Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 831–838

THE EFFECT OF MAGNESIUM CHLORIDE HYDRATE ON THE FIRE RETARDATION OF CELLULOSIC FIBERS

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(Received May 15, 2000; in revised form October 3, 2000)

Abstract

Thermal analysis was used to investigate the effect of the addition of magnesium chloride hexahydrate as a fire retardant to cellulosic fibers. The kinetics of the decomposition of the cellulosic material were first studied. The decomposition of the dry salt was also investigated and three steps disclosed. Then, the fabrics were impregnated into salt solutions of different concentrations and the loss in mass was followed by thermal analysis. The percent loss in mass was compared to that of pure cellulosic fabric at different temperatures. It was found that there is an appreciable improvement in fire retardation at a minimum percent add-on of the salt of 35%.

Keywords: cellulose, fire retardation, magnesium chloride hydrate

Introduction

Thermal analysis has been previously used to assess the possibility of using some inorganic salts as fire retardants for cellulosic fibers [1]. In this respect, non-isothermal kinetics were found to be more appropriate because of the high rate at which the temperature increases when a fabric is subjected to a flame [2]. Both integral and differential methods can be used to analyze the kinetic data although, in the present case, the latter one is more useful than the former one since it makes use of the available DTG traces. The method of Carroll and Manche was particularly useful in the analysis of data associated with fire retarding additions [13]. The degradation of cellulose has been studied by many authors [3–6] who proposed the same following general pattern: The first step of dissociation involves volatilization of moisture and other readily volatile materials. The second step consists of gradual degradation through depolymerization until the formation of the final compound *L*-glucosan. The final step is the carbonization step. The second step was found to follow a first order reaction. The values of activation energy varied from 140 to 260 kJ mol^{-1} [6, 7].

Normally, inorganic salts that are used as flame retarding agents decompose within the range of temperatures at which cellulose degrades so that they absorb part

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

of the available thermal energy for their decomposition, thereby delaying that of cellulose.

On the other hand, magnesium chloride hexahydrate has been mentioned by Kirk-Othmer [8] to have a fire retarding effect on cotton fabrics. The relevant properties have been studied by Hebeish *et al*. [9] using a standard technique (other than thermal analysis). The thermal decomposition of magnesium chloride hexahydrate has been studied by Dutte *et al*. [10] who found that MgOHCl was formed at temperatures below 450°C, under atmospheric pressure, then decomposes above 550°C to MgO and HCl. These findings were contradicted by Homma [11] who used combined TG and DTA to prove that the anhydrous chloride goes into solution in its own water of crystallization, which then evaporates above 200°C. Also, Todor [12] found out that after the loss of three molecules of water, the salt dissolves in them, thereby hydrolysing to MgO and HCl before the rest of the water molecules are eliminated. He concluded that the exact mechanism of decomposition was very complicated and could not be easily disclosed by thermal analysis alone.

In the present paper, the thermal analysis of cellulose was studied, as well as that of the pure salt. Then, the effect of adding the salt – at different concentrations – on the TG and the DTG patterns of the fabric was followed.

Experimental

The cotton fabric consisted of pure cotton strips cut from cotton cloth manufactured in Egypt by the JIL Company. Their physical properties were determined by the authors to be: a) number of threads=38 and number of knots=52 (per square inch), b) humidity at 25°C and 35% *RH*=3.3%, c) thickness=0.53–0.56 mm, d) dry density per unit area=0.0195 g cm^{-2}.

The salt was supplied by the Gomhouria Company for Chemicals (Cairo) and was stated to be of 99.3% purity. It was ground prior to thermal analysis to pass 150 mesh screen.

The application of the salt on the fabric was performed by washing the fabrics in warm water then drying at 110°C for 3 h and weighing. A saturated solution of the salt (280 part per 100 part water) was prepared in which the fabrics were impregnated with continuous stirring. After half an hour, they were allowed to dry overnight in a desiccator. They were then weighed and the amount of dry salt deposited on the dry fabric determined. The ratio between the mass of the salt and that of 100 parts of dry cloth is expressed as % add-on.

The thermal analyser used is of the type Shimadzu TG-50 where all operating functions have been incorporated in single compact instrument including temperature sensor with computer interface and data processor. The sample holder is made of platinum and can accommodate few milligrams of the material to be tested. The rate of heating used varied from 2 to 15°C min^{-1}.

Kinetic calculations

The basic kinetic equation used in thermal analysis is:

$$\frac{dw}{dt} = Ae^{-E/RT} w^n \quad (1)$$

where w – mass of sample, mg; T – temperature, K; t – time, s ; E – apparent activation energy, J mol^{-1}; n – apparent order of reaction and A – pre-exponential factor.

If the equation is differentiated with time and d^2w/dt^2 is equated to zero, we get:

$$\frac{E}{n} = \frac{RT_i^2 (dw/dt)_i}{\varphi w_i} \quad (2)$$

where φ – the heating rate dT/dt and the subscript i denotes the inflection point.

This point can be easily obtained from the DTG trace as it corresponds to a local peak on this curve. All the parameters of the RHS of this equation can be readily taken from a combined TG-DTG plot. To get the activation energy, it is proposed to apply the method of Carroll and Manche [13]. In this method, values of T and dw/dt are taken at different heating rates for the same value of conversion (say 0.5) so that the value of w in the following equation is constant.

$$\frac{dw}{dt} = Ae^{-E/RT} f(w) \quad (3)$$

Hence a plot of $\ln(dw/dt)$ *vs*. $1/T$ should give a straight line of slope equal to $-E/R$. In this method one need not know the value of n in Eq. (1). If the value of n is desired, it can be obtained by substitution in Eq. (2).

Results and discussion

Pure cotton fabric

The thermal analysis of the pure cotton fabric was performed at a 4 different heating rates in the thermal analyser: 2, 5, 10 and 15°C min^{-1}. The results at 10°C min^{-1} are shown in Fig. 1. Three steps are apparent: a slight loss in mass at about 100°C corresponding to the evolution of physical water and other possible volatile impurities; a second step at about 300°C representing the degradation step (ending with the formation of *L*-glucosan). The third step begins at about 350°C and ends at about 450°C with an abrupt loss in mass associated with an extremely sharp peak on the DTG probably due to rapid carbonization. Similar curves were obtained at the 3 other rates. They only differ in the temperatures at which each peak starts and ends (Table 1).

The kinetics of decomposition of the 2nd step were calculated using the previously mentioned method to get the value of E/n. These values were found to be almost equal for heating rates of 2 and 5°C min^{-1}: 275 and 290 kJ mol^{-1}, resp. The value was slightly higher at a heating rate of 10°C min^{-1}: 365 kJ mol^{-1} and much higher at the highest heating rate investigated (15°C min^{-1}) where it equalled 850 kJ mol^{-1}. The

value of E was obtained by plotting $\ln(dw/dt)$ at different rates of heating *vs*. $1/T$ for the same fractional decomposition of 0.5. The plot is shown in Fig. 2. From this figure, the slope equals $-E/R=-30800$ corresponding to $E=258$ kJ mol^{-1}. This value is comparable with those previously reported [6, 7]. If the values of E/n obtained at low heating rates are adopted, this would suggest a value of $n=1$. This is in accordance with the previously reported fact that the decomposition of cellulose to *L*-glucosan follows first order kinetics [6, 7].

Table 1 Temperatures corresponding to the beginning and the end of each decomposition step of cellulosic fabric

Rate/°C min^{-1}	2	5	10	15
Step 1	33–104	40–104	37–100	40–105
Step 2	280–335	280–376	320–360	340–370
Step 3	350–460	380–464	380–465	380–468

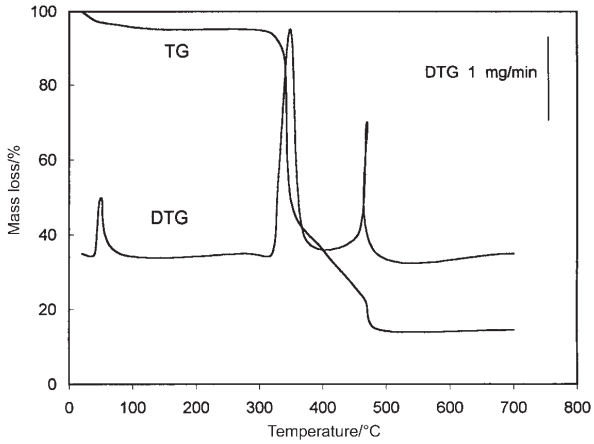

Fig. 1 TG and DTG curves for cotton fabric (heating rate=10°C min^{-1})

Pure magnesium chloride hexahydrate salt

The thermal analysis of the pure salt is very complicated and trials to elucidate the detailed mechanism were not successful [12]. In spite of this, it was possible, by mass loss calculations, to split the decomposition of the salt into three distinct steps:

Decomposition to the dihydrate:

$$MgCl_2 \cdot 6H_2O = MgCl_2 \cdot 2H_2O + 4H_2O$$

Decomposition to the monohydrate:

$$MgCl_2 \cdot 2H_2O = MgCl_2 \cdot H_2O + H_2O$$

Decomposition to the oxide:

$$MgCl_2 \cdot H_2O = MgO + 2HCl$$

The other curves obtained at heating rates of 5 and 15°C min^{-1} had the same pattern as the previous curve except for a slight shift in the temperatures at which each step begins and ends.

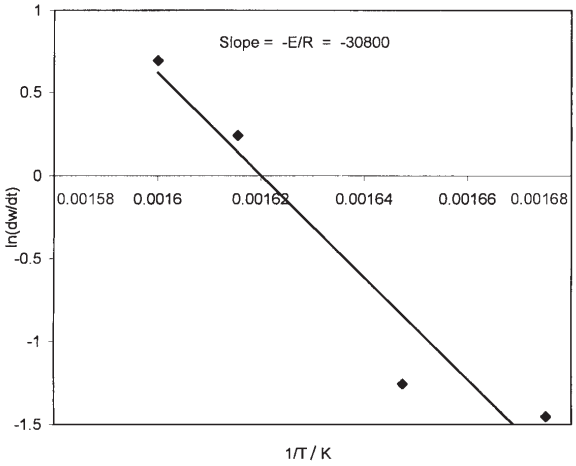

Fig. 2 Plot of ln(d*w*/d*t*) *vs*. 1/*T* for the second step of cellulose decomposition

Effect of adding magnesium chloride hexahydrate on the fire retardation of cotton fabrics

Cotton fabrics were treated with solutions of the salt with the following add-ons: 10.2, 17, 26.5, 35, 56, 63 and 122%. The thermal analyses for an add-on of 17, 10.2 and 26.5% were similar: After a slight loss up to about 220°C, there is a gradual loss in mass reaching its highest value at 330°C corresponding to about 50% loss in mass. The rate of loss then decreases up to 460°C where the final decomposition is completed. This behaviour is close to that of pure cotton (Fig. 1). We deduce, therefore, that at such low add-ons, the thermal decomposition behaviour is similar to that of pure cotton.

The behaviour is, however, quite different when the add-on exceeds 26.5%. The pattern of the thermal behaviour is shown in Fig. 3, which shows the combined TG-DTG at a heating rate of 10°C min^{-1} with a 56% add-on. As can be seen from this figure, the values of loss in mass at temperatures around 400°C are lower than the corresponding values for 17% add-on. To emphasize this point, the % loss in mass was plotted as a function of the exposure temperature for four different cases: 0% add-on, 26.5, 56 and 122% add-on. This is shown in Fig. 4. This loss was calculated by subtracting each time the loss due to the dissociation of the salt taking in account its percentage in each case. So, this is the loss due only to cellulose degradation. From this figure, it can be deduced that at temperatures above 350°C, the percent loss in case of treated fabrics is less than the untreated. However, the loss in case of 26.5%

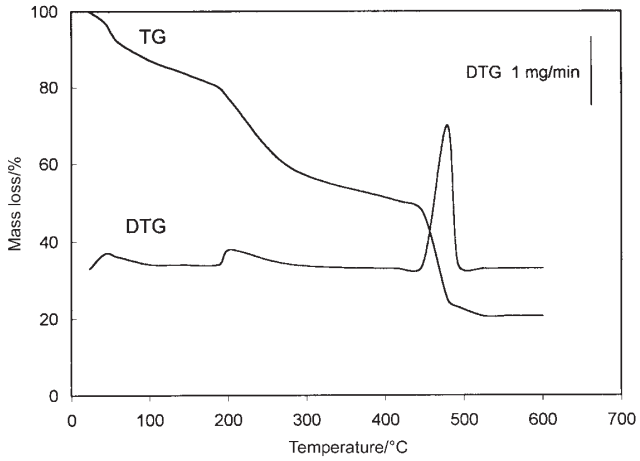

Fig. 3 TG and DTG curves for cotton fabric treated with salt at 56% add-on (heating rate=10°C min^{-1})

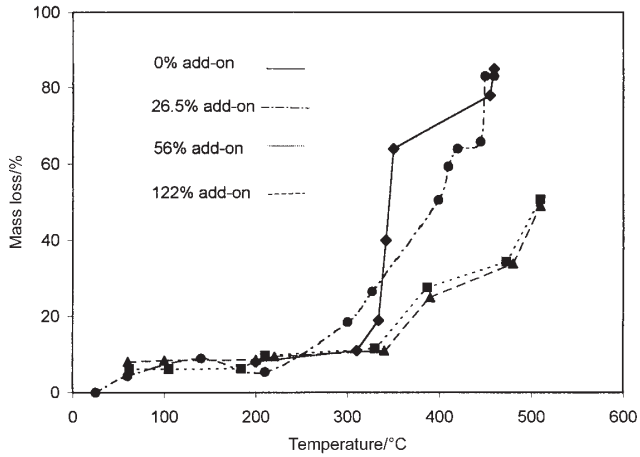

Fig. 4 Percent mass loss of cellulosic material in cotton fabric treated with different add-ons

add-on is comparable to that of the untreated fabric where as the two cases corresponding to 56 and 122% add-on show a marked improvement over that of the 26.5% case. At 400°C, while the loss is only 25% in case of treated fabrics (56 and 122%), it is about 70% in case of the untreated. Similar curves have been obtained for all the add-ons investigated, although not shown in the figure. The general pattern is close to that of the fabrics with 26.5% add-on as long as the percent add-on is below 35%. Starting from that percentage, all percent loss curves become similar to those corresponding to the two treated fabrics with 56 and 122% add-on. We conclude that, to obtain a fire retarding action, it is sufficient to use an add-on of 35%. This is in con-

tradiction with the work of Kirk-Othmer [8] according to whom an add-on of 16.5% is sufficient to obtain a reasonable fire retarding effect. We believe that this discrepancy may be due either to the use of textiles having different properties (such as number of knots or threads) or to different experimental conditions (such as the rate of heating). These authors have mentioned neither the properties nor the conditions.

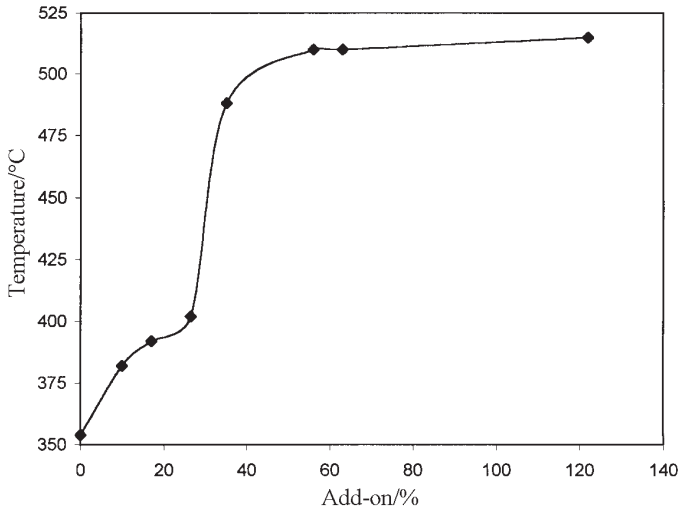

Fig. 5 Effect of percent add-on on the temperature corresponding to 50% mass loss

To summarize the previous findings, a plot was made to show the effect of the % add-on on the temperature at which 50% of the loss in mass takes place. The choice of this particular percentage is arbitrary. This plot is shown in Fig. 5 where the effect of the salt on the retardation of the final decomposition step of cellulose is obvious (for add-ons >35%).

Conclusions

The treatment of cotton fabrics with magnesium chloride hexahydrate salt is beneficial for fire retardation. It was proved, by use of thermal analysis, that a minimum add-on of 35% is necessary to improve this property. The percent loss in mass at temperatures around 400°C is much lower in case of treated fabrics than in case of the untreated (25 compared to 70% respectively). Also, the temperature at which the second degradation step is completed increases from about 360°C, in the case of pure cellulose, to 460°C when a 35% add-on used.

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