

The Synergistic Effect of Benzhydrylation and Iodination of the Flammability of Alpha-Cellulose

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Synopsis

Cellulose samples modified by iodination, benzhydrylation, and benzhydrylation followed by iodination were pyrolyzed to investigate the potential flame retardance of such treatments. Their effect on crystallinity, rate of thermal degradation, char production, and pyrolysis products was determined. Results indicate that in general the crystallinity index varies inversely with the percentage of substitution, rate of weight loss, and amount of residual char. Although the rates of weight loss of the substituted samples increased from 0.3%/min to 108%/min, depending on the type and percentage of substitution, the overall weight loss pattern of the treated cellulose was similar to that of the untreated samples. Of the three treatments, iodination appears to offer the best flame retardance in that the residual char is increased by a much larger factor for a given weight loss rate. On the other hand, addition of the benzhydryl to the iodinated sample decreases the char. All three treatments drastically reduce the number of degradation products of molecular weights lower than 150; untreated cellulose gave 59 components, whereas the substituted cellulose produced five major compounds: water, acetic acid, furfural, 5-methyl-2-furaldehyde, and 1,5-anhydro-2,3-deoxy- β -D-pent-2-eno-furanose. Of these, water and the furanose derivatives were the major components.

INTRODUCTION

Since cellulose is commonly found in areas of high fire hazard and plays a major role in most destructive fires, the effect of fire retardants on its mechanism of thermal decomposition is of fundamental interest in developing flame-resistant clothing and other cellulosic materials. Two basic ways in which a retardant may act are (1) to decrease the quantity of the gases produced and (2) to decrease the flammability of these gases. The standard retardant treatments increase the amount of residual char and thus decrease the quantity and flammability of the degradation products. However, at the same time they increase the rate of thermal degradation of the material at a given temperature and thus reduce its heat stability.^{1,2}

Experiments with gamma-radiation from ⁶⁰Co on aromatically substituted cellulose indicate that there is a decreased yield of free-radical sites in the aromatically substituted cellulose as compared with those in unsubstituted cellulose.³ It has been suggested that the substitution of aromatic groups on the carbohydrates affects energy transfer, particularly localization of

energy. The energy from the secondary electrons is directly absorbed by the aromatic groups and the energy reirradiated without localizing at a chemical bond causing decomposition or induced free-radical formation.

Experiments attempting to block the formation of levoglucosan (one of the major constituents of tar from cellulose, which provides the bulk of its volatile fuel) have been conducted in the past by esterifying the hydroxyl groups of cellulose with methanesulfonyl chloride.⁴ Since the levoglucosan decomposes into volatile and flammable products, the mesyloxy groups were partially replaced with halogens, particularly bromine and iodine, which are very effective flame retardants.

The results of past studies⁵ indicated that the substituted cellulose definitely deviates from its normal decomposition scheme. However, existing information does not show how the rate of pyrolysis and the amount of residual char are affected by these retardants. Furthermore, nothing conclusive has been ascertained about the effect of the treatments on the composition of the degradation products formed during pyrolysis.

The present work seeks to elucidate the combined effects of benzhydrylation-iodination on the degradation process of white alpha-cellulose. The work is conducted under isothermal conditions to simplify interpretation of the data. The cellulose used in this work is composed of a blend of 25% southern pine, purified sulfite pulp, and 75% sweetgum-purified pulp. The samples are 0.07 cm thick with a density of 0.70 g/cm³.

The scope of this study includes: (1) development of the most efficacious means of incorporating the benzhydryl and iodine groups into the cellulose molecule without producing undesirable side effects, (2) x-ray diffraction measurements of the treated cellulose to determine the extent of crystallinity change produced by the various degrees of substitution, (3) measurements of weight loss for benzhydrylated cellulose pyrolyzed in a nitrogen-fluidized sand bath at 288°C to determine the effect of benzhydrylation in terms of degree of substitution on the rate of degradation and the amount of residual char, (4) measurements of the weight loss for the iodinated cellulose pyrolyzed at 288°C to determine the effect of iodination in terms of degree of substitution on the rate of degradation and the amount of residual char, (5) measurements of weight loss of benzhydrylated and iodinated cellulose (of various degrees of substitution) to determine the most effective combination of these retardants which would produce the lowest rate of degradation and the highest residual char, and (6) analysis, by means of a gas chromatograph-mass spectrometer combination instrument, of the degradation products of the benzhydrylated, iodinated, and the combined benzhydrylated-iodinated cellulose to determine the effect of the various treatments on the type of degradation products formed during combustion.

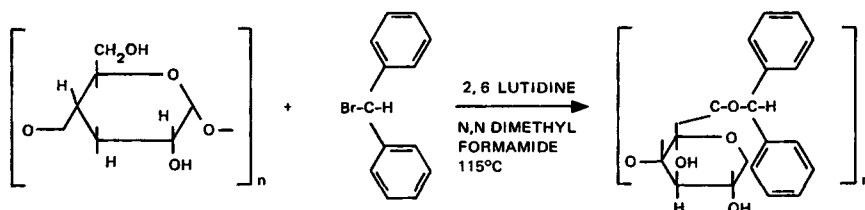
EXPERIMENTAL

To facilitate substitution, white alpha-cellulose disks (2.0 cm in diameter) were first soaked in 20% NaOH solution for various intervals ranging from 10.0 sec to 15.0 min. The samples were washed free of excess NaOH, soaked for 5.0 min in a 5.0% acetic acid solution, and washed again with

water until the wash water was at pH 5.5 as measured with a pH meter. To study the effect of alkaline pretreatment on the degree of substitution and the crystallinity index, at least 2.0 g of cellulose from each pretreatment were used in each substitution. The procedure for the synthesis of the derivatives was as follows:

Benzhydrylation⁵

Four grams cellulose was suspended in pyridine to remove most of the water and then washed with 2,6-lutidine. The samples were then placed in a mixture of 18.4 ml N,N-dimethylformamide, 18.4 ml 2,6-lutidine, and 31.7 g benzhydryl bromide. The reaction was carried out at 115°C under reflux for 20.0 min.

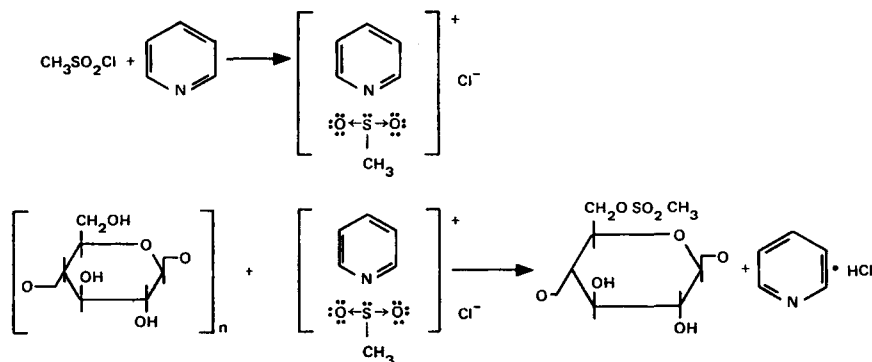


The crude samples were purified by first washing them with pyridine and then extracting for 24 hr with methanol in a Soxhlet extractor to remove a brown discoloration. The resulting white derivatives were washed with water, air dried, and stored for subsequent studies.

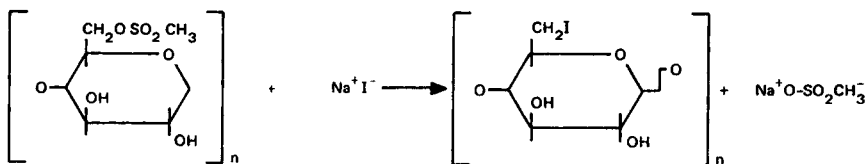
Iodination⁴

Preferential iodination of the primary hydroxyl group was attempted by replacing the primary mesyloxy group with iodine. The general procedure for mesylation was as follows:

A mixture of methanesulfonyl chloride and pyridine was prepared by carefully adding 8.5 ml methanesulfonyl chloride to 40.0 ml redistilled pyridine, cooled to 15°C. After 5.0 min, the mixture was removed from the ice bath and was allowed to stand at room temperature until a deep amber color developed. To this mixture were added 2.0 g pretreated and pyridine-soaked cellulose. The temperature of the reactants was slowly raised to 65°C and was maintained around 65°C ± 1.0°C for 20.0 min by alternately placing the reaction flask in hot and cold water baths.



The mesylated cellulose was first washed with formamide; then the brown discoloration was removed by extraction with methanol in a Soxhlet extractor for 24 hr. The resulting white derivatives were washed with water and were ready for iodination. The substitution was carried out in a 20% NaI solution in the presence of solid BaCO₃ for 5.0 hr under reflux using a heating mantle.



The derivatives were washed with water, air dried, and stored for subsequent studies.

Benzhydrylation-Iodination

To determine the combined effect of both treatments on the degradation rates, decomposition products, and char formation, a number of alkaline pretreated samples were subjected to 20.0 min of benzhydrylation, followed by 20.0 min of mesylation and 5.0 hr of iodination. The ratios of the reactants and the experimental procedure were kept the same as in the individual substitutions described above. A number of measurements were performed on the substituted samples.

Elemental Analysis. Carbon, hydrogen, and iodine analyses were performed on the samples by the Micro-Tech Laboratories in Skokie, Illinois, to determine the percentage of substitution. The expected and found values are summarized in Table I. The results were correlated with the crystallinity indices, rates of weight loss, and final char measurements.

X-Ray Diffraction. Diffractograms of substituted, alkaline-soaked, and untreated cellulose were obtained with a General Electric Model XRD-3 diffractometer equipped with a copper target to produce the Cu-K alpha radiation. Relative diffraction intensities as a function of angle were recorded on a strip chart recorder, and the intensity of the peaks was measured by a Geiger counter with a scaling circuit.

Weight Loss Rates. The isothermal pyrolysis chamber (a nitrogen-fluidized sand bath) used in the degradation studies was described earlier.^{6,7} It was designed to meet the following requirements: (1) rapid and uniform heating of the samples to the controlled temperatures, (2) uniformity of temperature throughout the pyrolysis chamber, (3) constancy of temperature to within $\pm 0.2^\circ\text{C}$ over prolonged time intervals, (4) continuous removal of volatile products and rapid recovery of solid residue, and (5) intermittent sampling of the volatile degradation products for gas-chromatographic analysis.

The cellulose samples were raised to the pyrolysis temperature within 10 sec and were kept isothermal within $\pm 0.12^\circ\text{C}$ throughout the length of all

TABLE I
Elemental Analysis of Substituted Samples

Sample description	C, %		H, %		I, %	
	Calculated	Observed	Calculated	Observed	Calculated	Observed
10.0 sec in 20% NaOH and benzhydrilated	44.0	44.65	6.00	6.16		
30.0 sec in 20% NaOH and benzhydrilated	45.95	46.12	6.00	6.12		
15.0 min in 20% NaOH and benzhydrilated	44.50	44.74	6.00	6.15		
10.0 sec in 20% NaOH and iodinated					2.82	2.81
75.0 sec in 20% NaOH and iodinated					5.95	5.90
2.5 min in 20% NaOH and iodinated					2.42	2.42
15.0 min in 20% NaOH and iodinated					2.95	2.97
10.0 sec in 20% NaOH benzhydrilated and iodinated	37.30	37.32	4.85	4.92	10.89	10.86
30 sec in 20% NaOH benzhydrilated and iodinated	39.00	39.68	4.90	4.92	8.40	8.44
2.5 min in 20% NaOH benzhydrilated and iodinated	41.00	41.03	5.69	5.69	6.35	6.30
15.0 min in 20% NaOH benzhydrilated and iodinated	42.40	41.99	5.84	5.82	2.75	2.81

the runs. The temperature variation throughout the pyrolysis chamber at any one time was no greater than $\pm 0.1^\circ\text{C}$. Accumulation of the degradation products in the chamber was prevented by continuous removal of the volatiles through a vent and by changing the fluidizing medium with each cellulose sample. The pyrolyzed sample was recovered from the reaction chamber in 5 sec or less at the conclusion of each heating period.

The arrangement of the pyrolysis chamber and the outer oven is shown in Figure 1. The temperature in the stripped-down Aerograph Model 600 gas chromatography oven is controlled by their Model 328 isothermal pro-

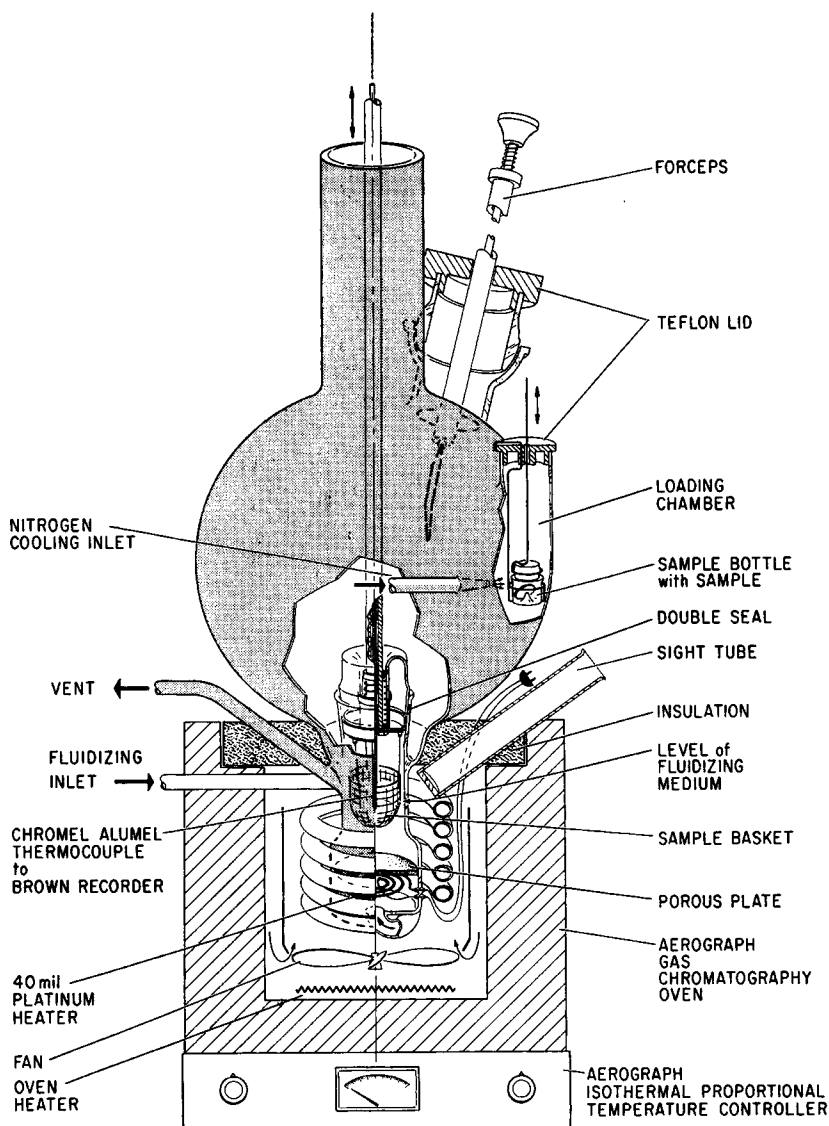


Fig. 1. Apparatus for the study of the isothermal degradation of cellulosic materials.

portional temperature controller and is maintained to within $\pm 0.2^\circ\text{C}$ from ambient to 400°C .

The glass pyrolysis unit consists of the sample loading chamber and the reaction chamber. The sample loading chamber is separated from the reaction chamber by a retractable double-seal plug. The reaction chamber is constructed from a 50.0-mm sintered glass funnel. It contains 60–80 mesh, thoroughly cleaned Monterey sand, a 0.05-cm nichrome wire sample holder, and a Chromel–Alumel thermocouple. The reaction chamber is

fluidized by 99.997% pure nitrogen, which is initially preheated to 250°C by passage through a preheater oven. The gas is then brought to the desired temperature by the Aerograph oven and maintained within $\pm 0.1^\circ\text{C}$ by a 0.1-cm platinum wire heater inside the nitrogen-fluidized inlet coil. The volatile reaction products are vented to the atmosphere through a glass side arm, which leads from the reaction chamber and serves as a gas sampling inlet to the gas chromatography unit.

Prior to the actual pyrolysis, each sample was evacuated for 30 min, dried to constant weight in nitrogen in the presence of phosphorus pentoxide, transferred in a covered, tared weighing bottle to the loading chamber, and then inserted into the reaction chamber. Since the object of this study was to determine the effect of the degree of substitution on the degradation rate and char formation, the samples were all pyrolyzed only at 288°C. This temperature was chosen because it was low enough for detailed kinetic studies and high enough to be well in the 276–350°C temperature range, where the mode of degradation follows a specific pattern. Below 276°C, the scheme of degradation is different. At the end of each run, the sample residue was removed from the reaction chamber, returned to its weighing bottle desiccated, and reweighed to obtain the amount of sample converted into volatiles.

To determine amounts of final chars, the variously substituted samples were heated in an oven at 600°C. Air oxidation was minimized by sandwiching the weighed samples between two index cards wrapped with aluminum foil. The index cards protected the samples from possible detrimental effects on the char-forming processes of direct contact with the aluminum foil. The samples were then pyrolyzed for 12.0 min and reweighed.

Analysis of Degradation Products. For a better understanding of the effect of chemical substitution on the mechanism of degradation, gas-chromatographic/mass-spectrometric analysis was performed on the pyrolysis products of the substituted and untreated samples. A Beckman GC-4 analytical gas chromatograph and a modified Bendix Model 14 time-of-flight mass spectrometer were used in this study. A detailed description of the analytical techniques was given earlier.^{2,3} Briefly, cellulose samples were rolled into cylinders and burned in air. To collect the degradation products (excluding the fixed gases and more volatile compounds), one end of the cylinder was placed in a liquid nitrogen-cooled centrifuge tube and the other was ignited. This method allowed the pyrolysis products to flow down the center of the cylinder and condense out on the bottom of the centrifuge tube. Aliquots of 10 μl were then injected with a syringe onto a 10-ft by 0.25-in. o.d. stainless steel column packed with 10% by weight of Carbowax-20M on Chromosorb-T 40–60 mesh, obtained from the Varian Aerograph Company at Walnut Creek, California. The column was then ballistically temperature programmed from 90° to 220°C in 40 min. The helium flow rate was 60 cc/min, the thermoconductivity detector oven was maintained at 225°C, and the injection port, at 240°C. The gas-chromatographic peaks were identified with the aid of the time-of-flight mass spectrom-

eter, which was linked to the gas chromatograph by means of the Watson-Bieman helium separator. To facilitate identification of the components, mass spectra were taken at both 15 and 70 eV.

RESULTS AND DISCUSSION

The effect of substitution on crystallinity, rates of degradation, and char build-up is summarized in Table II. For better correlation of the results, the effects of alkaline soaking on crystallinity, rate of weight loss, and final char are also included. The crystallinity indices were calculated by an empirical method based on Segal et al.⁹ In this method, the diffractogram heights above a baseline at $2\theta = 19^\circ$ and 22.6° for the untreated samples and $2\theta = 16.0^\circ$ and 21.7° for the treated samples were used to calculate the index of crystallinity from the relationship

$$\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100$$

where CrI is the crystallinity index, I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction (22.6° for the untreated and 21.7° for the treated), and I_{am} is the intensity of diffraction in the same units for the amorphous background—in our case at $2\theta = 19.0^\circ$ for the untreated cellulose and $2\theta = 16.0^\circ$ for the treated cellulose. This difference in angles is due to different crystalline structures in the untreated and treated material. The treatment changes the structure from cellulose I to cellulose II.

As stated earlier, alkaline pretreatment of the samples is necessary for efficient substitution. Unfortunately, such soaking leads to the transformation of the crystalline lattice as well as decrystallization of the samples which in turn increases the rate of degradation. Table II shows that the crystallinity indices of the 20% NaOH-treated samples gradually decrease with the length of soaking. The index varies from 80.5 for the 10.0-sec-soaked samples to 75.0 for the 15.0-min-soaked samples. Figure 2 compares a number of diffractograms of the variously treated samples with a diffractogram of an untreated sample (curve A). Alkaline treatment for as short an interval as 10 sec changes the native crystalline pattern of $2\theta = 19.0^\circ$ and 22.6° to that of $2\theta = 16.0^\circ$ and 21.7° (curve B), which is the characteristic pattern of cellulose II. In view of these findings, a number of samples, which were soaked in 20% NaOH for 5.0 min, were subjected to nitrogen pyrolysis at 288°C for various lengths of time. The rate of weight loss in the linear region of pyrolysis was three times that of the untreated sample, and the final char residue remained essentially unchanged. The increased rate in the linear region suggests loosening of the macromolecular packing of the molecule by the NaOH treatment, which would make the sample less heat resistant.

An optimum soaking time of 30 sec in 20% NaOH produced the highest degree of benzhydrylation and also the lowest crystallinity index. Although this degree of substitution is not high enough to destroy the cellulose

TABLE II
Effect of Substitution on Crystallinity, Rates of Weight Loss, and Char Build-up

Sample description	Substitution, %	Crystallinity index	Angles used in calculating the crystallinity index, degrees	Rate of wt loss, %/min	Final char, %
Untreated sample	0	81.0	19 and 22.6	0.3	9.23
10.0 sec in 20% NaOH	0	80.5	16 and 21.7		
30.0 sec in 20% NaOH	0	80.0	16 and 21.7		
75.0 sec in 20% NaOH	0	78.0	16 and 21.7		
2.5 min in 20% NaOH	0	77.5	16 and 21.7		
5.0 min in 20% NaOH	0	75.2	16 and 21.7	1.0	9.40
10.0 min in 20% NaOH	0	75.2	16 and 21.7		
15.0 min in 20% NaOH	0	75.0	16 and 21.7		
10.0 sec in 20% NaOH and benzhydriylated	4.1	80.5	16 and 21.7	14.0	16.22
30.0 sec in 20% NaOH and benzhydriylated	34.0	77.0	16 and 21.7	60.0	18.80
15.0 min in 20% NaOH and benzhydriylated	6.0	82.0	16 and 21.7	18.0	16.47
10.0 sec in 20% NaOH and iodinated	3.6	76.0	16 and 21.7	7.5	23.08
75.0 sec in 20% NaOH and iodinated	8.0	78.0	16 and 21.7	19.0	31.29
2.5 min in 20% NaOH and iodinated	3.0	84.0	16 and 21.7	9.0	20.88
15.0 min in 20% NaOH and iodinated	4.0	78.2	16 and 21.7	15.0	22.96
10.0 sec in 20% NaOH then benzhydriylated and iodinated	27.0	amorphous	16 and 21.7	108.0	21.35
30.0 sec in 20% NaOH then benzhydriylated and iodinated	20.29	amorphous	16 and 21.7	96.0	19.89
2.5 min in 20% NaOH then benzhydriylated and iodinated	15.0	55.0	16 and 21.7	8.0	26.43
15.0 min in 20% NaOH then benzhydriylated and iodinated	8.0	82.0	16 and 21.7	6.0	22.09

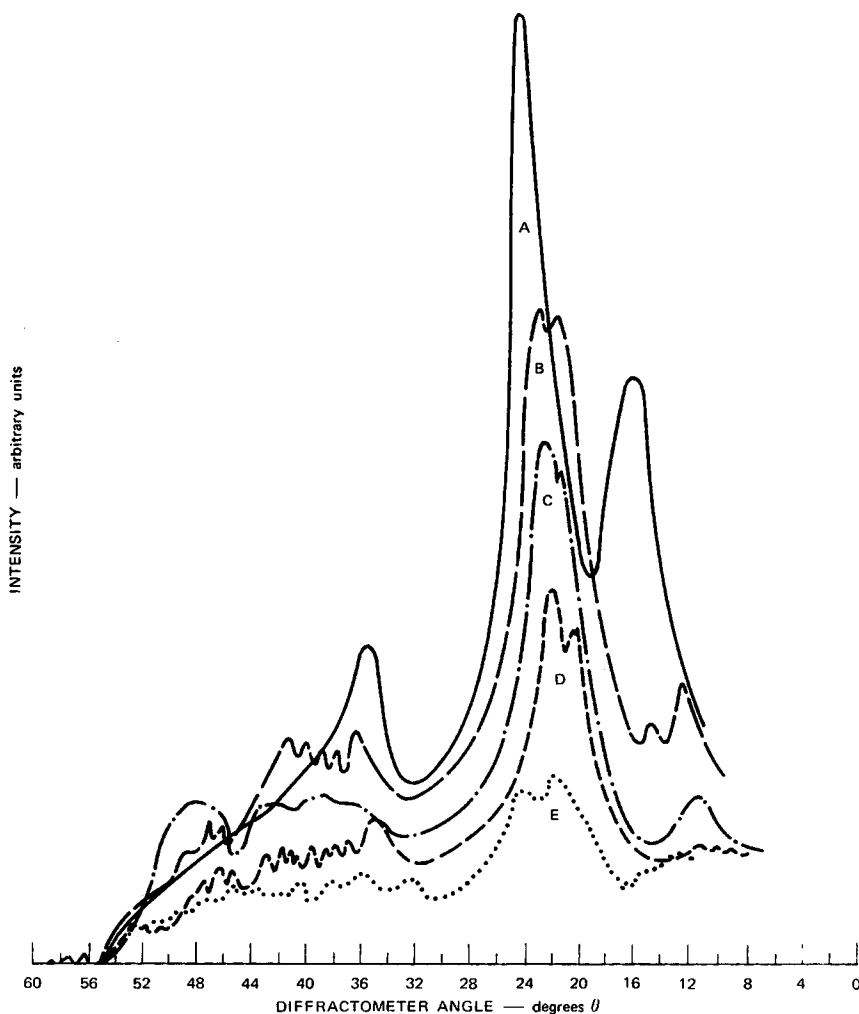


Fig. 2. Effect of NaOH soaking and substitution of crystallinity: (A) control; (B) cellulose soaked in 20% NaOH for 10 sec; (C) benzhydrylated cellulose after 30 sec swelling 20% NaOH; (D) iodinated cellulose after 75 sec of swelling in 20% NaOH; (E) benzhydrylated then iodinated cellulose after 10 sec of soaking in 20% NaOH.

II pattern (Fig. 2, curve C), it definitely lowers the crystallinity index. The highest percentage of iodination, and also the lowest crystallinity index, was achieved after 75.0 sec of soaking time in 20% NaOH (Fig. 2, curve D). Benzhydrylation followed by iodination not only lowered the crystallinity index but, at higher percentages of substitution, reduced the crystalline regions to an essentially amorphous state (Fig. 2, curve E).

Figure 3 shows the remaining weights of benzhydrylated cellulose as a function of time and percentage of substitution. The overall shape of the curves follows that observed for both the unsubstituted cellulose and for

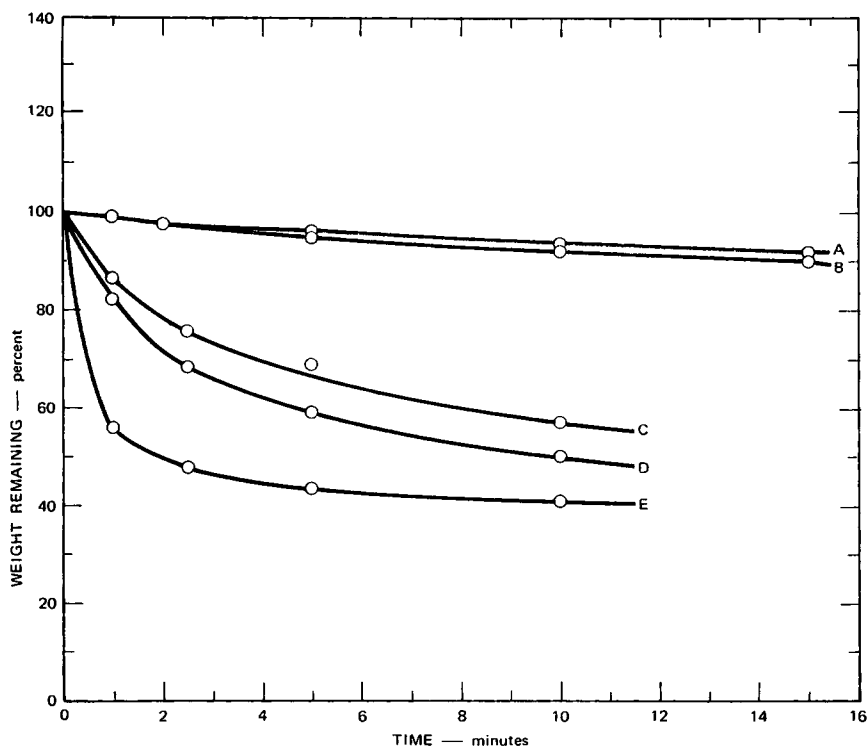


Fig. 3. Isothermal pyrolysis of benzhydrylated white alpha-cellulose in nitrogen at 288°C; (A) untreated cellulose; (B) soaked in 20% NaOH for 5.0 min but not substituted; (C) 4.1% substitution; (D) 6.0% substitution; (E) 34.0% substitution.

samples treated with basic and acidic salts. All of the retardant-treated samples display markedly increased rates of degradation and a considerable increase in the final char. Correlation of the pyrolysis results with the x-ray diffraction measurements shows that, in general, the rates of degradation and amount of final char vary inversely with the crystallinity indices.

The remaining weights of the iodinated samples as a function of time and percentage of substitution are shown in Figure 4. The general shape of the curves follows the same pattern as that of benzhydrylated samples. Although the rate of weight loss relative to the degree of substitution is essentially the same for benzhydrylated and iodinated samples, the increase of char relative to the degree of substitution for the iodinated samples is considerably greater than for the benzhydrylated samples. Thus, in the series of iodinated samples, a substitution of 8% leads to the highest production of char (approximately 31%), while in the benzhydrylated series, even a substitution of 34% gives only 19% of char.

Although the exact mechanism of the action of these retardants, as well as basic and acidic salts, on the breakdown of the cellulose molecule is as yet not fully understood, experiments with fire-retardant products on treated levoglucosan suggest that the primary action of the retardant is on

the levoglucosan, formed during the decomposition of cellulose, rather than on the cellulose molecule itself; i.e., it is thought that the retardant breaks up levoglucosan into char and decreases the amount of flammable species. If the rate of decomposition of the retardant itself is faster than the char formation process, then the amount of the char produced will naturally be lower due to the depleting concentration of the retardant. This might be applicable to the benzhydryl group; although scission of the iodine does occur during pyrolysis, the iodine atom could still cause the levoglucosan molecule to break down into char.

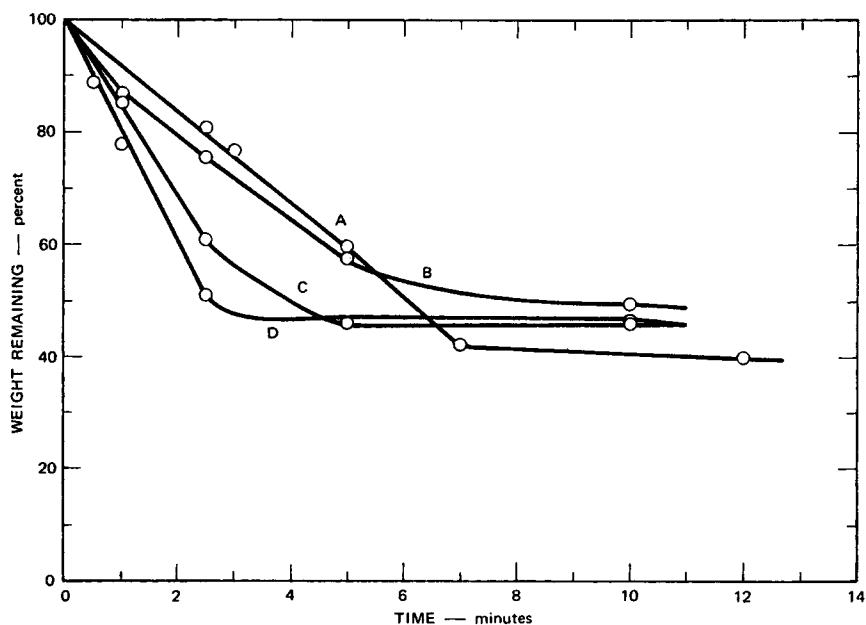


Fig. 4. Isothermal pyrolysis of iodinated white alpha-cellulose in nitrogen at 288°C: (A) 3.0% substitution; (B) 3.6% substitution; (C) 4.0% substitution; (C) 8.0% substitution.

Figure 5 shows the residual weights of benzhydrylated-iodinated samples. The rate of degradation is directly proportional to the percentage of substitution and crystallinity indices, which is comparable to the overall effect of the singly derivatized samples seen in Figures 3 and 4. However, the rate of degradation relative to the degree of combined substitution in the more highly substituted samples is faster than that produced by either benzhydrylation or iodination alone. At the same time, the char produced by this combination is lower relative to the degree of substitution than in samples subjected to either benzhydrylation or iodination.

These findings as well as those from the singly substituted derivatives imply that, of the three types of treatments tried, iodination renders the most effective retardance in terms of rate of weight loss and char production.

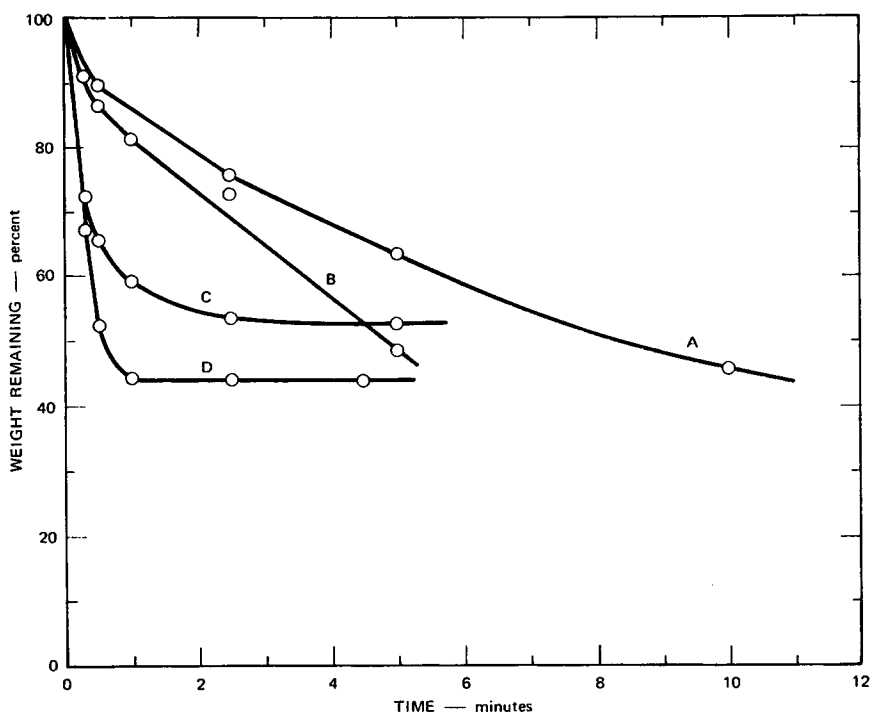


Fig. 5. Isothermal pyrolysis of benzhydrylated then iodinated white alpha-cellulose in nitrogen at 288°C: (A) 8.0 substitution; (B) 15.0% substitution; (C) 20.3% substitution; (D) 27.0% substitution.

The addition of the benzhydryl to the iodinated sample seems to decrease rather than increase its char-producing property.

Figure 6 compares a chromatogram of the degradation products of untreated cellulose with those of chemically bonded cellulose. The percentages of substitution used for the analysis were 6% benzhydrylation, 4% iodination, and 5% benzhydrylation followed by 4% iodination. A typical chromatogram of the degradation products of untreated cellulose shows 39 peaks which represent at least 59 compounds as analyzed by the time-of-flight mass spectrometer. These vary from CO and CO₂ to benzene and furan derivatives. Since no silyl derivatives have as yet been prepared for the identification of higher molecular weight components, the gas-chromatographic analysis involves only compounds with molecular weights less than about 150. The degradation products of the chemically substituted compounds consist of only five prominent peaks, identified as water, acetic acid, furfural, 5-methyl-2-furaldehyde, and a previously unidentified compound (peak 31a). Of these, water is the dominant peak and appears as the largest peak in the combined benzhydrylated-iodinated samples.

Since the size of peak 31a is markedly increased in the treated cellulose as well as in treated levoglucosan, it was decided that identification of this peak was important. Therefore, the compound comprising peak 31a was sepa-

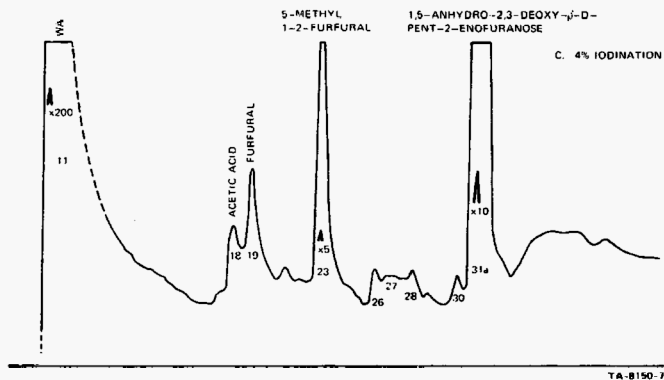
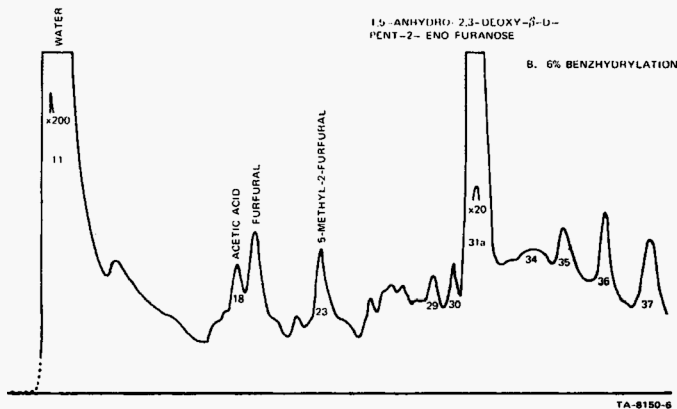
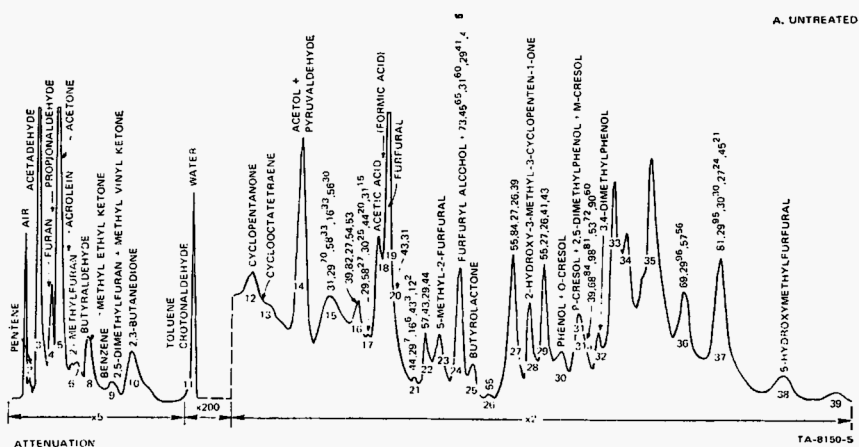


Fig. 6 (continued)

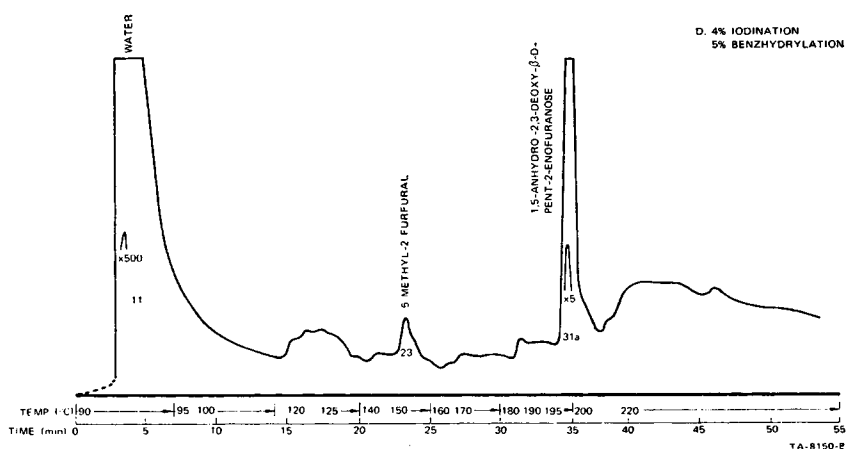


Fig. 6. Gas chromatograms of the volatile products from the pyrolysis of untreated and chemically substituted alpha-cellulose: (A) untreated; (B) 6% benzhydrylation; (C) 4% iodination; (D) 5% benzhydrylation followed by 4% iodination.

rated in the gas chromatograph, trapped in a cooled glass tube (4 in. long and $1/10$ in. in diameter), and then subjected to various analyses.

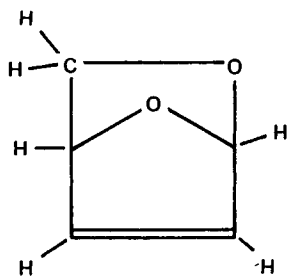
Low- and high-resolution mass spectra, as obtained by Bendix Model 14 time-of-flight and the CEC 110 fast-scanning mass spectrometers, respectively, indicated a possible mixture, with the main compound having a molecular weight of 98 and an empirical formula of $C_5H_6O_2$. The sample was optically inactive when dissolved in chloroform and measured by the Rudolph polarimeter. Examination of the infrared spectrum of the liquid film on an NaCl window led to the following tentative assignments:

cm^{-1}	Assignments
2800-2900	CH_2 stretching
1680-1725	$C=C$ stretching
1090-1100	$C-O$ stretching
960-975	$C-H$ bending
873-893	
825-833	

The NMR spectrum, recorded and integrated at 100 MHz using $CDCl_3$ as solvent, consisted of:

ppm (δ)	Number of protons
3.85	2 multiplet
5.02	1 triplet
5.35	1 singlet
6.12	1 doublet
6.30	1 multiplet

Based on the above results, a tentative structural formula was assigned to this compound as follows:

1,5-anhydro-2,3-deoxy- β -D-pent-2-eno-furanose

TA-8150-10

It is now important to isolate and purify this compound, to determine the mechanism of its formation, and to establish its role in the scheme of decomposition of cellulose.

CONCLUSIONS AND RECOMMENDATIONS

1. There is an optimum swelling time in the 20% NaOH to achieve the highest percentage of substitution. Longer pretreatments result in extensive changes in the crystalline lattice which in turn seem to lower the accessibility of the hydroxyl groups to the chemical reagents. For benzhydrylation, the optimum length of alkaline soaking was 30 sec, which led to 34% substitution; for iodination, 75 sec with 8% substitution; and for benzhydrylation followed by iodination, the optimum soaking time was 10 sec, which gave 27% as a total per cent of substitution. The possibility of using another swelling agent such as Cadoxen¹⁰ should be investigated for higher percentages of substitution.
2. The overall weight loss pattern of the chemically substituted samples is similar to that of the untreated ones. The increased rate of weight loss in the treated cellulose is due partly to an increased percentage of the amorphous regions in the samples and probably to a reduction in the molecular weight. Measurements of the molecular weight distribution of the substituted samples and cellulose soaked in NaOH should be performed to determine the extent of the reduction.
3. Of the three types of treatments tried, iodination provides the most effective retardance, because it causes the cellulose to produce the largest amount of char without drastically increasing its rate of weight loss.
4. The addition of benzhydryl groups to the iodinated samples decreases rather than increases char production.
5. Since the action of the chemically bonded retardants on the rate of degradation is similar to that of basic and acidic salts, it is reasonable to assume that the action of the chemically bonded retardants on the char is also similar to that of the basic and acidic salts. Thus, it is speculated that the action is primarily on the levoglucosan rather than on the cellulose molecule itself. Char determinations on benzhydrylated and iodinated levoglucosan might clarify this action.
6. In general, the three kinds of derivatives have a drastically decreased number of thermal degradation products of molecular weights lower than

150. The compounds identified with the dominant peaks from chemically bonded cellulose were water and a furanose derivative. The largest amount of water is produced by the combined treatment. Additional differences in the action of these retardants might be detected by the gas-chromatographic analysis of the trimethyl-silyl derivatives of the degradation products of molecular weight higher than 150.

7. Since the furanose derivative appears only in the degradation products of treated cellulose (chemically bonded as well as treated with basic and acidic salts) and also increases in amount in the products of levoglucosan, it is important to determine the mechanism of formation of the main component and its role in the decomposition of cellulose. At this point, the possibility that the furanose might be formed by the action of the retardants on 1,6-anhydro- β -D-glucofuranose or 1,5-anhydro- β -D-ribofuranose should not be excluded. Since these compounds have been identified among the degradation products of treated and untreated cellulose, gas-chromatographic analysis of the pyrolysis products of treated and untreated 1,6-anhydro- β -D-glucofuranose and 1,5-anhydro- β -D-ribofuranose should be performed. On the other hand, the furanose derivative might be one of the primary decomposition products of levoglucosan, which is stabilized by the presence of a retardant and hence appears in larger quantities in treated samples. Therefore, gas-chromatographic analysis of the degradation products of treated and untreated furanose derivative should also be performed.

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