

STUDIES OF PYROLYSIS AND AIR HEATING OF RAYON BY INVERSE GAS CHROMATOGRAPHY

HENRY L. FRIEDMAN and BERNARD MILLER

Textile Research Institute, Princeton, NJ 08540 (U.S.A.)

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ABSTRACT

Inverse gas chromatography using water probing at 110°C was carried out to characterize rayon yarns after prior heating at 200 and 250°C in both inert (nitrogen) and oxidative (dry air) atmospheres for successively longer time intervals. During the early stages of heating in either atmosphere, the affinity of the rayon for water drops rapidly. However, whereas continued heating in N₂ results in a further loss of activity, data have been obtained showing that after an initial period yarns heated in air at 250°C exhibit an increasing attraction for water even while losing more weight.

INTRODUCTION

Inverse gas chromatography (IGC) is a technique used to study polymer properties through interpretation of interactions with volatile solutes as revealed by gas chromatography. The polymer is used as the stationary phase and the volatile solute is known as a probe. This method was first used by Smidsrød and Guillet [1] and was recently reviewed by Braun and Guillet [2]. It is reported to be useful for determining glass transitions, melting transitions, qualitative information on the temperature coefficient of free volume increase above the glass transition, polymer solution thermodynamics, crystallinity, adsorption isotherms, heats of adsorption, surface area, diffusion coefficients, diffusion of plasticizers, degree of curing, and composition of mixed polymers.

A considerable amount of research on fibers by inverse gas chromatography has been carried out at the Center of Research for Silk and the Textile Industry, and the Chemistry Department of the Université Claude Bernard in Lyon, France, by Chabert and co-workers [3–6], but no results for cellulose were reported. Inverse gas chromatography has been applied to cellulose by Gray and co-workers [7–9] in an attempt to measure the solid surface area. The technique involved measuring retention times for different small volumes of probe, and fitting the data to the BET equation for adsorption [10].

In preliminary studies we observed that a conventional spun rayon yarn heated in an inert atmosphere exhibited decreased retention times for an injected water charge as preheating time and temperature were increased.

This led to a systematic investigation in which weighed IGC rayon yarn columns were heated for various time intervals in flowing nitrogen or air in an oven at 200 or 250°C. After cooling, the columns were installed in the gas chromatograph, and IGC water probe measurements were made at 110°C. These studies are described below.

EXPERIMENTAL

The gas chromatograph (GC) used is the Hewlett Packard Model 5730A dual column unit with a differential thermal conductivity detector. One- μ l water probes are injected from a 10- μ l syringe into an injection port at 150°C, with the column temperature at 110°C. Because small injection volumes are difficult to measure accurately, and since the flow-through time for each water injection as well as data processing time is lengthy, it was decided to stay with a single probe volume for semiquantitative intercomparison purposes. Nitrogen carrier gas is used with a flow rate of 40 ml min^{-1} at a tank regulator pressure of 50 psig. Signals were recorded with a Leeds and Northrup Speedomax XL 620 Series dual channel recorder with 10 speeds ranging from 1 in. h^{-1} to 6 in. min^{-1} .

The 1/8-in. o.d. stainless steel GC tubes are filled with rayon yarn by the following method. First, a nylon leader yarn which is longer than the column is pulled through the straightened column with the aid of a vacuum pump. A predetermined number of rayon yarn loops are then wound between two rods which are separated by a distance that is greater than column length. The leader is knotted to an end of the loop bundle, and the latter is pulled through the column by the leader. After being cut to fit, the column ends are packed with short lengths of fiberglass wool.

Samples of Avtex Fibers Inc. SN 2544 bright regular spun rayon (1.5 denier, $1\frac{9}{16}$ in. long filament) were extracted with chloroform and isopropanol (three times each), and 52 strands of yarn were drawn into each column. Each fresh IGC column was put into the GC and allowed to dry at 110°C in flowing N_2 until a flat baseline (indicating no more water evolution) was achieved. A water probe was injected at the inlet septum and the IGC curve was recorded. This was done three times to establish the initial water retention capability of the rayon. The dried column was weighed after removal from the GC. Specific retention volumes, in ml g^{-1} , of column packing material were determined from

$$V_g = F (273.2/T) [(t_R - t_M)/W]$$

where F = carrier gas flow rate (40 ml min^{-1}), T = column temperature (383.2 K), t_R = average retention time of probe molecules (H_2O) in the gas phase (peak time in min), t_M = average retention time of an undetained molecule (peak time for O_2 in min), and W = mass of column packing (in g). Some of the pertinent properties of fresh rayon columns dried at 110°C are listed in Table 1. Note that the reproducibility of V_g from column to column is about $\pm 5\%$ (based on results for five columns).

A pair of columns was then connected, one to a regulated tank of N_2 and the other to air, and flow was adjusted to 40 ml min^{-1} . The columns were

TABLE 1

Properties of dried fresh rayon columns related to inverse gas chromatography *

Property	No. of columns	Ave value
Break-through time **	9	3.26 ± 0.37 min ***
Peak time (t_R)	9	5.45 ± 0.24 min ***
Dry weight of rayon (W)	5	0.2661 ± 0.0067 g
Specific retention volume (V_g)	5	579 ± 28 ml g ⁻¹

* $\frac{1}{8}$ -in. o.d. × 1-ft. rayon column at 110°C, 1- μ l H₂O probe, N₂ carrier flow 40 ml min⁻¹ at 50 psig.

** Time to first detection of water.

*** Average deviation for each of three readings on the same column = ±2.8%.

put into an isothermal oven for a predetermined period of time, then removed and cooled. Gas flow was maintained during cooling. For the long duration heating experiments it was necessary to adjust gas pressure to keep the flow rate constant, presumably because loss of fiber mass had reduced packing. When the columns were cool, they were reweighed and reinserted into the GC for IGC measurements at 110°C (again in triplicate). Two series of experiments were performed, one at 200 and another at 250°C, as described below.

RESULTS

Weight changes for the rayon samples as a function of time for the 200°C heatings in N₂ and air in the GC tubes and, for comparison, in the DuPont 951 thermobalance, are shown in Fig. 1. The isothermal thermogravimetric

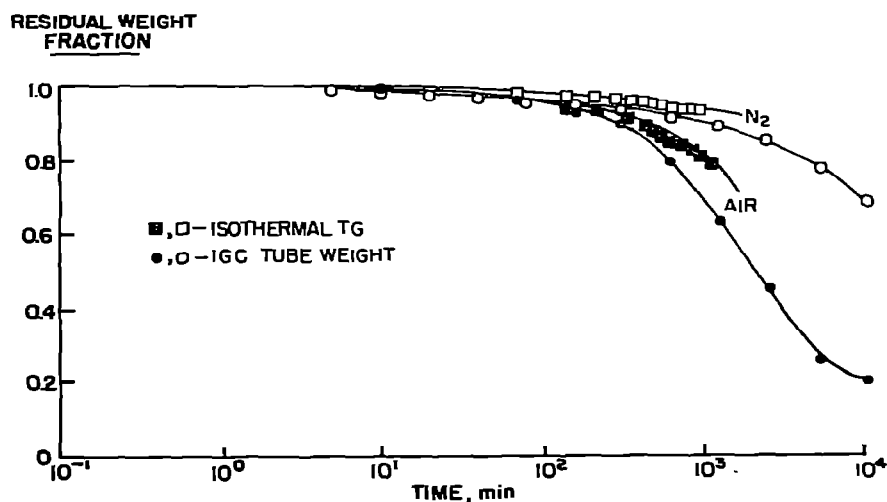


Fig. 1, Weight loss of rayon yarn samples with time of heating at 200°C in air and N₂ in GC tubes and in a thermobalance.

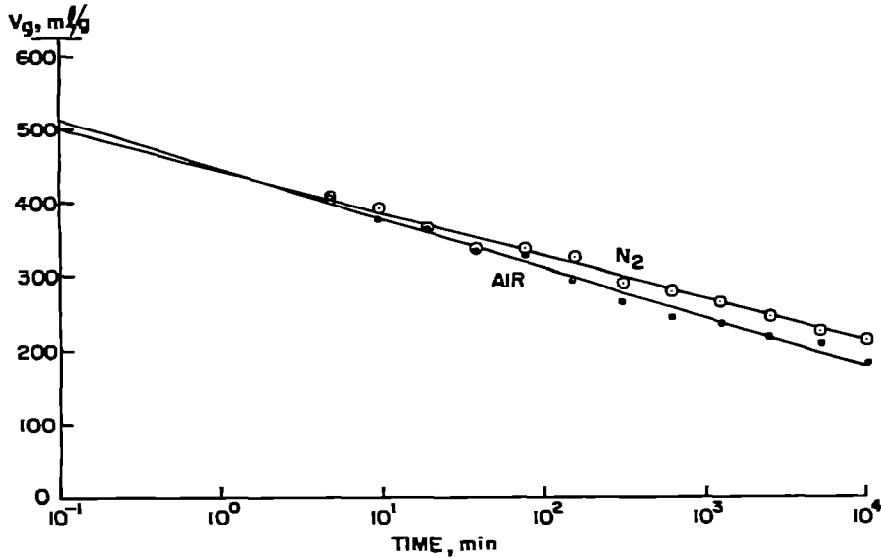


Fig. 2. Specific retention volume for water probing at 110°C of rayon yarns in Fig. 1 as a function of heating time at 200°C in air and in N₂.

(TG) experiments were carried out at flow rates of 50 ml min⁻¹. In each case, weight loss was faster in air than in N₂, and faster in the GC tubes than in the thermobalance. Despite the faster volume flow rate in the thermobalance, the larger cross-section of that instrument made the linear flow velocity much slower than in the GC tubes, so that faster removal of decomposition products in the GC tubes resulted in higher weight loss rates.

The results of the IGC measurements for the samples heated at 200°C are shown in Figs. 2 and 3. The time axis of Fig. 2 is logarithmic in order to

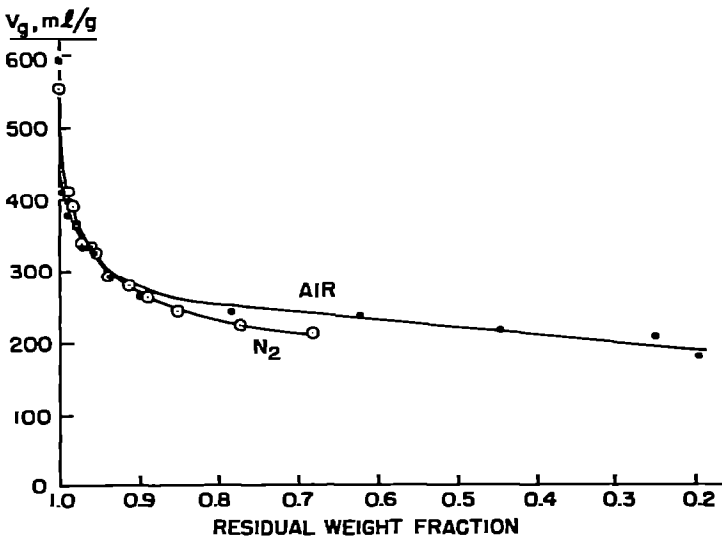


Fig. 3. Specific retention volume measured as in Fig. 2 as a function of weight loss on heating at 200°C in air and in N₂.

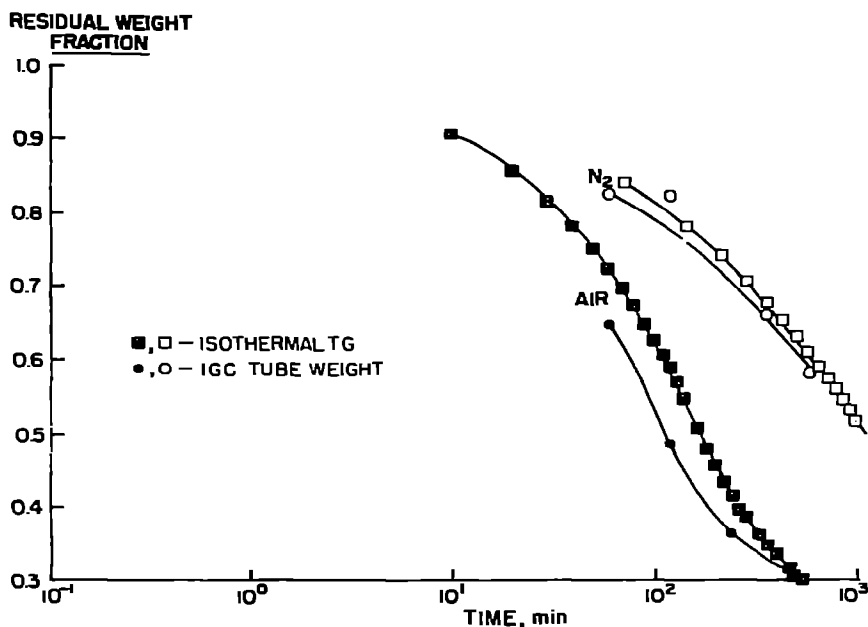


Fig. 4. Weight loss of rayon yarn samples with time of heating at 250°C in air and N₂ in GC tubes and in a thermobalance.

make the data readable, and the data were fitted with straight lines within the precision of the individual measurements. The slopes of the N₂ and air lines ($\Delta V_g/\Delta \ln t$) were -25.31 and -29.08 , respectively. From this it appears that V_g drops more rapidly for air than for N₂; however, when plotted as a function of residual weight fraction (Fig. 3), the V_g values start out pretty

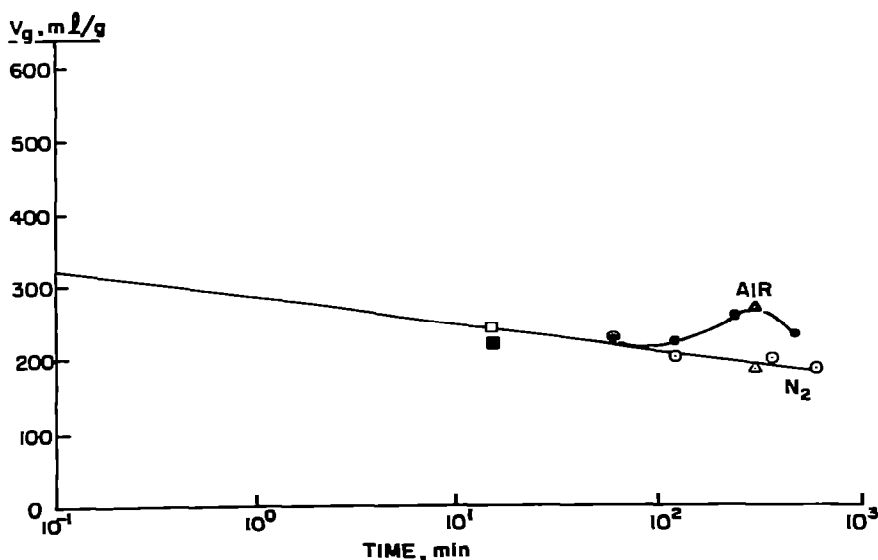


Fig. 5. Specific retention volume for water probing at 110°C of rayon yarns in Fig. 4 as a function of heating time at 250°C in air and in N₂. ■, □ and ▲, △ denote measurements on fresh columns.

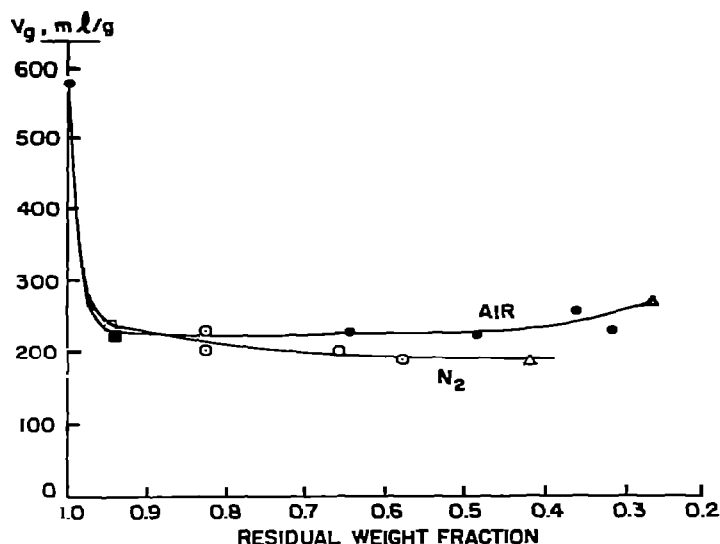


Fig. 6. Specific retention volume measured as in Fig. 5 as a function of weight loss on heating at 250°C in air and in N_2 . □ (estimated), ■ and ▲, △ denote measurements on fresh columns.

much together, but after 10% weight loss, the values for air exceed those for N_2 .

Residual weight fractions at 250°C for the GC tubes and isothermal TG measurements are shown in Fig. 4. Note that the relative positions of the various curves are the same as at 200°C (see Fig. 1). (The displaced value for 120 min of heating in N_2 in the GC tube is considered to be the result of a weighing error, since the TG results show only a consistent weight loss.) The IGC results are shown in Figs. 5 and 6. (Note that separate experiments on fresh columns were performed for 15 and 300 min of heating, which seem to give values in reasonable agreement with the cumulative heating experiments performed on single columns.) In this case, as for 200°C, the plot of V_g vs. $\ln t$ (Fig. 5) is linear for N_2 , with slope = -15.77 . For air, the V_g values seem to rise after ~ 70 min, showing a significant increase in surface activity. The N_2 and air curves in Fig. 6 seem to coincide up to about 10% weight loss (as in Fig. 3), after which the air curve once again shows higher V_g than for N_2 . In this plot the V_g values for heating in air increase during the later stages, in contrast with the results for N_2 at 250°C, and for both N_2 and air at 200°C.

DISCUSSION

One significant finding is that during the early stage of thermal decomposition, the affinity of the rayon surface for water drops quickly at 200 and 250°C regardless of whether it is in an inert or oxidizing environment. After about 10% weight loss, the drop in activity is greater for N_2 than for air at any given extent of weight loss. In air at 250°C, the surface activity increases

even as extent of decomposition increases after approximately 10% volatilization. These data suggest that early decomposition in both environments may be simply pyrolytic. Perhaps the products and/or the rate of volatilization are such as to prevent oxygen from reaching the rayon surface. During further heating, the surface may start to oxidize, and the resultant functional groups may be more interactive towards water than the pyrolyzed surface.

The production of more interactive locations was not observed at 200°C, and further work is in progress to establish more closely where, between 200 and 250°C, the behavior shifts from one mode to the other. In addition, an attempt is being made to correlate the results of IGC studies with isothermal TG kinetics [11].

CONCLUSIONS

Inverse gas chromatography appears to be an effective technique for studying changes in activity of cellulose (and probably other polymers) as a result of pyrolysis and oxidative heating.

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