VISCOSE CARBONS: MODIFICATION OF THERMAL DECOMPOSITION OF VISCOSE BY INORGANIC ADDITIVES

A. Capon and F.A.P. Maggs
Chemical Defence Establishment, Porton Down, Salisbury, Wiltshire, UK

Introduction

The yield of carbon char from cellulosic precursors may be augmented by treatment of the cellulose with inorganic additives prior to carbonisation. The effect on the thermal decomposition and on the char yield of impregnating viscose rayon with inorganic chlorides has been studied using DTA and TGA techniques.

Experimental

Rayon cloth samples were impregnated by immersion in salt solutions by a reproducible technique. Analysis showed that the uptake of salt during preparation could be calculated from the equation, weight of salt (mg/g) = solution strength (mg/ml) x volume occluded (ml/g). (By the technique used 1.4 $\pm$ 0.1 ml/g of solution were occluded). Samples were carbonised in flowing nitrogen (5 ml/min) at 5°C/min using Stanton Redcroft TGA and DTA apparatus. Char yields were recorded at 450°C and on occasions at 850°C. Samples were not dried prior to use.

Char Yield

The char yield of unimpregnated viscose was 22% at 450°C and 13% at 850°C (dry basis). In all cases examined prior treatment with a 5% w/w solution augmented the char yield. Yields obtained with different metal chlorides at 450°C varied as follows.

20 - 30% Au
30 - 40% Na, K, Ni, Al, Sn, Hg, NH_4
40 - 50% Li, Mg, Ca, Sr, Ti, Cr, Mn, Cu, Zn, Cd

For six salts the effect of strength of the impregnation solution on char yield at 850°C was examined. The results (Fig.1) show that small amounts (10 - 20 mg/g) of impregnant have a marked effect on yield and that the rate of yield increase diminishes with increasing impregnation.

Thermal Decomposition

The DTA and TGA curves obtained exhibited a wide variety of behaviour. All salts with the exception of Na and K caused a lowering of the decomposition temperature, and in general chlorides within each periodic grouping gave rise to reaction in the same temperature zone. (Li was an exception, causing a substantial lowering of the decomposition temperature). The results may be superficially grouped according to the number of reaction zones observed (cf. Fig.2). In one group a single temperature zone of reaction (zone B, $\sim$ 200 - 330°C) at or near the zone shown by untreated viscose, was observed. Other impregnants gave rise to two zones of reaction, one in the 100 - 200°C region (zone A), the second in zone B. In a few cases (e.g. $HgCl_2$) more complex behaviour was observed. In all cases a maximum in the rate of weight loss coincided with a peak in the DTA curve.

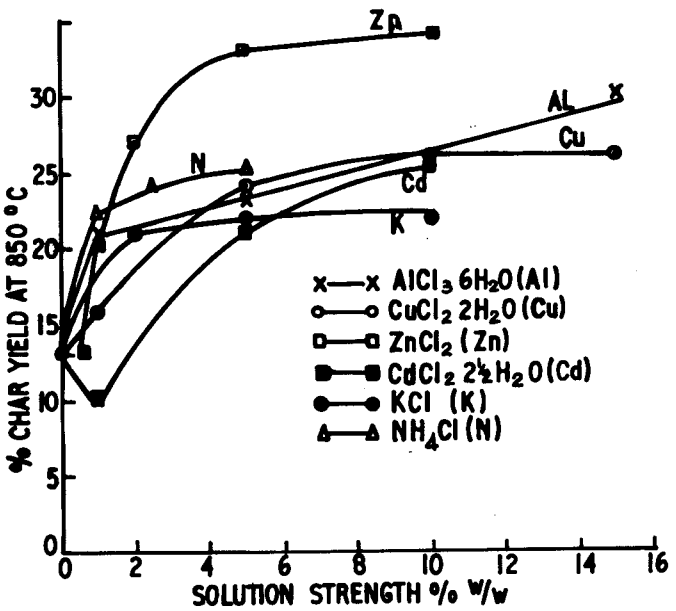

Figure 1. Variation of Char yield with impregnation solution strength.

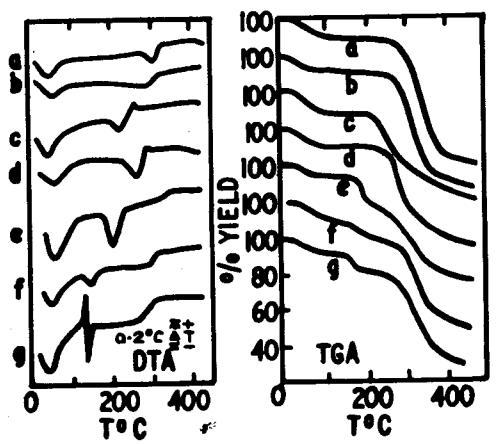

Figure 2. DTA and TGA curves for (a) Untreated viscose and treated with 5% w/w solns. of (b) KCl, (c) $ZnCl_2$, (d) $CdCl_2$, (e) NH_4Cl, (f) $AlCl_3$, (g) $CuCl_2$. N_2 Atmosphere: 5°C/min.

Further distinctions were disclosed by varying the quantity of impregnant (1). For KCl the zone B temperature remained unchanged, but the extent of the energy changes diminished with increasing impregnation.

For $ZnCl_2$ and $CdCl_2$ the zone B temperature was reduced, the temperature of decomposition being lower the greater the amount of impregnation. For NH_4Cl, $CuCl_2$ and $AlCl_3$, increasing the extent of impregnation increased the extent of the zone A reaction and reduced the extent of the zone B reaction, the reaction temperature of both zones being essentially unaltered.

Several reaction mechanisms have so far been distinguished: (i) Reaction of impregnant in zone B with thermally unstable viscose (e.g. KCl, NaCl); (ii) Catalytic enhancement of the initial dehydration reaction at the expense of a depolymerisation process in zone B (e.g. $ZnCl_2$, $CdCl_2$); (iii) Decomposition of the salt to yield HCl, partial reaction of the viscose in the released HCl, followed by completion of the decomposition at higher temperatures (e.g. NH_4Cl, $AlCl_3$); (iv) Formation of a viscose/salt complex followed by breakdown of the complex and further decomposition at higher temperatures (e.g. $CuCl_2$).

Mixed Impregnants

Experiments have also been carried out with mixed salt impregnations. In general the DTA and TGA results showed peaks attributable to the individual components of the reaction mixture. This is illustrated in Figure 3 where the reactions of $ZnCl_2$ and $CuCl_2$ are clearly visible in the DTA and TGA traces of the mixed impregnant sample. Decompositions at higher temperatures tend to be diminished, however, in the presence of salts reacting at lower temperatures.

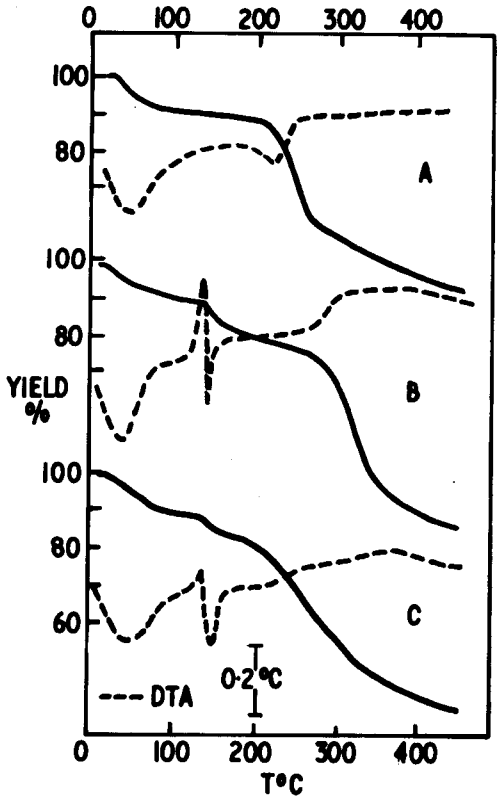

Figure 3. DTA and TGA curves for viscose rayon impregnated with 5% w/w solns. of (A) $ZnCl_2$, (B) $CuCl_2$ and (C) 2.5% w/w each of $ZnCl_2$ and $CuCl_2$.

Reference

(1) Capon A. and Maggs F.A.P., *Proc. 1st. ESTA, Salford, UK, Sep 1976*, p.176. D. Dollimore (Editor), Heyden (1976).