

DSC, DTA, and TG of cellulose untreated and treated with flame-retardants

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Abstract

DSC of untreated cellulose and cellulose treated with diammonium hydrogen phosphate, sodium tetraborate decahydrate, boric acid, ammonium sulfamate, or guanidine sulfamate, was conducted in a nitrogen atmosphere. In addition, DTA and TG under vacuum were performed for untreated cellulose and cellulose treated with the above first two salts. Two endotherms were found on both DSC and DTA curves, and these as well as the effects of the chemicals on the DSC and DTA behavior were explained by a pyrolysis chain reaction mechanism. The endothermic heat due to the weight loss was reduced by treatments with ammonium sulfamate and guanidine sulfamate, and was increased by treatment with boric acid. The decrease in heat may be due to depropagation accelerated by the addition of salts. The increase is ascribable to the termination accelerated by boric acid.

INTRODUCTION

Cellulose, a linear polysaccharide polymer, consists of glucose units linked through β -1,4-glucosidic bonds (see Fig. 4 below). It is a major component of plant cell walls and makes up approximately a third to a half of the dry weight of plants. Cellulose therefore constitutes the largest amount of naturally synthesized material.

Thermal analyses of cellulose in most cases have been concerned with the development of fire-retardant wood and cellulosic materials, energy resources, and chemical and industrial materials. The most frequently reported cellulose thermal analysis studies have involved TG (thermogravimetry), DTA (differential thermal analysis), and DSC (differential scanning calorimetry). These studies have yielded a number of Arrhenius parameters. The parameters as well as the thermal analysis behavior, however, have not been satisfactorily explained or interpreted based on reaction mechanisms of the thermal decomposition. Therefore, the aim of this study is to correlate thermal analysis behavior of untreated and chemically treated cellulose with the pyrolysis mechanisms and the Arrhenius parameters.

EXPERIMENTAL

The cellulose sample used was purified fibrous cotton linter whose weight average degree of polymerization (DP) was 2971. The flame-retardants used were diammonium monohydrogen phosphate, sodium tetraborate decahydrate, boric acid, ammonium sulfamate, and guanidine sulfamate (CP grade). The cellulose samples were first immersed in a 0.5 or 1% aqueous solution of the retardants for about 90 min, then filtered and freeze-dried. Finally, the treated samples were held in a vacuum desiccator before runs. The mean percentages of retardants added, in the above order, were 4.4, 7.5, 1.6, 6.3, and 4.9 to each original weight of cellulose.

Initial weights of samples of approximately 50 mg under vacuum (1–4 mbar) were subjected to simultaneous TG and DTA measurements using a Sinku Riko TGD-1500. The DSC runs were carried out with initial sample weights of 4.5–9.0 mg in a nitrogen gas atmosphere, at a heating rate of $8^{\circ}\text{C min}^{-1}$, using a Perkin-Elmer DSC-1B calorimeter.

RESULTS

The DSC curves for untreated samples and samples treated with ammonium phosphate and sodium borate are shown in Fig. 1. The DSC behavior as well as the results of DTA may be determined by the relationships between the endothermic and exothermic changes as both changes can occur simultaneously in the samples.

In addition to a broad and shallow endotherm which occurred in the temperature range of $200\text{--}300^{\circ}\text{C}$, untreated cellulose showed a large endotherm in the $320\text{--}390^{\circ}\text{C}$ range on the DSC curve. Many workers [1–11]

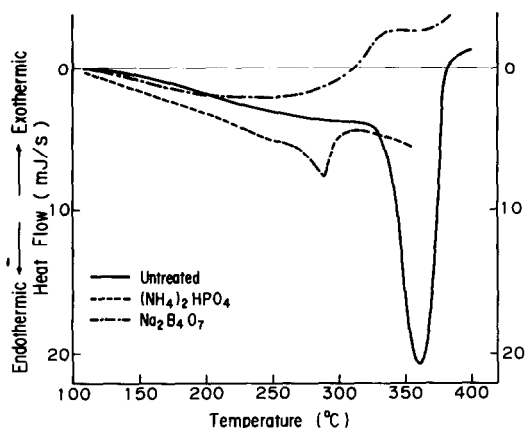


Fig. 1. DSC curves of untreated cellulose and cellulose treated with ammonium phosphate and sodium borate. Heating rate $8^{\circ}\text{C min}^{-1}$, atmosphere nitrogen.

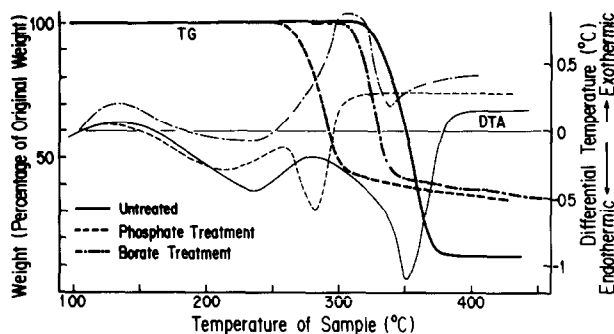


Fig. 2. DTA and TG curves of untreated cellulose and cellulose treated with ammonium phosphate and sodium borate under vacuum. Heating rate $5^{\circ}\text{C min}^{-1}$.

have observed large and sharp endothermic peaks in the same temperature range on various samples of untreated cellulose. The sample treated with ammonium phosphate produced very small and sharp endothermic changes in the ranges $220\text{--}260^{\circ}\text{C}$ and $270\text{--}300^{\circ}\text{C}$, respectively. The latter endothermic peak may correspond to the large peak for the untreated sample, shifted towards the lower-temperature side by the ammonium phosphate treatment. Similar results for cellulose samples of Avicel and filter paper treated with phosphoric acid have been shown by Kumagai et al. [7]. The curve for the sodium borate treated sample seems to have two small endotherms which are divided by an exothermic peak at about 340°C .

The onset temperature for weight loss is found to have been lowered by ammonium phosphate and sodium borate, as seen in the TG curves in Fig. 2. Similar findings have been reported by many workers (too many to be quoted here). Furthermore, from comparison between the TG and DSC curves the endotherms in the high-temperature ranges are given by the active weight losses. The behavior on DTA for each sample, as shown in Fig. 2, is basically the same as that found by DSC, but the former is more sensitive than the latter, probably as a result of the larger initial sample amount for DTA. Before a main endothermic peak caused by an active weight loss, a few small endothermic DTA peaks, which are accompanied by a slow weight loss, have been observed for cellulose treated with ammonium phosphate [12,13]. In the present work, however, before the active weight loss, a broad endothermic region, which was not differentiated into peaks, was obtained without discernible weight loss. This may be due to the low salt content of the sample.

To obtain endothermic heat of pyrolysis of untreated cellulose and cellulose treated with boric acid, ammonium sulfamate, and guanidine sulfamate, the DSC curves were constructed from the differences between the curves of sample runs and the base-line (blank) runs. The base-line runs were performed before each sample run. The curves obtained yielded sharp endothermic peaks, as shown in Fig. 3. These peaks were found to be

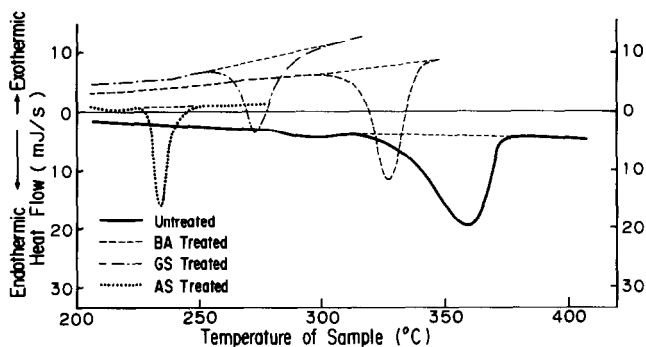


Fig. 3. DSC curves of untreated cellulose and cellulose treated with boric acid (BA), guanidine sulfamate (GS), and ammonium sulfamate (AS). Heating rate $8^{\circ}\text{C min}^{-1}$; atmosphere nitrogen.

ascribable to the weight losses in comparison with the TG curves (data not shown). All the samples except the boric acid treated one produced a small endotherm before the main endotherm. The areas of the sharp peaks were determined by drawing base-lines (as shown in Fig. 3) and the areas were reduced to the endothermic heat using heats of fusion of indium, tin, lead, and zinc for calibration. The values obtained are listed in Table 1. The endothermic heat for untreated cellulose falls within the range of values reported for Avicel and filter paper [7], and cotton cellulose [3]. This heat, however, has been shown to depend on fine structures such as crystallinity and orientation of the polymer [5]. The endothermic heat per unit weight loss decreased with the ammonium sulfamate and guanidine sulfamate treatments, and increased with boric acid. On the other hand, the heat per unit initial weight was reduced by all treatments. Additives to and chemical modification of cellulose have been reported to cause decreases [1–3,7,10] and increases [2] in the endothermic heat.

DISCUSSION

Changes in mechanical properties of cellulose with heating, which were obtained by sonic pulse velocity measurements [14] and torsional braid

TABLE 1

DSC endothermic heat for untreated cellulose and cellulose treated with boric acid (BA), ammonium sulfamate (AS), and guanidine sulfamate (GS)

Samples	Untreated	BA treated	AS treated	GS treated
ΔH_1^a (J g^{-1})	691	733	503	557
ΔH_2^b (J g^{-1})	553	415	142	222

^a Endothermic heat per unit weight loss.

^b Endothermic heat per unit initial weight.

analysis [15], have been referred to as the glass transition. Furthermore, the possibility of melting of cellulose has been presented [16]. However, these transitions, as well as other physico-chemical changes such as softening, seem to have rarely been detected by DSC and DTA techniques, as concluded from a survey of the literature. Therefore, the DTA and DSC peaks shown in Figs. 1 and 2 are thought to be the results of chemical reactions.

From many DP measurements and product analyses the principal route of cellulose pyrolysis is thought to be a process proceeding from cleavage of glucosidic bonds to production of levoglucosan. In the low-temperature range (200–250 °C), the cleavage of glucosidic bonds causes reduction in the DP without accompanying substantial production of levoglucosan, which occurs at elevated temperatures and is responsible for most of the weight loss. The pyrolysis route is widely considered to be controlled by radical mechanisms. On the other hand, dehydration apart from the route does occur but is thought to be a side-reaction of lesser significance.

For an explanation of the reaction kinetics of cellulose pyrolysis, several models have been presented without [17] and with definite chemical mechanisms [18–20]. Hirata's model [20] is able to explain both the changes in the DP and the weight. His model shows a chain reaction mechanism consisting of random scission-initiation, grafting termination between a hydroxyl group and a resultant radical produced from the initiation, and depropagation to

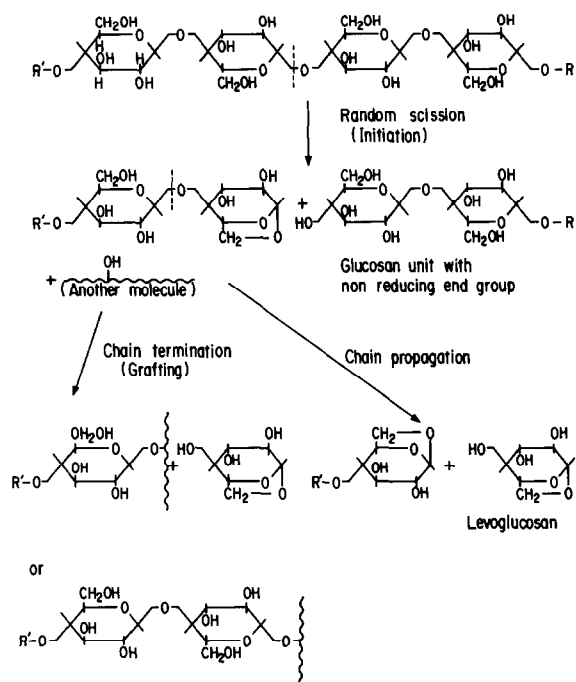


Fig. 4. Mechanism of chain reaction of pyrolysis of cellulose.

TABLE 2

Activation energies for pyrolysis reactions of untreated cellulose and cellulose treated with AP and SB ^a

Samples	Activation energies (kJ mol ⁻¹) ^b			
	E_w	E_i	E_{dep}	E_t
Untreated	187	159	160	132
AP treated	170	148	127	105
SB treated	209	124	171	86

^a Cited in ref. 20.

^b The subscripts w, i, dep, and t designate the weight loss, the initiation, the depropagation, and termination, respectively, and E designates the activation energy. AP, Diammonium hydrogen phosphate; SB, sodium tetraborate decahydrate.

produce levoglucosan, as shown in Fig. 4. According to Hirata's model the activation energy of Arrhenius for the weight loss at a stationary state between the initiation and the termination is expressed as

$$E_w = E_i + E_{dep} - E_t \quad (1)$$

where E is the activation energy, and the subscripts w, i, dep, and t designate the weight loss, the initiation, the depropagation, and the termination, respectively [20].

The activation energies for untreated cellulose and cellulose treated with ammonium phosphate or sodium borate have been determined from changes in the DP and weight with isothermal heating [20], and are listed in Table 2. The activation energies for the weight loss and depropagation were reduced by the treatment with ammonium phosphate and were increased by sodium borate. The activation energies for the initiation and termination were reduced by both treatments.

First the initiation occurs, which may form the first endotherms in low-temperature ranges before the weight losses, as shown in Figs. 1 and 2. The exothermic termination then follows, and neutralizes the endotherms to give the formation of DTA exothermic peaks, because of the higher reaction rates of the termination rather than the initiation, as seen from the comparison of activation energies for the two processes in Table 2. By increasing the temperature, however, depropagation of the higher activation energy occurs, and overcomes the termination. Therefore, the exotherms are rapidly turned into the main endothermic peaks. In fact, the main endotherms are ascribable not only to the weight loss, but also to vaporization of the pyrolysis products.

Progress of the termination would result in formation of a thermally stable network of cellulose molecules. The sodium borate treated sample showed a large DTA exothermic peak at the beginning of weight loss and also a DSC exotherm in the same range. These might be given by the

termination accelerated by the salt. The monomers (levoglucosan) from these stabilized structures would be produced with a high activation energy of the depropagation, as shown in Table 2. Nevertheless, the weight loss occurred in a lower temperature range than for the untreated sample. This could be explained by the accelerated initiation. In the case of the ammonium phosphate treated sample, despite the lower E_i , the E_{dep} is lower than that of the untreated sample. This may imply that this retardant accelerates the depropagation as well as the termination.

For the boric acid treated sample, the larger endothermic heat per unit weight loss compared with that of the untreated sample may be due to cellulose structures stabilized by the termination accelerated by this retardant. This inference agrees with findings that the start of weight loss of fiberboard with isothermal heating was delayed by boric acid mixed with sodium borate [21]. The decreases in this heat by ammonium sulfamate and guanidine sulfamate may be due to the depropagation accelerated by these salts.

CONCLUSIONS

(1) Cellulose samples untreated and treated with ammonium phosphate or sodium borate yielded two endotherms on the DSC and DTA curves. The main endotherms in high-temperature ranges are ascribable to weight losses caused by the pyrolysis. The broad endotherms in low-temperature ranges are probably due to the random chain scission.

(2) The sample treated with sodium borate yielded a noticeably large exothermic peak between the two DTA endotherms, which might be attributable to termination accelerated by this salt.

(3) Endothermic heat caused by the weight loss decreased on treatment with ammonium sulfamate and guanidine sulfamate, and increased with boric acid. The decreases in the heat are ascribable to depropagation of a chain reaction accelerated by the two salts. The increase in the heat is probably due to cellulose structures being stabilized by the termination accelerated by boric acid when heating.

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