

Pyrolysis of Treated Rayon Fiber

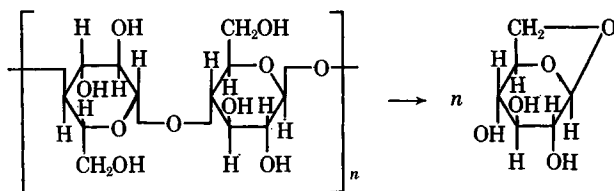
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Synopsis

The thermal decomposition behavior of rayon yarn which had been treated with various chlorosilanes and boron-phosphorus compounds was determined at temperatures up to 800°C. It was found that 70% of the available hydroxyl groups in rayon would react with dichlorodiphenylsilane and that the treated yarn had an initial decomposition temperature 125°C higher than that of untreated rayon. The weight loss of the treated yarn at 800°C was dependent on the nature of the chlorosilane and the type of posttreatment used. Alkylchlorosilanes produced higher weight losses than did the arylchlorosilane-treated rayons. Treatment of rayon yarn with bis(chlorodiphenylphosphine)decaborane (BCDPD) or dimeric chlorophospha(III)-*o*-carborane (DCPC) resulted in an increase in the char yield of the pyrolyzed yarns. In the case of untreated rayon, weight retention at 800°C was 20%, whereas the treated yarns yielded boronated residues of 42-53%. Carbon yields as high as 28% were obtained with the BCDPD treatment. This treatment also resulted in substantial improvement in the oxidative stability of rayon at temperatures up to 250°C.

INTRODUCTION

The development of high strength-high modulus graphite fibers from rayon began in this country in the early 1950s. Rayon yarn was the precursor of choice because of its availability, low cost, and nonmelting character. The graphitization of rayon is carried out in three distinct stages: (1) preoxidation in air at low temperatures, (2) carbonization up to 1300°C, and (3) graphitization under tension at 2800-3000°C. A great deal of information is available in the literature regarding the thermal decomposition of cellulose¹⁻⁵ which can be applied to the low-temperature pyrolysis of rayon (stage 1). Kilzer and Broido⁶ have shown, for example, that low-temperature pyrolysis of cellulose causes random dehydration of hydroxyl groups producing dehydrocellulose, which is the principal source of char at elevated temperatures. A second pyrolysis reaction, which competes with the dehydration reaction, leads to the formation of levoglucosan(1,6-anhydro-β-D-glucopyranose III),⁷ as follows:



Volatilization of levoglucosan and its degradation products produces large weight losses as the decomposition temperature is raised. It is apparent that control of these two reactions in the initial stages of pyrolysis is essential to the preparation of high-quality graphite fiber.

Shindo and co-workers⁸ were able to form dehydrocellulose exclusive of any levoglucosan by conducting the cellulose pyrolysis in an atmosphere of hydrogen chloride. Their analytical results showed that all of the weight which was lost up to 200°C was due to volatilization of water, and no carbon-containing gases were detected. Char yields of 37% were reported in contrast to only 20% when the pyrolysis was carried out in an inert atmosphere. Schwenker and Pascu⁹ also reported an increase in char yield when cellulose was subjected to a preoxidation treatment. The oxidation of the C-6 methylol group to a carboxylic acid prevents the formation of levoglucosan and leads to a highly crosslinked intermediate which yields more char.

It was the intent of this work to determine whether or not selected chemical treatments for rayon would promote the formation of higher char yields. Treatments were selected which had high carbon contents and functional groups which were capable of interacting with the hydroxyl groups in rayon to form new chemical bonds.

EXPERIMENTAL

Villwyte 1650/720 yarn was supplied by Midland-Ross Corporation of Cleveland, Ohio. The yarn was a two-ply, 720 filament/ply yarn having a denier of 1650. The yarn, as received, contained a hydrocarbon lubricant, which was removed by continuous extraction with trichloroethylene followed by ethyl alcohol. The pyridine used was "Baker Analyzed" reagent grade and was dried where indicated by distillation under nitrogen from potassium hydroxide pellets.

Dichlorodiphenylsilane, dimethyldichlorosilane, and cyclopentamethylenedichlorosilane were all supplied by Peninsular Chemresearch, Inc., and were used without further purification. Bis(1,4-dimethylchlorosiloxy)benzene was prepared in this laboratory from resorcinol and dimethyldichlorosilane using a sodium methoxide catalyst. The waxy solid was stripped of unreacted chlorosilane before being used. The two treatment compounds, bis(chlorodiphenylphosphine)decaborane and dimeric chlorophospha (III)-*o*-carborane, were supplied by the Olin Corporation.

The chlorosilane treatments were carried out in refluxing pyridine. The treated yarn was thoroughly washed with fresh pyridine and dried under vacuum before thermal analysis was determined.

The procedure used to treat Villwyte with the boron-phosphorus compounds was an adaptation of that reported by Schwenker and Pascu.⁹ A continuous length of yarn (1 to 100 meters) was stretched between two bars and tied at the ends exactly 1 meter apart. The yarn was then immersed in a 6% sodium hydroxide solution without tension for a period of

1 min. The mercerization process resulted in an increase in the fiber cross section and a corresponding decrease in the fiber length. Mercerization was terminated by washing with water for a period of 30 min. After press drying to remove the bulk water, the yarn was placed in pyridine and soaked for a period of 15 min. The yarn was press dried again and placed in fresh pyridine for another 10-min soak. At this point, it was assumed that the pyridine had replaced most of the water in the yarn bundle.

After removal from the pyridine, the yarn was pressed and placed in a 10% treatment solution at 25°C. The total weight of the treating agent present in the solution was always two or three times the amount required for a 20% pickup based on the weight of the yarn used. The treatment time was 15 min, and, after light pressing, the yarn was stretched under tension while air drying. Finally, the yarn was vacuum dried for 2 hr at 100°C. The shrinkage caused by the treatment was determined by measuring the distance between the ties which originally were placed 1 meter apart. Shrinkage amounted to 10%–15% by this process. The per cent weight pickup was calculated by weighings before and after treatment.

The thermogravimetric analysis (TGA) equipment used in this study was described in detail by Anderson.¹⁰

RESULTS AND DISCUSSION

Chlorosilanes

Schuyten and co-workers¹¹ showed that chlorosilanes such as trimethylchlorosilane would react readily with cellulose in refluxing pyridine. Group substitutions as high as 2.75 trimethylsilyl groups per glucose unit (91.5% conversion) were obtained with cotton linters, but no thermal stability data were reported. Other examples of chlorosilane treatment of cellulose and poly(vinyl alcohol) can be found in the literature.^{12–15}

Theoretical calculations were made based on the change in the elemental composition of rayon with respect to crosslinking with dichlorodiphenylsilane (Fig. 1). The results showed two important changes in the factors which affect the char yield of the treated yarn. The carbon content increases from 44% to 67% for a completely crosslinked rayon, while the oxygen content decreases from 49% to 19%. This shift in elemental balance creates a condition which favors greater retention of carbon in the char residues if the thermal decomposition behavior follows a favorable course.

Initially, a study was made to determine the effect of reaction time on the pyrolysis of dichlorodiphenylsilane-treated Villwyte. One-meter lengths of yarn were treated in 10% pyridine solutions of dichlorodiphenylsilane at 115°C for various periods of time. Samples were withdrawn at intervals of 0.25, 0.50, 1.0, and 3.0 hr, washed in pyridine, dried, and submitted for elemental and thermogravimetric analysis. Results from these experiments (Table I) show that the carbon content of treated rayon increases with reaction time. Yarn which had been treated for 3 hr showed an in-

TABLE I
Elemental Analysis of Dichlorodiphenylsilane-Treated Rayon^a

Reaction time, hr	Elemental composition, %			
	Carbon	Hydrogen	Silicon	Oxygen (by difference)
Untreated Rayon ^b	44.44	6.23	—	49.34
0.25	54.49	6.32	4.45	34.73
0.50	62.02	5.61	7.20	25.17
1.0	62.59	5.69	8.13	23.59
3.0	63.21	5.03	8.55	23.21

^a In pyridine at 115°C.

^b Theoretical calculations.

crease in carbon from 44.44% for untreated to 63.21% for the treated yarn, with a corresponding decrease in the oxygen content from 49.34% to 23.21% (calculated by difference). The silicon content of this treated yarn increased with reaction time to a final value of 8.55%. The elemental composition of the product indicated that the per cent conversion based on the data from the theoretical curves in Figure 1 was about 70%.

The TGA results (Fig. 2) show that the pyrolysis of the treated yarn is dependent on the extent of the hydroxyl reaction in rayon. In the case of

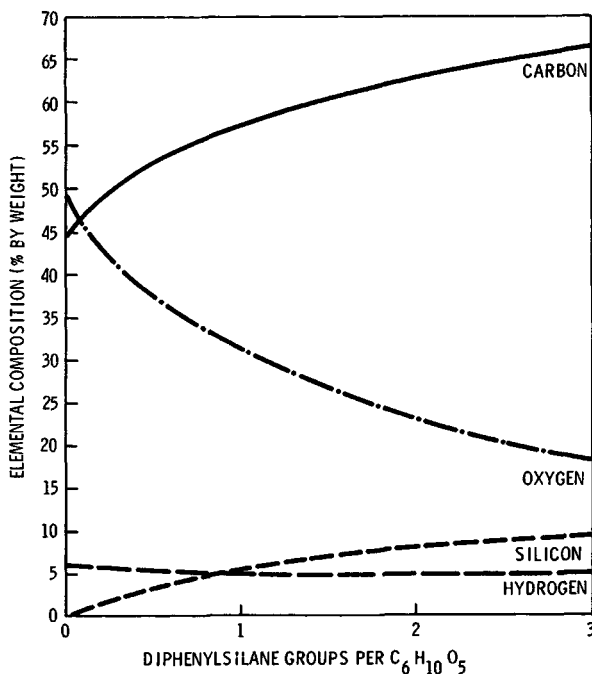


Fig. 1. Elemental composition of rayon crosslinked with dichlorodiphenylsilane (theoretical calculations).

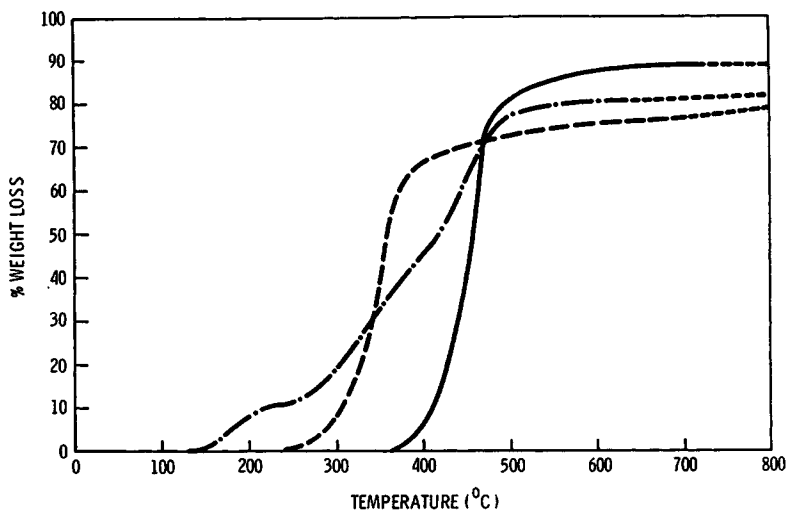


Fig. 2. Thermogravimetric analysis of rayon treated with dichlorodiphenylsilane. Rayon reacted with dichlorodiphenylsilane in refluxing pyridine for: (---) 0.25 hr; (—) 1.0 hr; (-·-·) untreated rayon.

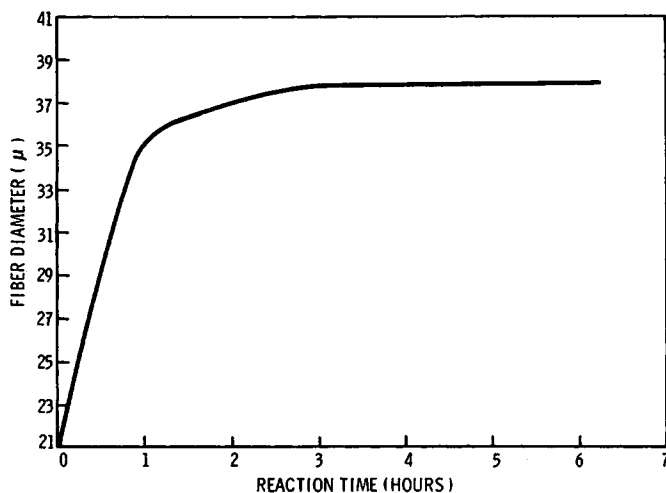


Fig. 3. Fiber diameter of dichlorodiphenylsilane-treated rayon vs. reaction time. Reacted in refluxing pyridine.

the 0.25-hr treatment (20% conversion), there is a stepwise decomposition which begins 100°C lower than the temperature of initial decomposition (TID) of rayon. The rate of weight loss in this case is lower than for rayon and actually occurs over a 350°C range. There is no change in the final weight loss of the treated material and untreated rayon. If reaction time is extended to 1 hr (70% conversion), the pyrolysis behavior is entirely different. The TID is now 125°C higher than that of untreated rayon, the

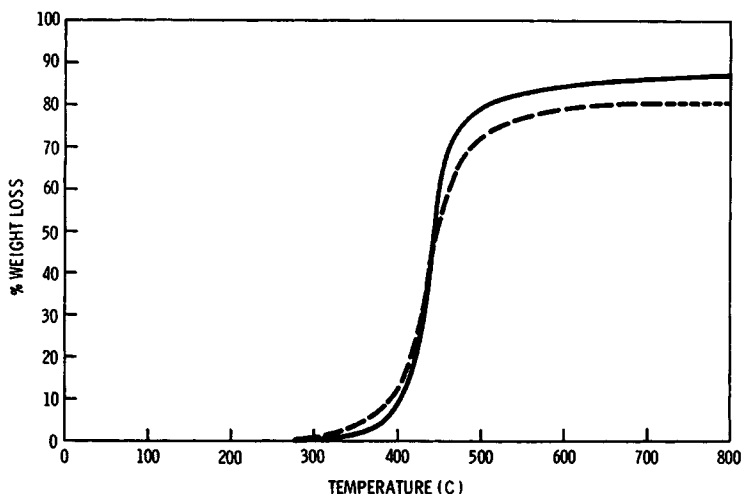


Fig. 4. Effect of chlorosilane endgroups on the pyrolysis of dichlorodiphenylsilane-treated rayon: (—) no extraction or pyridine extraction, vacuum dried; (---) pyridine-water extraction, vacuum dried.

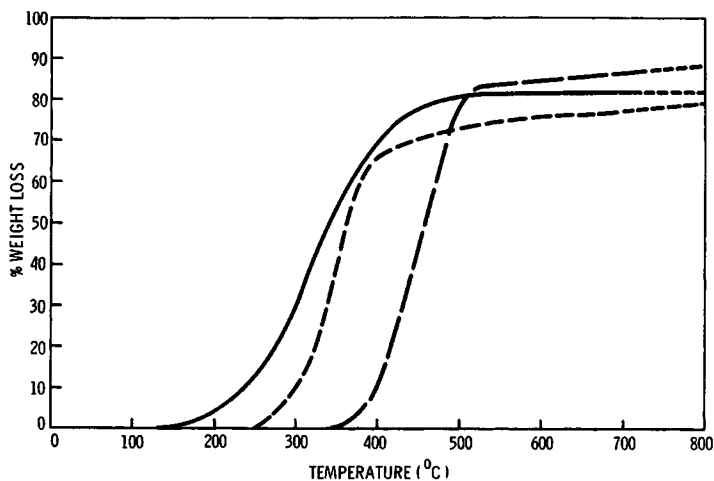


Fig. 5. Effect of moisture on the pyrolysis of dichlorodiphenylsilane (DCDPS)-treated rayon: (---) untreated rayon; (—) rayon treated with DCPS in dry pyridine; (- - -) rayon treated with DCDPS in wet pyridine (0.1% water).

rate of weight loss is similar, and the char yield is 10% lower. The increase in TID can be explained by the loss of hydroxyl groups from rayon due to reaction with the chlorosilane, while the explanation for the increased weight loss is more complex. Depolymerization of rayon probably occurs during the course of reaction with the chlorosilane, which leads to increased volatilization of polymer segments, or else the increased weight loss may be due to a catalytic decomposition caused by the presence of silicon at these

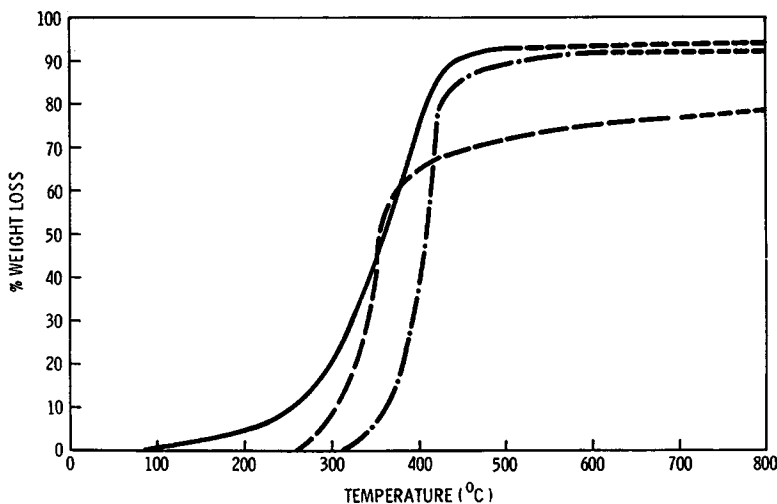


Fig. 6. Thermogravimetric analysis of rayon treated with chlorosilanes: (---) untreated rayon; (—) rayon treated with dichlorodimethylsilane; (— · —) rayon treated with cyclopentamethylene dichlorosilane.

temperatures. So that while the treatment was successful in raising the initial carbon content of the precursor, subsequent pyrolysis led to unfavorable losses which reduced the yield of carbon fiber at 800°C.

The increase in fiber diameter with reaction time (Fig. 3) was measured by means of an optical microscope, and the results can be correlated with the TGA results. After 0.25 hr of reaction, the fiber diameter increases about 20% and continues to increase rapidly for 1 hr. At this point, the monofilaments have increased in diameter from 21.0 to 35.2 microns and the rate of increase becomes much slower, until after 3 hr the diameter has levelled off at 37.6 microns and remains unchanged.

Chlorosilane endgroups were found to have an adverse effect on the pyrolysis of the treated yarn. Previously, dried rayon was placed in a pyridine solution containing an excess of dichlorodiphenylsilane and refluxed for a period of 3 hr. A sample of the resulting yarn was vacuum dried at 100°C, while a second sample was extracted continuously with pyridine to remove the unreacted dichlorodiphenylsilane before vacuum drying at 100°C. The TGA results (Fig. 4) indicate no difference in the pyrolysis of these two yarns. A third sample, which had been extracted continuously with an azeotrope of pyridine–water, showed an increase in char yield from 13% to 20% at 800°C, which can be attributed to the hydrolysis of residual chlorosilane endgroups.

Moisture was found to have an effect on the rate of the condensation reaction between dichlorodiphenylsilane and rayon. In one case, pyridine was dried by distillation over potassium hydroxide pellets, and in the second case it was used in the “as received” condition. Analysis of this “as received” pyridine indicated a moisture content of 0.1%. TGA results (Fig.

5) show that when the reaction was carried out in dry pyridine for a period of 3 hr at 115°C, the resulting rayon shows a weight loss behavior similar to that of untreated rayon. However, when the reaction is carried out in "as received" pyridine under the same conditions, the TID of the treated yarn is raised by 100°C, which indicates that reaction has taken place. The char yield in the case of the dry pyridine run was 18% compared to only 12% for the "as received" pyridine.

In order to determine the effect of chlorosilane structure on the decomposition behavior, a series of compounds were screened as potential rayon treatments (Figs. 6 and 7). Dichlorodimethylsilane in pyridine for 3 hr at reflux (70.3°C) led to extensive degradation of the rayon, which produced a

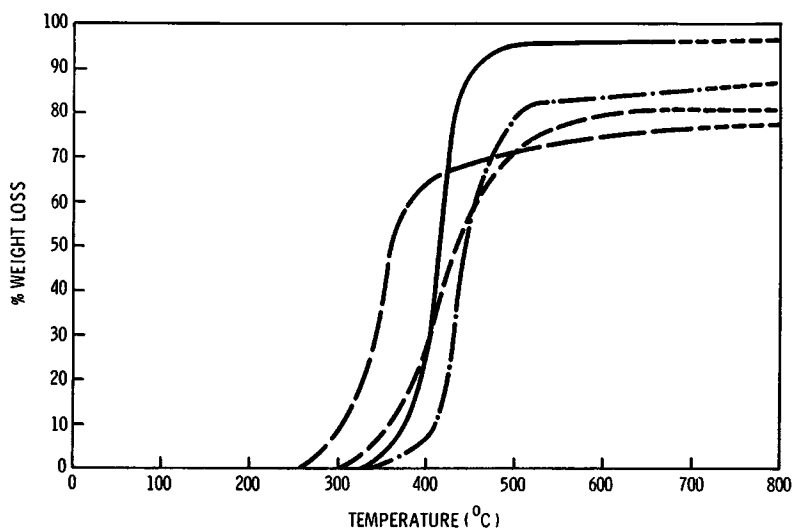


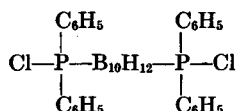
Fig. 7. Thermogravimetric analysis of rayon treated with various chlorosilanes. Rayon treated with: (—) dichlorodiphenylsilane in refluxing pyridine; (---) dichlorodiphenylsilane after sodium hydroxide swelling; (-·-) bis(1,4-dimethylchlorosiloxy)benzene; (—) untreated rayon.

high weight loss (94%). The TID and rate of loss approximate those of untreated Villwyte. The restriction of a lower reaction temperature (70.3°C) in this system compared to the higher-boiling chlorosilanes, where the reaction temperature was 115°C, may be responsible for the lack of reaction. In the case of cyclopentamethylenedichlorosilane and bis(1,4-dimethylchlorosiloxy)benzene, the TID is raised slightly (75°C), but the final weight losses of 93% and 97%, respectively, indicate extensive fiber degradation. Thus, it appears that the alkylchlorosilanes, in addition to reacting at hydroxyl sites, also cause depolymerization, probably by attack at the ether linkages in the polymer backbone. This depolymerization produces greater volatilization through a series of complex reactions at elevated temperatures.

In the case of dichlorodiphenylsilane, it was found that the weight loss could be reduced by carrying out the treatment at 25°C with rayon that had been preswollen in a sodium hydroxide solution. At 800°C, the weight loss amounted to only 81% for the mercerized treatment, compared to 86% for the same reaction in pyridine at 115°C.

Boron-Phosphorus Treatments

Prior to experimental evaluation of the boron-phosphorus-containing treatments, calculations were made to determine the effect of the treatment on the elemental composition of the yarn. The results for the bis(chlorodiphenylphosphine)decaborane (BCDPD) treatment (Fig. 8) showed that



in the case of complete reaction the carbon content of the treated yarn increases from 44% to 57%, while the oxygen content decreases from 49 to only 9%. This represents an increase in the carbon/oxygen atomic ratio from 1.2 to 8.4. The boron and phosphorus contents of the treated yarns based on complete reaction are 18% and 11%, respectively, while the hydrogen level remains at 6%. This set of theoretical curves can be used to

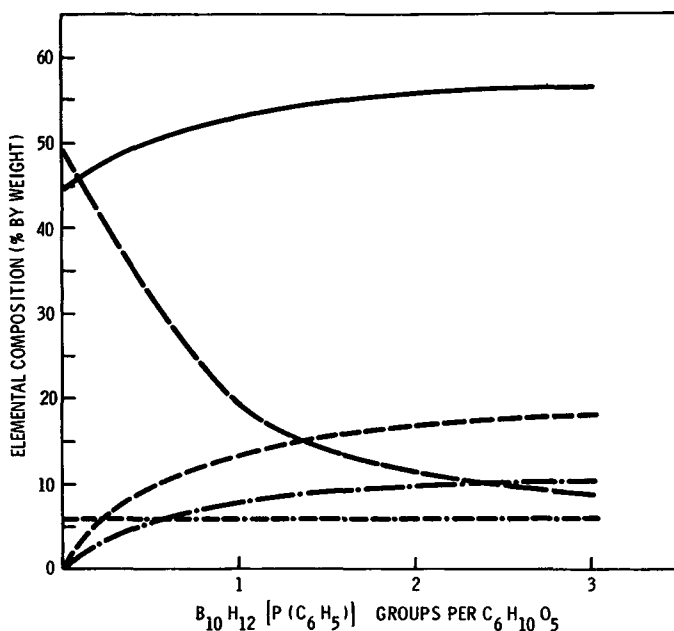


Fig. 8. Theoretical elemental composition of rayon treated with bis(chlorodiphenylphosphine)decaborane (BCDPD): (—) carbon; (---) boron; (-·-) phosphorus; (— —) oxygen; (- - - -) hydrogen.

determine the extent of reaction after the elemental composition of the treated yarn has been determined.

The BCDPD and DCPC treatments were carried out at 25°C on rayon which had been preswollen in caustic solution. However, it was found that extended periods of swelling would yield a stiff, brittle yarn which was not suitable for carbonization. It then became necessary to determine the effect of caustic concentration on swelling and also on the physical properties of the yarn. Short lengths of Villwyte 1650/720 yarn were placed in sodium hydroxide solutions of varying concentrations (6%–20%) for a period of 5 min in air at 25°C. The yarns were removed from the caustic solutions and thoroughly washed with water to remove the residual base. Monofilament diameters were then measured by means of an optical microscope, equipped with a vernier eyepiece, while the yarn was still wet. The results (Table II) are the average of five to ten measurements on different fila-

TABLE II
Effect of Caustic Concentration on the Swelling of Rayon

NaOH Concentration, wt-%	Monofilament diam, μ	Yarn condition after drying
—	17.9	“as received” yarn
6	29.0	soft, flexible, no filament fusion
8	34.3	stiff, weak, filament fusion
10	36.4	stiff, weak, filament fusion
12	34.2	stiff, weak, filament fusion
16	33.8	stiff, weak, filament fusion
20	36.3	stiff, weak, filament fusion

ments. The fiber diameter increases quite rapidly from a value of 17.9 microns for the “as received” fiber to a maximum of 36.4 microns after treatment in a 10% sodium hydroxide solution. Fiber swelling goes through a minimum point at a concentration of 13%–14% but begins to increase again at higher concentrations. After the fiber diameters had been measured, the yarn was air dried and examined for flexibility and softness. It was found that caustic concentrations above 6% produced weak yarns which showed partial fusion of the monofilaments. The 6% alkali rayon was soft and flexible, and this concentration was used in all subsequent experiments.

Conversion of Villwyte to alkali rayon (6% NaOH treatment) had an adverse effect on the thermal decomposition properties. The temperature of initial decomposition for alkali rayon (Fig. 9) was about 50°C lower than that of untreated rayon, and the final weight retention of alkali rayon at 800°C is only 13% compared to 20% for untreated rayon. This decrease can be explained by the fact that in the swollen condition, alkali rayon is subject to depolymerization caused by air oxidation. The result is that any chemical treatment which requires swelling in caustic to insure reaction

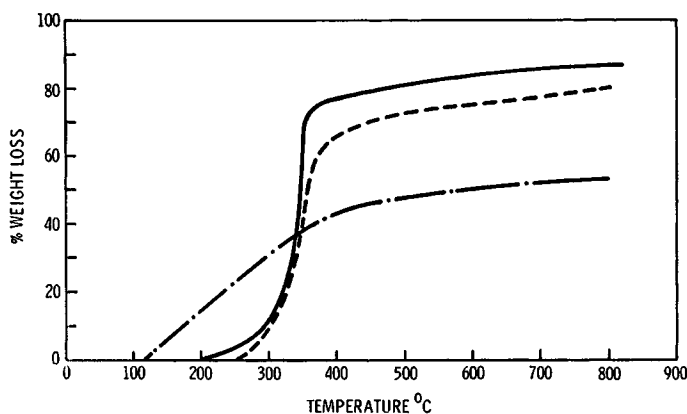


Fig. 9. Thermogravimetric analysis of rayon treated with bis(chlorodiphenylphosphine)decaborane (BCDPD): (—) alkali rayon; (---) untreated rayon; (-·-) BCDPD-treated rayon.

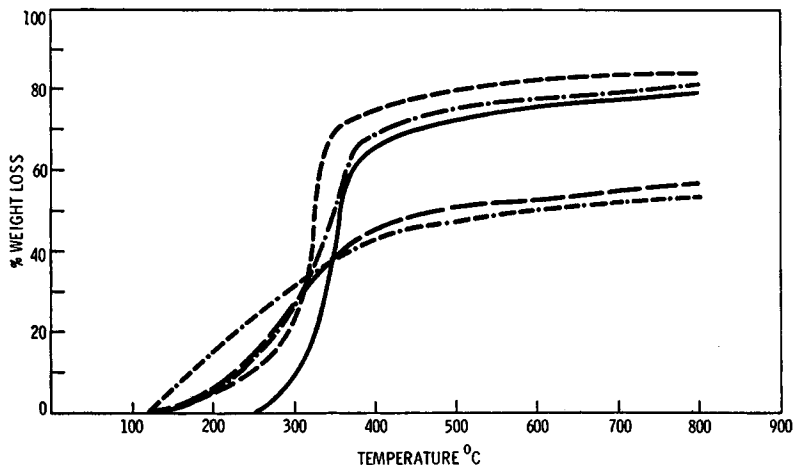


Fig. 10. Effect of bis(chlorodiphenylphosphine)decaborane (BCDPD) loading on the pyrolysis of rayon. Rayon treated with: (---) 3% BCDPD; (-·-) 5% BCDPD; (—) 18% or 22% BCDPD; (----) 33% BCDPD; (—) untreated rayon.

suffers a weight loss penalty on pyrolysis. In spite of this penalty, char improvements were obtained with both the BCDPD and the DCPC treatments used in this method.

In the case of alkali rayon treated with bis(chlorodiphenylphosphine)decaborane (BCDPD), the thermal decomposition behavior is entirely different from that of the untreated yarn (Fig. 9). Decomposition starts at 100°C for the treated yarn, which is 150°C below that for untreated rayon, but the rate of initial weight loss is slower for the treated yarn. The final weight retention increases from 20% for untreated rayon to 47% for the BCDPD-treated yarn at 800°C. Elemental analysis of the residue (Table

TABLE III
 Elemental Analysis of Residues from the Pyrolysis of Bis(chlorodiphenylphosphine)decaborane (BCDDP)-Treated Rayon

NaOH used in merceriza- tion, %	Loading of BCDDP on Rayon, wt-%	Residue at 800°C, %	Residue analysis				Carbon in residue at 800°C, %
			C, %	H, %	B, %	P, %	
6	11.8	34.7	68.14	1.46	3.82		23.6
6	16.5	37.6	61.71	1.61	9.04	1.65	23.2
6	21.0	47.0	54.69	1.58	7.57		25.7
10	—	33.0	79.14	1.26	4.22	1.65	26.1
16	—	35.0	79.36	1.17	4.29		27.8

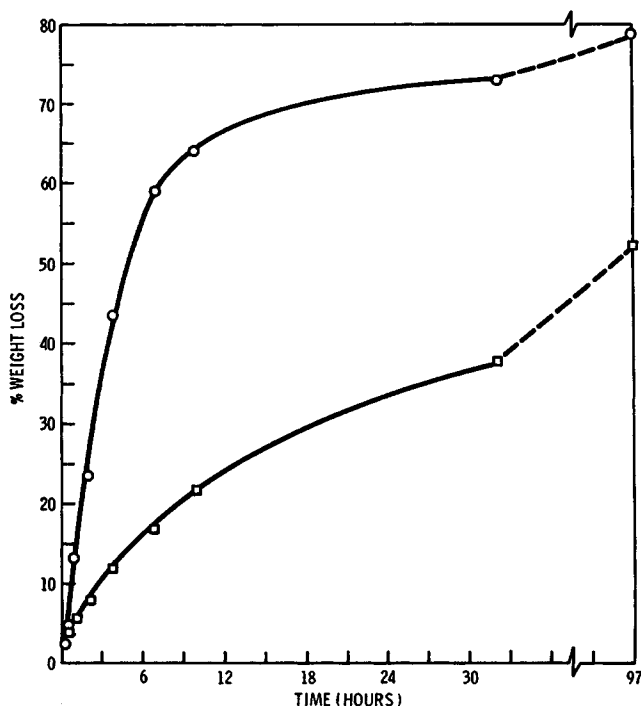


Fig. 11. Isothermal (250°C) weight loss in air of rayon treated with bis(chlorodiphenylphosphine)decaborane (BCDPD): (O) untreated rayon; (□) BCDPD-treated rayon.

III) shows a carbon content of 54.69%, which means that the actual weight retention of elemental carbon after pyrolysis was 26%. An additional undetermined quantity of carbon is probably complexes with the 7.57% boron present in the residue. While no quantitative mechanical data were obtained on the carbonized yarn, it was inherently strong and flexible and maintained these properties after heating to 2250°C.

The per cent loading of this treatment (BCDPD) on rayon has an effect on the pyrolysis behavior of the treated yarns (Fig. 10). Weight retentions of 42%–47% were obtained with loadings of 18%, 22%, and 33%, while 3% and 5% loadings produced retentions of only 15% and 19%, respectively. The reason for this increased weight loss in the latter case compared to untreated rayon is the result of air oxidation of the alkali rayon, as previously discussed (Fig. 9). Treatment loadings of 20% are comparable to those used commercially to flame-proof cellulose yarn. Some of the representative elemental analysis data for these treated yarns are presented in Table III.

The effect of air oxidation on BCDPD-treated yarns is important since, as was indicated previously, commercial graphite fiber producers subject the rayon precursor to a preoxidation treatment. Results at 250°C in air (Fig. 11) show a more gradual loss of weight for the treated yarn. After 8

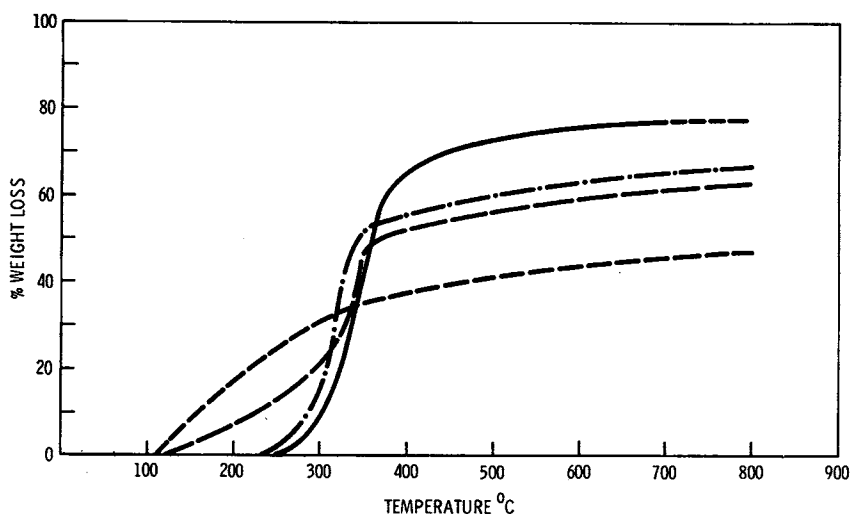
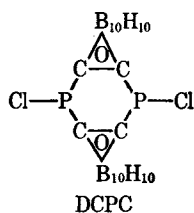


Fig. 12. Thermogravimetric analysis of rayon treated with dimeric chlorophospha(III)-*o*-carborane (DCPC): (—) untreated rayon; (---) mercerized rayon treated with dimeric carborane; (-·-) posttreatment extraction with pyridine; (—) unmercerized rayon treated with dimeric carborane.

hr, untreated rayon had lost 62% of its weight while the BCDPD-treated rayon had lost only 19%. Final losses after 97 hr were 79% untreated and 52% treated. Thus, it appears that this treatment might be of use in preventing excessive weight losses during the preoxidation step of the graphitization process.

The second boron-phosphorus treatment compound studied was dimeric chlorophospha(III)-*o*-carborane (DCPC):



The TGA results for the DCPC-treated yarn show an initial weight loss at 100°C (Fig. 12) similar to that of the BCDPD treatment and a final weight retention of 53% at 800°C. The effectiveness of this treatment was reduced by extraction with pyridine. The temperature of initial weight loss and the rate of loss after pyridine extraction resemble those of untreated rayon, while in the case of treated yarn without extraction, the results suggest that an "in situ" reaction occurs at a temperature below 250°C. The fact that the rate of weight loss for the DCPC rayon does not increase at the normal dehydration temperature (250°C) indicates that the hydroxyl groups are probably involved in the reaction, which starts at 100°C.

The effect of the BCDPD and DCPC treatments is to stabilize the rayon structure by reaction at lower temperatures, which then leads to a more controlled series of decomposition reactions and, consequently, higher weight retention. This also means that the DCPC treatment was only deposited on the surface of the yarn without any etherification occurring prior to pyrolysis.

When rayon was not mercerized prior to treatment with DCPC, the thermal decomposition behavior was a composite of the two extremes. There was both low temperature weight loss at 100°C and also dehydration between 325°–350°C. In order to ensure optimum char yields, it appears necessary to first swell the fiber to permit the treatment to penetrate and be deposited between the micelles and then "set" the treatment on the yarn by an appropriate heat curing process.

CONCLUSIONS

Dichlorodiphenylsilane treatment of rayon produced a fiber in which 70% of the available hydroxyl groups had reacted. The carbon content of the treated yarn was significantly increased, while the oxygen content undergoes a corresponding decrease. Alkylchlorosilanes yielded higher weight losses than did arylchlorosilanes at 800°C. The char yields of the treated yarns were either the same or lower than those of untreated rayon.

Rayon yarn treated with bis(chlorodiphenylphosphine)decaborane (BCDPD) or dimeric chlorophospha(III)-*o*-carborane exhibited increased weight retentions on pyrolysis. Rayon treated with BCDPD had a higher carbon yield at 800°C than did the untreated yarn and showed substantial improvement in oxidative stability at 250°C. The pyrolyzed yarns were strong and flexible and showed no signs of filament fusion.

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