DTA and IR Studies on Cellulose Treated with a Formulation Based on Phosphorus, Nitrogen and Sulphur Synergism*

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Received 22 June 1978; accepted 14 October 1978

DTA studies were made on cellulose treated with THPC and thiourea in the presence of trace amounts of ammonium dihydrogen orthophosphate as a function of hydrogen ion concentration in air and nitrogen atmospheres. The thermograms showed differences in the decomposition temperatures, depending upon the pH of the formulations. The thermograms of the treated cellulose had sharp and well defined peaks in air atmosphere, whereas in nitrogen atmosphere, double peak patterns were observed. Infrared spectra of some selected samples, which had been partially or completely charred near the peak temperatures, gave an indication of dehydration and skeletal rearrangement of the thioamide linkage in the adduct.

The function of a flame retardant is to alter the course of decomposition, so that a lower percentage of flammable volatiles is produced and a correspondingly larger quantity of char is formed. Reid1 reported that the treated fabrics left much larger residues when heated above 250°C as compared to those left by untreated fabrics. Analysis of the residual chars showed reduction in the volume of carbonaceous gases and a shift towards the production of ideal products, namely carbon and water.

A number of flame retardant formulations for cotton developed in recent years are based on tetrakis(hydroxymethyl) phosphonium chloride (THPC). In our earlier communications2, a new formulation based on THPC, thiourea (TU) and a small quantity of ammonium dihydrogen orthophosphate (ADP) for imparting flame retardancy to cotton textiles was reported. The reaction between cellulose powder and THPC + TU + ADP was also studied under different conditions of pH and thermal curing. IR studies carried out on these systems showed two sharp bands at 1530 cm⁻¹ and 1350 cm⁻¹, which were absent in the spectra of any of the individual components of the formulations. The bands have been identified as being due to thioamide (II) linkage. The data were used for understanding the mechanism whereby THPC-based formulations impart flame resistant characteristics to cellulose.

In the present study, the DTA technique has been used to follow the path of thermal degradation of cellulose made flame resistant by treatment with THPC-TU-ADP formulations prepared under varying conditions of pH (4.0-6.5) as a function of temperature. The thermograms were obtained in nitrogen and air atmospheres. Thermograms of the treated samples were compared with those of untreated controls. Chars of certain selected samples were also investigated by the IR technique.

Materials and Methods

The method of treating cellulose samples at different pH values and conditions of curing, drying and storing has been described elsewhere3.

Samples of the charred pure cellulose and of the charred treated cellulose at pH 6.5 and 4.0 were prepared for IR studies by heating the mixture in a DTA cell under nitrogen. Heating was stopped in the vicinity where the DTA peaks were observed and the samples cooled rapidly to stop further reaction.

The thermograms were recorded on a DTA-02 Universal Model (VEB Laborelektronik Halle, GDR). The instrument could be operated in the range of ambient temperature to 1200°C and programmed to maintain a preselected upper temperature, or shut off at any temperature. Data could be presented on an X-Y recorder with block temperature as the X-axis and ΔT as the Y-axis. A heating rate of 12.5°C/min was adopted throughout. Most of the samples were investigated in the range 100-500°C.

The sample to be analysed was ground thoroughly and placed in the sample holder. γ-Alumina was used as the reference material.

*Research project supported by the U.S.D.A.-A.R.S., USA under project No. UR-A(7)-219.
Results and Discussion

Schwenker and Beck\textsuperscript{4} observed that at high temperatures, DTA curves in oxygen atmosphere were poorly defined due to many overlapping reactions. Therefore, to get more information, thermograms were obtained in nitrogen atmosphere also. In the present study also, nitrogen atmosphere was used in addition to air atmosphere. Thermograms of single components were obtained for systems consisting of the desired combinations of these compounds. The thermograms of cellulose-THPC-TU-ADP systems under varying conditions of pH in air and dynamic nitrogen atmosphere are presented in Figs 1 and 2 respectively. The values of maxima for the systems studied in the two atmospheres (nitrogen pressure 2 kg/cm\(^2\)) are presented in Table 1.

An inspection of the peaks of the individual components and their combinations shows that the decomposition temperatures of cellulose are around 340° and 310°C in air and nitrogen atmospheres respectively. The system cellulose-THPC-TU-ADP gave exotherms in the range 200-250°C, depending upon the pH. At the lowest pH, the exothermic peak was observed at the lowest temperature of 200°C, indicating that the adduct formed was better in so far as the non-flammability was concerned. Since pyrolysis of the treated and untreated cellulose is a complex process, degradation of the residue, which would be an endothermic reaction, is overshadowed by the exothermic reactions, as two or more competing reactions might be taking place simultaneously.

It is seen from Table 1 that the decomposition temperature of cellulose-THPC-TU-ADP system decreases with fall in \(\text{pH}\) of the formulations; this results in the formation of lower volumes of flammable volatiles and a correspondingly larger quantity of char. However, the advantage that could have been gained by adopting a lower \(\text{pH}\) for the treatment of cellulose is offset by other factors, such as lowering in tensile and

![Fig. 1—DTA curves of cellulose treated with THPC-thiourea adduct](image1)

![Fig. 2—DTA curves of cellulose treated with THPC and TU under dynamic nitrogen flow of 2 kg/cm\(^2\)](image2)

Table 1—Maxima in the Thermograms of Different Compounds and Systems

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak temperature, °C</th>
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<tbody>
<tr>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>Cellulose</td>
<td>325 (endo)</td>
</tr>
<tr>
<td>Thiourea</td>
<td>160, 240 (endo)</td>
</tr>
<tr>
<td>ADP</td>
<td>210, 290 (endo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 6.5)</td>
<td>250 (exo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 6.0)</td>
<td>220 (exo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 5.5)</td>
<td>220 (exo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 5.0)</td>
<td>210 (exo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 4.5)</td>
<td>200 (exo)</td>
</tr>
<tr>
<td>Cellulose + THPC + TU + ADP (pH, 4.0)</td>
<td>200 (exo)</td>
</tr>
</tbody>
</table>
tear strengths, as observed by Beninate and coworkers. They showed that fabrics with the maximum durability were those treated with formulations having higher pH values (6.9-9.0). Thus, in the formulations with low pH values, although the samples had lower decomposition temperatures, they did not improve the durability of fabrics.

The thermograms in nitrogen atmosphere under dynamic gas flow conditions were similar to those in air, except that the exotherms were somewhat smaller, and the thermogram exhibited the double peak pattern in all cases. The second exotherm appeared in each case in the range 270-250°C, depending upon the pH of the sample. The first exothermic peak may be the result of exothermic changes due to decomposition and the second one may be attributed to bond formation.

Infrared examination of chars obtained in nitrogen atmosphere—IR spectra of the untreated cellulose specimens which had been heated to different temperatures (300-500°C) in nitrogen atmosphere indicated that the changes observed with respect to various bands were, in general, common to any char of cellulose; at 360°C, the char pattern showed almost complete decomposition.

The cellulose samples treated at pH 6.5 were prepared for IR examination after heating them in a DTA cell in nitrogen atmosphere to different temperatures, namely 200, 220, 240, 250 and 260°C; samples treated at pH 4.0 were prepared similarly after heating to 180, 200, 220, 240 and 260°C. The IR spectra of the residues gave an indication of dehydration and skeletal rearrangement, as evidenced by the decrease in the absorption attributed to the O-H stretching at 3400 cm⁻¹ and the aliphatic C-H stretching at 2900 cm⁻¹ respectively. A new peak observed in the cellulose-THPC-TU-ADP system at 1530 cm⁻¹ reported earlier started disappearing with increase in the temperature of the charred samples; it disappeared completely at about 300°C. This indicates some skeletal rearrangement of the thioamide linkage in the adduct. However, in the case of the charred samples, the sharp band at 1350 cm⁻¹ disappeared only above 450°C.

It may be concluded that the treated cellulose decomposed at a lower temperature and consequently yielded higher quantities of residues. Degradation in air was more complete and proceeded at lower temperatures. The presence of two exothermic peaks in the DTA curves for treated cellulose in nitrogen atmosphere may be taken to mark decomposition and formation of new bonds during the process of pyrolysis.

Acknowledgement

The authors are grateful to the United States Department of Agriculture, Far Eastern Agriculture Research Service for supporting the research project through the grant of research fellowships to two of them (SB and JCG).

References