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THE FIRE RETARDANT BEHAVIOR OF VARIOUS CHLORIDES ON CELLULOSE

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Abstract

TG, DTA, and TMA data on the pyrolysis of α-cellulase powder in air is reported together with the modified pyrolysis behavior of the cellulose impregnated with between 2–3% (w/w) of calcium, potassium, sodium and zinc chlorides. The lower temperature of onset of the pyrolysis (as shown by TG and TMA), the increased peak areas of the DTA exotherms, and the elimination of an initial endotherm present in the pure cellulose, all suggest an increased flammability for the impregnated samples. Other properties of the impregnated celluloses however favor a fire retardancy effect; these are an increase in the temperature of the first exothermic peak on the DTA, a reduction in the maximum rate of mass loss, a reduction in the % mass loss occurring in the first mass loss period, and an increase in the % ash remaining at 800°C. The relative effect of the various chlorides is examined and shown to correlate with other data already published.

Keywords: cellulose, flammability

Introduction

At least four theories have been put forward to explain the fire retardation of cellulosic materials effected by the addition of impregnated materials [1]. These four theories suggest that the retardation occurs by either chemical, coating, thermal or gas evolution effects. In this study, four chlorides are studied which have from previous reports been suggested as possible fire retardants. These are calcium chloride, potassium chloride, sodium chloride and zinc chloride.

In considering fire retardation by chemical effects it is necessary to outline the probable mechanism of pyrolysis of cellulose. Tamaru [2] outlined a pyrolysis mechanism for cellulose by which depolymerisation occurred first, followed by the competing reactions of destructive distillation and char fortnation. He suggested that the main effects of added salts was to reduce the yield of organic vapors. Schwenker and Pascu [3] contend that the first and the rate determination step in the pyrolysis of cellulose is depolymerisation to levoglucosan believed to be the major inflammable product, and that a flame retardant inhibits the formation of this product. Madorsky, *et al.* [4] showed that sodium chloride increased the yield of carbon dioxide and water whilst decreasing the yield of the tar fraction. They suggest that

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this is due to the catalytic effect of the sodium chloride on the dehydration and bond scissions taking place in the cellulose material. Fung *et al.* [5] however cast some doubt on the general hypothesis and could find no relationship between the yield of levoglucosan and the amount or type of fire retardants.

More recent studies on cellulose and wood investigated the kinetic aspect of the change, using the isothermal techniques [6] or rising temperature analysis [7]. A rising temperature study by Dollirnore and Hoath [8] established that pyrolysis in air progressed through three stages, combustion of volatile material, glowing combustion af carbonaceous residue and in some cases a combustion of product gases from the glowing combustion.

Experimental

Material

The cellulose used was Whatman CC31, a white microgranular powder, supplied by Messrs W. and R. Balston Ltd. This cellulose powder is manufactured from high purity cotton containing 98% α-cellulose. The manufacturing process consists of acid treatment which modifies the internal structure and renders the cellulose "ashless", followed by controlled grinding which ensures a high packing density. The powder has a rod-like form is free flowing when dry and has the following contents: ash (max.) 0.01%. Iron 5 ppm Copper 2 ppm.

Impregnation

Calcium, potassium, sodium and zinc chlorides were used to impregnate the cellulose. They were used in high purity (Analar) form. An impregnation level of 2–3% (*w/w*) was chosen for each of the salts since this concentration appeared to be typical of earlier work. After the impregnation, the treated cellulose was dried for 1 day at 110°C and then stored in a desiccator over silica gel. The actual chloride content in each of the impregnated samples was as follows: calcium chloride sample 2.96% (determined as % chloride *w/w* in cellulose), potassium chloride 2.54%, sodium chloride 2.67%, zinc chloride 2.67%.

Apparatus

The thermogravimetric (TG) and differential thermal analysis (DTA) results were obtained simultaneously using a Stanton-Redcroft TR/STA661. In addition, the samples were subjected to a TG analysis using the Stanton 691TMA. On the simultaneous TG and DTA unit a heating rate of 8°C min^{-1} was used in a static atmosphere of air. The sample weight was 20 mg, the crucible made of platinum/rhodium, the DTA reference was simply an empty crucible and the sample was not diluted. The heating rate on the TMA unit was 10°C min^{-1}, the atmosphere was static air, and the sample weight 0.03 g in an aluminum foil crucible, packed with powder and the movement registered is the overall movement of the powder mass.

Results and discussion

The data for the pure cellulose are shown in Fig. 1. The behavior of the impregnated samples are given in Fig. 2 for CaCl$_2$-impregnated cellulose, in Fig. 3 for KCl-impregnated cellulose, in Fig. 4 for NaCl-impregnated cellulose, and in Fig. 5 for ZnCl$_2$-impregnated cellulose.

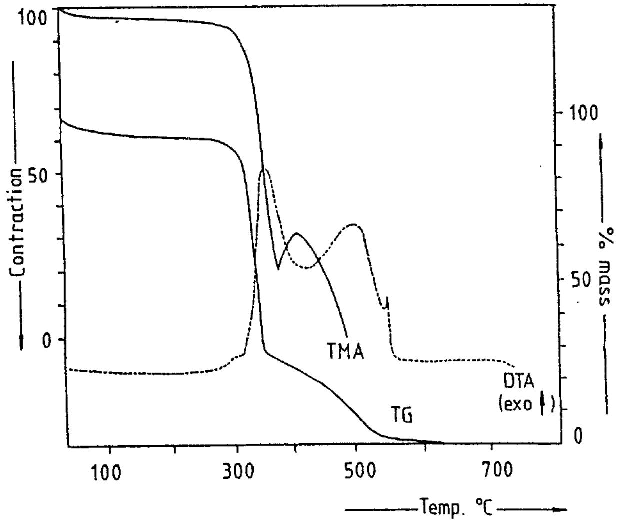

Fig. 1 Simultaneous DTA/TG and additional TMA results for pure cellulose in air. In the DTA plot, the scale can be read from the % mass plots, 100% mass=10°C. This holds for Figs 1–5

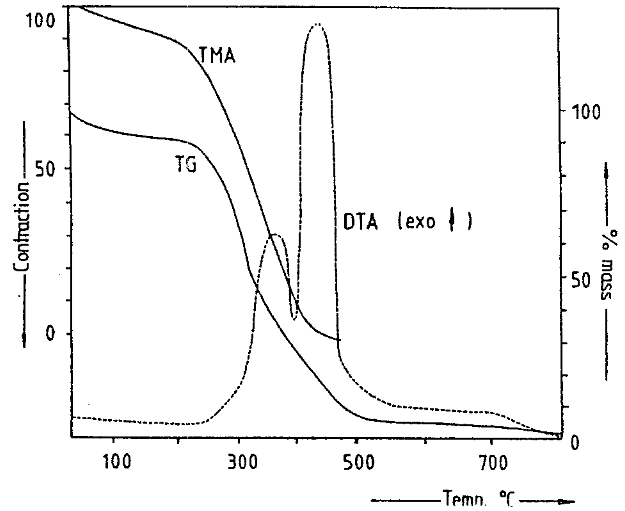

Fig. 2 Simultaneous DTA/TG and additional TMA results for CaCl$_2$-impregnated cellulose in air

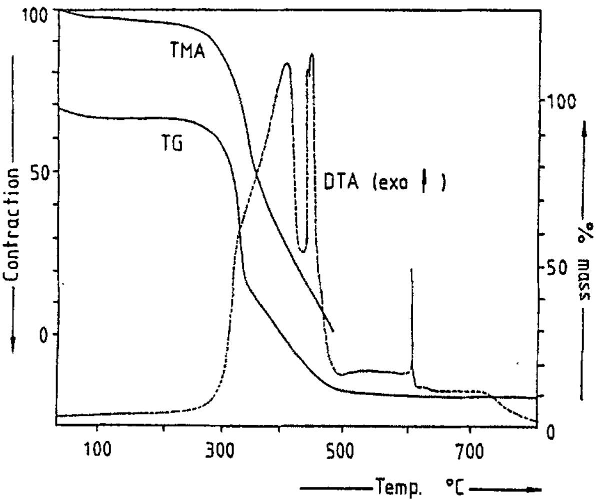

Fig. 3 Simultaneous DTA/TG and additional TMA results for KCl-impregnated cellulose in air

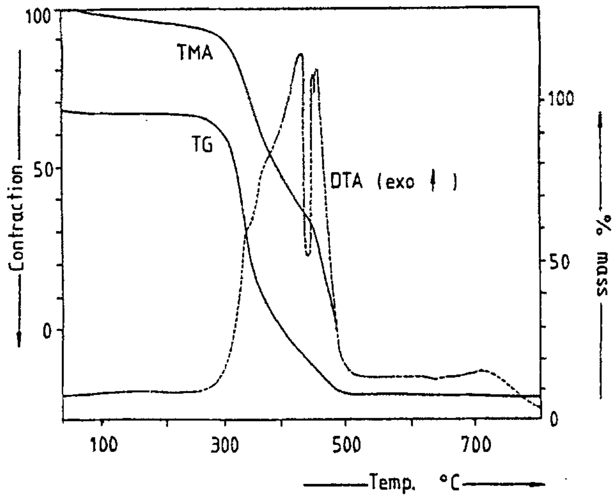

Fig 4 Simultaneous DTA/TG and additional TMA results for NaCl-impregnated cellulose in air

Comparison of the $CaCl_2$-impregnated sample with that for the pure sample shows that the first exothermic peak occurs at a slightly higher temperature in the impregnated sample. The pure cellulose shows two broad exotherms and a smaller third exotherm at a higher temperature, but in the $CaCl_2$-impregnated sample only two broad exotherms are to be seen; it is reasonable to assign the first to the flaming combustion of the decomposing sample and the second to the glowing combustion of the char. The third exotherm in the pure cellulose could be caused by subsequent

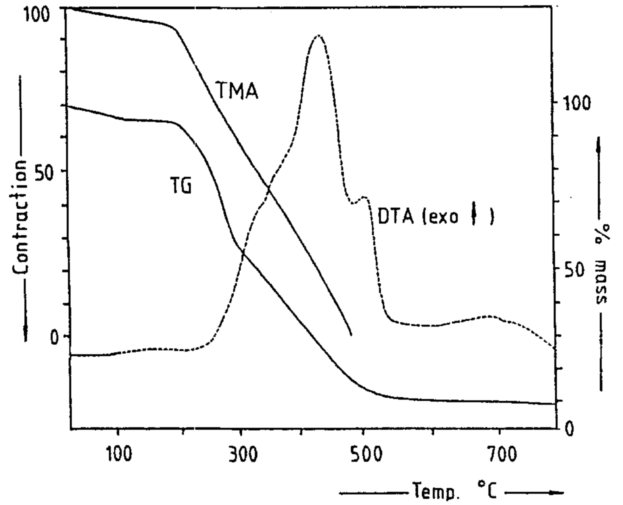

Fig. 5 Simultaneous DTA/TG and additional TMA results for $ZnCl_2$-impregnated cellulose in air

(but not necessarily consequent) combustion in the gas phase. It would appear that the presence of calcium chloride causes an enhancement of both the glowing combustion and the flaming combustion in that the area of both peaks was increased but particularly the former. The TG results reflect the lower temperature start of the reaction in the impregnated sample, which is also seen in the DTA results. The rate of mass loss is significantly slower than that of pure cellulose. This is the only feature of the TG results which suggests any increased fire retardance. The TG data on the impregnated sample indicates a two stage decomposition, with the first exothermic peak corresponding to the end of the rapid mass loss and the second peak corresponding to the slower mass loss. TMA shows a continuous shrinkage of the $CaCl_2$-impregnated sample from about 60°C upwards; in fact prior to this temperature the sample expanded slightly. The TMA shows only a single stage process in the $CaCl_2$-impregnated sample as opposed to the TMA for the pure cellulose which shows two regions of contraction. The TMA on the $CaCl_2$-impregnated sample does not show the swelling seen for pure cellulose at 370–405°C.

The behavior of the other impregnated samples can differ in kind as well as in degree with each other. The DTA curve for the KCl-impregnated cellulose shows, for example, three endotherms as for pure cellulose. There are differences, the first exotherm has a prominent shoulder preceding its main peak; the second exotherm although sharp divides into two; whilst the third exotherm occurs over a very narrow temperature range. TG results show that the maximum rate of mass loss is less than that of pure cellulose but more than that of the sample doped with calcium chloride. The maximum rate of mass loss coincides with the shoulder on the first exotherm, whilst a second slower mass loss corresponds to the peak itself. It seems probable that the assignments given to the three exotherms for pure cellulose are inapplicable in this case. Although. the $CaCl_2$-impregnated sample shrank considerably at temperature lower than 250°C, the TMA curve for the KCl sample shows little contraction occurring in this temperature region. TMA suggests a two stage decomposition with a slower second stage and this is supported by the TG results.

The results for the NaCl-impregnated sample are similar to those of the KCl sample. There is, however, an additional shoulder on the first peak and the third sharp exotherm is not present. The temperature of the maximum rate of mass loss corresponds to the first of the two shoulders. Although TG suggests that only one process is involved TMA shows an initial decomposition which accelerates to a maximum and then decreases, followed by a second, initially accelerated reaction.

The data for the $ZnCl_2$-impregnated sample are least like the original cellulose. The TG and the TMA results show that the reaction starts at a lower temperature than that of the other samples. The first stage occurs at a slower rate than for the other impregnated samples but it is faster than the second stage (see both the TG and TMA results). The main mass loss, which for cellulose is only complete at 75% mass loss, is over at 45%. The majority of the entire weight loss is therefore the result of the second slower process. The weight of ash remaining at 800°C is slightly higher for this sample than for KCl and NaCl-impregnated samples. The DTA curves consist of two exothermic peaks and two inflections prior to the first peak which is itself higher than in the other samples. All the DTA phenomena occur after the first mass loss region. This makes it difficult to correlate the data since the peaks or periods of rapid change do not correspond.

Several features of the results presented here suggest that the addition of these chlorides to the cellulose has actually increased its flammability; these are:

(i) the onset of the decomposition (shown by TMA and TG) occurs at a lower temperature after treatment.

(ii) The peak areas of the exotherms are greater for the treated samples – particularly the second peak of the $CaCl_2$-impregnated sample.

(iii) An endotherm which for pure cellulose often precedes the first exotherm is generally absent from the DTA curves of the treated samples.

The effect of the treatment on the DTA curves is far-reaching; the impregnated samples have very different DTA curves from pure cellulose. Only the KCl-impregnated sample has three exothermic peaks like the untreated cellulose, whilst the other treated samples display only two exotherms; however, with the exception of the additional high temperature peak of the KCl sample, the DTA curves for the sample Areated with KCl and NaCl are almost identical.

The basic shape of the TG curves is less affected by chloride impregnation than the DTA, nevertheless there are significant differences in temperatures and percentages from the pure cellulose. The most obvious effect of impregnation is a diminution of both the average and the maximum mass loss although the temperature of the maximum rate is barely affected. The expansion of pure cellulose between 370 and 405°C is prevented by chloride impregnation; none of the treated samples expands during a TMA run between 60 and 500°C.

The effects of the impregnating cellulose with $CaCl_2$, KCl, NaCl and $ZnCl_2$ which appear to be associated with fire retardance are:

(i) the peak temperature of the first exotherm is increased, in the order:

$$\text{Pure} < \text{KCl} < \text{CaCl}_2 < \text{ZnCl}_2$$

(ii) The maximum rate of mass loss is reduced:

$$\text{Pure} > \text{KCl} > \text{CaCl}_2 > \text{ZnCl}_2$$

(iii) The % mass loss occurring in the rapid mass loss period is reduced:

$$\text{Pure} > \text{CaCl}_2 > \text{KCl} > \text{ZnCl}_2$$

(iv) The % ash remaining at 800°C is increased:

$$\text{Pure} < \text{CaCl}_2 < \text{KCl} < \text{ZnCl}_2$$

Generally the performance of NaCl was similar to that of KCl. The oxygen index results of Fung *et al.* [5] can usefully compared with the above data:

(v) inflammability

$$\text{Pure} > \text{CaCl}_2 > \text{KCl} > \text{ZnCl}_2$$

Since the oxygen index results reported by Fung show quite close values for cellulose treated with $CaCl_2$ and KCl, it is not surprising that the performance of these salts is occasionally transposed. It is concluded that thermal analysis may in certain cases be able successfully to predict fire resistance.

The mechanism by which these chlorides impart fire resistance is unclear; this work has produced no evidence to dispute the catalytic explanation endorsed by Madorsky *et al.* [4] and by Golova [9]. The criticism of the "levoglucosan theory" by Fung *et al.* [5] is completely dependent on their oxygen index tests and consequent flammabillity ratings. The results obtained here do not contradict this flammability data and therefore the evidence against the "levoglucosan theory" is still worth consideration.

Levoglucosan yields from the thermoanalysis of pure and treated cellulose have been obtained by Golova *et al.* [10]. The relative performance of each of the impregnated samples – obtained from these results – is shown below:

(vi) Levoglucosan yield

$$\text{Pure} > \text{ZnCl}_2 > \text{CaCl}_2 > \text{KCl}$$

Similar rankings can be constructed from the results of Tsuchiya and Sumi [11] for the yields of other products:

(vii) CO yield

$$\text{Pure} < \text{ZnCl}_2 < \text{CaCl}_2 < \text{KCI}$$

(viii) CO_2 yield

$$\text{Pure} < \text{ZnCl}_2 < \text{CaCl}_2 < \text{KCI}$$

(ix) H_2O yield

$$\text{Pure} > CaCl_2 > KCl > ZnCl_2$$

It is interesting to note that the grouping for levoglucosan and for CO and CO_2 yields are in identical – but reverse – order, whilst the water yields correspond exactly with the inflammability results ((v) above).

Addition of each of the chlorides renders the cellulose less inflammable, decreases the levoglucosan yield, and increases production of CO, CO_2 and water. However, it appears that the decreased levoglucosan and increased CO and CO_2 yields are not directly related to the reduced inflammability, whilst the water production and flame retardance may have a relationship to each other.

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