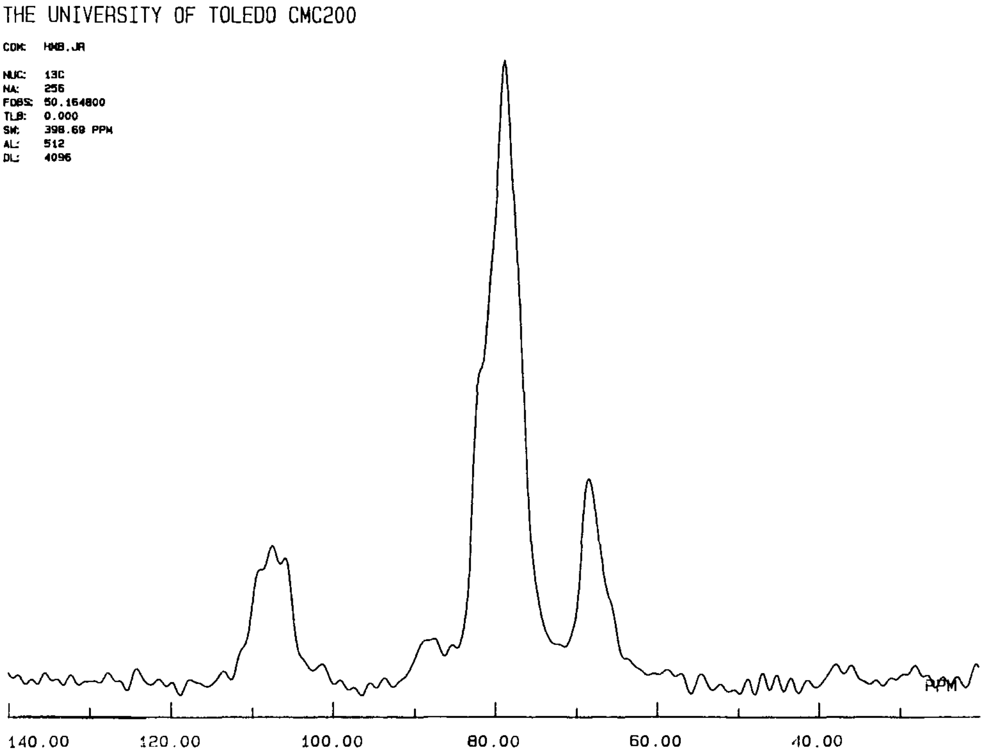

Fig. 1. ^{13}C NMR spectra of native corn starch obtained using solid-state NMR.

and cationic starch are shown in Figs. 5 and 6. It is seen that an initial peak appears in cellulose, followed by a greatly enhanced peak in the cationic starch. The data is tabulated for all sample investigations in Table 1. The enhancement is so great for the cationic amylose that the first peak is greater than the second peak. The other important comment is that the carbon residue is generally enhanced by the cationic treatment. There is also an effect observed in the values of T_i, T_p and T_f (where, T_i refers to the initial temperature, T_p to the peak temperature and T_f the final temperature of the DTG plot) which is apparent from the cationic modification.

All this data collected in nitrogen can also be correlated with the TG–DTA analysis of experiments in flowing air. Again, typical data are shown for cellulose and corn starch. The presentation however differs slightly. The degradation in nitrogen for all these materials showed a DTA endothermic peak. In air, the sample would ignite and heat generated from the combustion process with complications occurring in the conventional plots against temperature. The data are therefore presented as mass loss with a time scale imposed. For cellulose the DTG plot reveals two regions of combustion. The corresponding TG–DTG data for corn starch also reveals a two-stage process. This is more readily apparent on inspection of the DTA plots for the cellulose and corn starch shown in Figs. 7 and 8. The data in Fig. 8 for cellulose shows the start of an endothermic degradation being overtaken by the gaseous combustion of the gases being released in a large exothermic event. The second region of mass loss corresponds to the ignition of the solid carbonaceous residue in a self-sustained exothermic process leading to a second exothermic event or as a shoulder to the first peak in the region usually termed as a region of 'glowing combustion'. Figs. 9 and 10 show the behavior of the modified cellulose and corn starch in air in the form of TG–DTG plots.

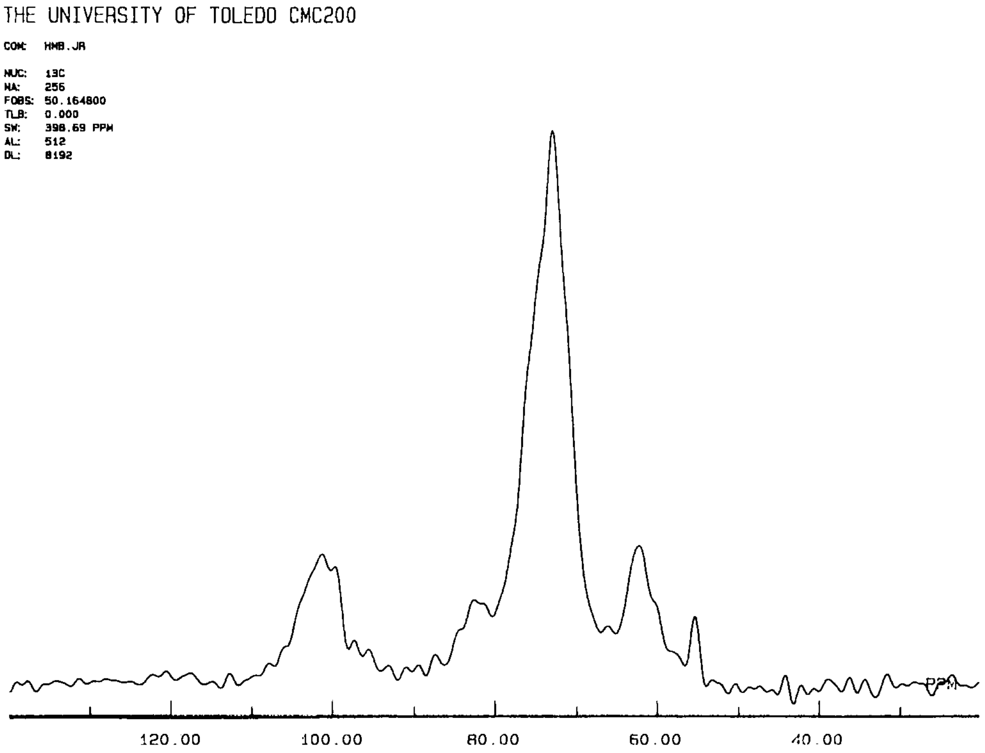

Fig. 2. ^{13}C NMR spectra of cationically modified corn starch obtained using solid-state NMR.

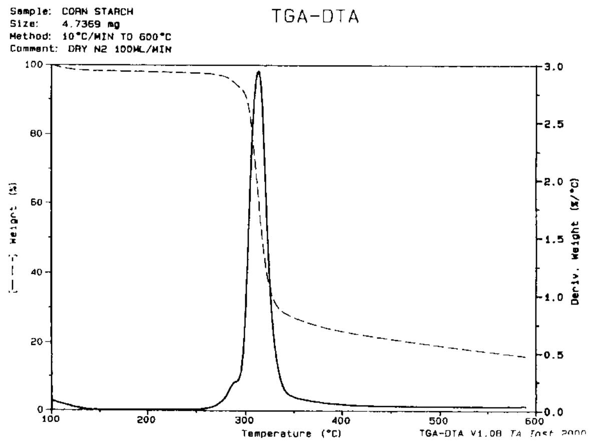

Fig. 3. TG–DTG plot of corn starch in an atmosphere of flowing dry nitrogen, at a heating rate of 10°C min^{-1}.

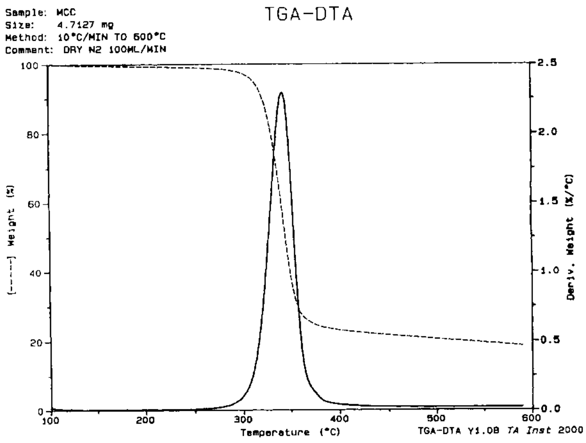

Fig. 4. TG–DTG plot of MCC in an atmosphere of flowing dry nitrogen at a heating rate of 10°C min^{-1}.

In order to compare the solid-state reactivity of the modified and the unmodified materials, the α_r–α_s method of comparison was used, as has been shown before [18]. In this method α_r refers to the fraction of the decomposition of the reference sample, and α_s to the fraction of sample under investigation decomposed. In this study, the data obtained from the degradation of corn starch on the TG unit was taken

Table 1
Height of the peak believed to be due to surface reactivity and the extent of carbonaceous residue at 500°C for the various samples in cationically modified and unmodified form, subjected to TG in an atmosphere of flowing dry nitrogen, where T_i, T_p and T_f refer to initial, peak and final temperature on the DTG plot.

Sample	Height of 1st and 2nd peak%/°C		T_i°C	T_p°C	T_f°C	% Residue of carbonaceous material at 500°C
MCC		2.292	250	345	400	20
MCC modified	0.2286	3.287	200	330	400	24
Corn starch	0.2476	2.943	250	325	400	19
Corn starch modified	1.067	1.431	225	310	400	32
Amylose	0.1857	2.868	250	315	350	28
Amylose modified	1.367	1.361	200	300	400	28
Amylopectin	0.207	2.814	250	325	400	10
Amylopectin modified	1.200	1.239	225	300	400	22

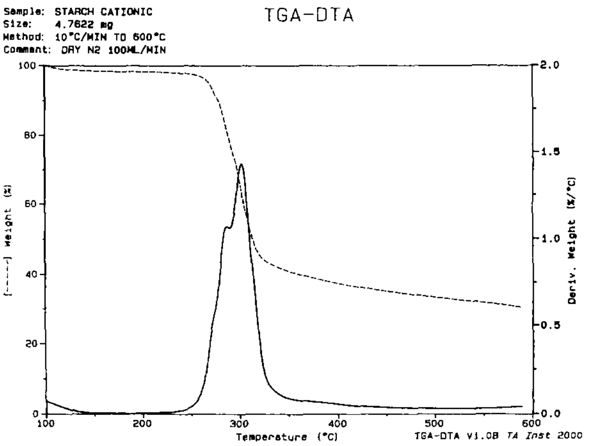

Fig. 5. TG–DTG plot of modified corn starch in an atmosphere of dry nitrogen at a heating rate of 10°C min^{-1}.

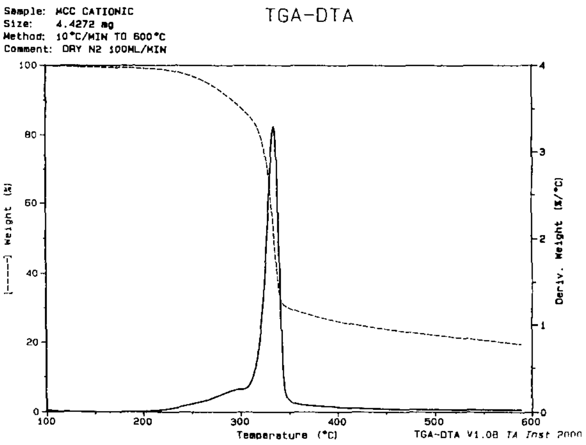

Fig. 6. TG–DTG plot of modified MCC in an atmosphere of dry nitrogen at a heating rate of 10°C min^{-1}.

as the reference and plotted against the fraction of the other native and modified materials. Depending on the reactivity of the materials being compared, the α_r–α_s plot will indicate which material is more reactive than corn starch, as that is considered to be the reference. A sample, less reactive than corn starch, will appear lower than corn starch on the α_r–α_s plot, whereas those that are more reactive will lie above it. As can be seen from the α_r–α_s plot in Fig. 11, in all the cases the cationic material appeared more reactive than the native unmodified material, until ~70% of the material had decomposed, after which the cationic material appeared less reactive than the unmodified materials in all the samples examined (Fig. 11). In case of the degradation of the materials in nitrogen, all the cationic starches appeared more reactive than their native counterparts. Tables 2 and 3 summarize the results for α_r/α_s at different values of α_r, where the modified and the unmodified materials were compared for each sample investigated, using the modified sample as the reference material (α_r).

4. Summary of results

1. It can be seen that characterization of the materials using NMR gave the degree of substitution of the modified starch and cellulose products.

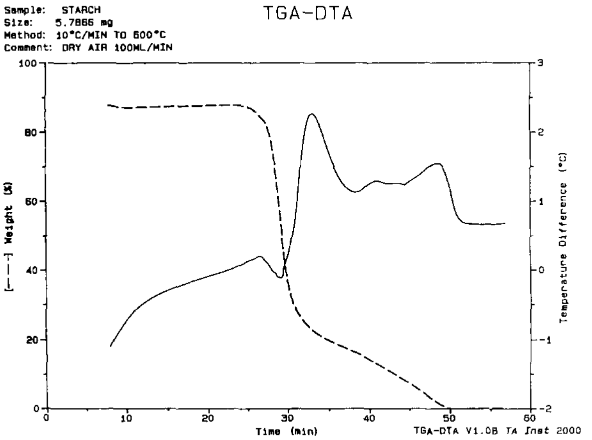

Fig. 7. TG–DTA of corn starch in an atmosphere of flowing dry air at a heating rate of 10°C min^{-1}.

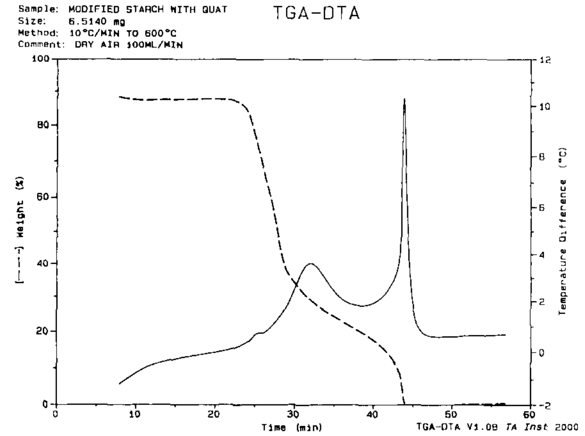

Fig. 9. TG–DTA of modified corn starch in an atmosphere of flowing dry air.

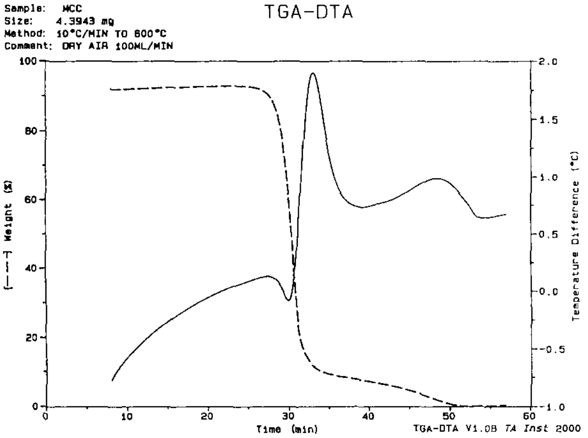

Fig. 8. TG–DTA of MCC in an atmosphere of flowing dry air.

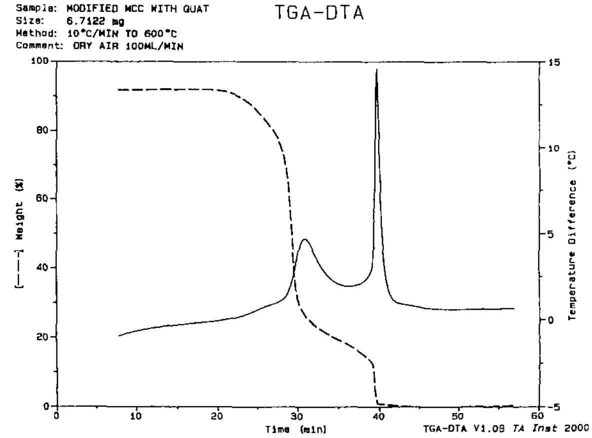

Fig. 10. TG–DTA of modified MCC in an atmosphere of flowing dry air.

2. The modification leads to a secondary overlapping peak on the DTG plot. This peak is attributed to the surface structural modification. It should be noted that some signs of surface modification are already apparent in the corn starch, amylose and the amylopectin, but the signal is greatly enhanced by the cationic modification.
3. In all cases the TG–DTG in nitrogen shows an endothermic degradation to carbon but generally the carbon residue is enhanced by the cationic treatment.
4. In air, quite clearly gaseous combustion is followed by glowing combustion, both being sufficiently exothermic to cause appreciable distortion in the imposed temperature program.
5. In using the α_r–α_s method, it is apparent that the reactivity in air at 0.5 α_r is of the following order: modified amylose > modified corn starch > modified amylopectin > amylose > corn starch > modified MCC > amylopectin > MCC. It is seen that the cationic modifications are more reactive than the unmodified materials, and this is borne by examination of Table 2.
6. At higher α_r values, the difference in reactivities caused by the modifications disappear (see Table 2).

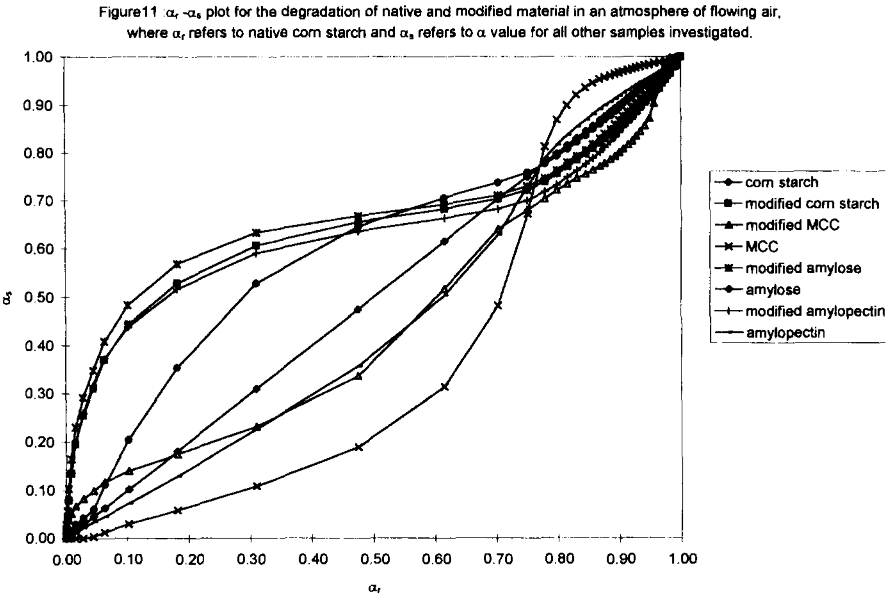

Fig. 11. α_r–α_s plot of all the materials investigated from the TG data in an atmosphere of dry air, with corn starch used as reference.

Table 2

α_r/α_s values at different values of α_r, where α_s is the cationic material in each case, for all the materials examined from data obtained from the TG plots in an atmosphere of flowing air

Material	α_r/α_s at $\alpha_r = 0.5$	α_r/α_s at $\alpha_r = 0.8$
Modified corn starch – α_r, native material – α_s	4.50	0.95
Modified – α_r, native amylopectin – α_s	6.25	0.90
Modified – α_r, unmodified amylose – α_s	2.80	0.95
Modified – α_r, unmodified MCC – α_s	1.79	0.81

Table 3

α_r/α_s values at different values of α_r, where α_s is the cationic material in each case, for all the materials examined from data obtained from the TG plots in an atmosphere of flowing nitrogen

Material	α_r/α_s at α_r=0.5	α_r/α_s at α_r=0.8
Modified corn starch – α_r, native material – α_s	5	1.03
Modified – α_r, native amylopectin – α_s	8.1	0.93
Modified – α_r, unmodified amylose – α_s	3.85	1.14
Modified – α_r, unmodified MCC – α_s	1.85	1.8

7. The same general observation is borne out by the behavior in nitrogen.
8. It can be speculated that the modification affects the surface; once this surface region is gasified, the greater reactivity imposed by the modification disappears.

5. Conclusions

From the study it can be seen that for all the materials cationically modified, the reactivity of the modified material was higher than those of unmodified materials. This indicated that the presence of the cationic group, at the surface, increases the reactivity of the materials under consideration. Also for the order of the reactivity, it was found that modified amylose appeared more reactive than all the rest because it is mainly linear, which makes it more susceptible to thermal degradation as compared to the branched corn starch and amylopectin. In the case of cellulose there are linkages which are more difficult to break, contributing to cellulose being the least reactive amongst the rest. This is the first time such a comparative based study between modified and unmodified starch and cellulose has been introduced.

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