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Small-scale heat-treatment of rayon precursors for stress-graphitization

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A method for the routine stabilization and heat-treatment of rayons to prepare them for carbonization and graphitization has been developed. After treatment by this method, which employs either air or pure oxygen, the yarn is suitable for fast, continuous stress-carbonization and stress-graphitization. Routine processing conditions yield "carbon fibres" with a filament modulus of fifty million psi*. This procedure, which produces a carbon yield between 16 and 21%, has been successfully applied to rayons produced by five different manufacturers. The steps necessary to accommodate the process to different sources of precursor materials are discussed, and the final product properties obtained are presented.

1. Introduction

The processing required to convert a rayon textile material into a graphite† yarn can be logically divided into three domains. The temperature domains involved are heat-treatment involving temperatures below 400°C, carbonization to temperatures between 1000 and 1500°C, and graphitization to temperatures in the range of 2500 to 3000°C. Although the carbonization and graphitization can be performed rapidly with times, at temperature, measured in seconds, the heat-treatment process can require times ranging from minutes to days. In addition to the time factor, which makes the heat-treatment the production limiting step in any attempt to produce more than subgram quantities, the ultimate weight yield of the process and the flexibility of the yarn bundle after final graphitization are essentially fixed at the completion of the heat-treatment stage.

The carbon content of the rayon precursor used for the production of graphite fibres is 44% on a dry basis and the yield would be 44% if no carbon were lost. Processing methods can cause variation in yield from $< 10\%$ if the processing is performed in vacuum or inert atmosphere to above 30% when substances such as "fire retardants" are employed as catalysts during pyrolysis. This report relates work that was undertaken to develop and use for the evaluation of rayon precursors a process intermediate between the conventional low yield laboratory inert atmosphere process and the high yield catalysis processes which are used in large scale production, but are extremely difficult to control satisfactorily for laboratory experiments.

When the ultimate objective of the pyrolysis of rayon is the production of graphite yarn with tensile modulus of the order of 50×10^6 psi, rather stringent limits are placed on the physical characteristics of the yarn during processing. Although it is possible to produce short sections of a few inches length of high-modulus yarn by static methods, attention here will be limited to the production of long lengths suitable for composite fabrication. The necessary continuous stress-graphitization involves significant elongation of the yarn at temperatures in excess of 2800°C, temperatures at which the yarn undergoes plastic deformation. Clearly, any non-uniformity in the yarn encountered in this type of drawing operation will lead to non-uniform stretch or frequent breaks in the yarn passing through the high temperature furnace. Addi-

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*10^3psi = 6.89Nmm^{-2}.

†Current usage often includes all fibres made of carbon in the term "carbon fibres". In this paper, differential is made between carbon fibres and graphite fibres according to whether they have been processed to carbonizing or graphitizing temperatures, respectively.

tionally, the yarn must be transported by means of rollers and pulleys. When the modulus of the yarn is high, the filaments must be free to move relative to each other in the yarn bundle; cementation of filaments early in the processing causes stiffness and subsequent breakage of the yarn.

To be an effective process for the evaluation of precursor rayons, heat-treatment must be capable of consistently producing uniform yarn which is free from cementation. Minimum processing times and high carbon yeild would be desirable; however, in a laboratory process for which only fractions of kilograms of material are needed, these factors are not of major importance. With the heat treatment process which has been developed, once the processing parameters have been established for one rayon precursor, the modification of the process for alternate rayon precursors is easily achieved by monitoring weight loss.

To establish the relationship between the properties of rayon precursors and the suitability of these precursors for the production of high modulus graphite yarn, we have subjected a number of rayons produced commercially to this process. Although it was not possible to specify from this experience exactly how to improve on the standard precursor (Villwyte, produced by IRC Fibers Company), it has been possible to define some precursor characteristics which fundamentally influence either the processibility or the end-product properties.

2. Heat-treatment process

When the many heat-treatment methods for rayon which might be employed in the laboratory were considered, two factors dominated. First, the process should be essentially continuous and, second, the time for the completion of the process should fall between the very rapid, complex commercial process involving catalysts and the very slow inert atmosphere low yield process. Since oxygen is a known pyrolysis promoter for cellulose [1] and is convenient to use, it would be a likely candidate for a laboratory process. Previous experiments had demonstrated that rayon could be heat-treated in a pure oxygen atmosphere to produce a stress-graphitized, high-modulus product [2]. The total time for the heat-treatment in oxygen was slightly over 20 min for our standard 1650/720 Villwyte rayon, and the weight yield to graphite was approximately 20%.

Two variations of the heat-treatment process have been employed. The first process involves multiple passes of the yarn through a tube furnace in pure oxygen atmosphere. The second process involves pre-treatment of the yarn by a long, low-temperature batch bake in an air oven, followed by one or two continuous passes in the oxygen tube furnace. Batch treatment is not desirable, because of the danger of non-uniformities arising from uneven temperature in the oven and from contact by the yarn with the supports necessary to hold the yarn. However, this method of pyrolysis was employed because of the increased productivity made possible by the considerable reduction in residence time in the pure oxygen atmosphere. The problems intrinsic to batch treatment were minimized by winding the yarn loosely on a graphite rack and then rotating the rack slowly in the oven during the heat-treatment.

For the purpose of monitoring the progress of pyrolysis, three types of measurements were employed: X-ray diffraction, weight loss, and shrinkage. Fortunately, after gaining some experience with the processing of diverse yarns, we found that, under normal processing conditions, we were able to rely on the weight loss, which is easily measured.

According to the appearance of the X-ray diffraction patterns, the pyrolysis of rayon from precursor to high modulus end-product can be divided into two regions: first, the crystalline structure of the Cellulose II starting material is gradually degraded until the Cellulose II characteristic diffraction pattern disappears and all that remains is an amorphous pattern; second as pyrolysis continues, the diffuse bands of the diffraction pattern sharpen and shift in position consistent with the growth of a condensed ring structure and reduction of interlayer spacing until the diffraction pattern characteristic of turbostratic graphite develops. Parallel with the development of the condensed ring structure is the development of fibre-type anisotropy [3]. Below 900°C, the diffraction pattern exhibits almost no preferred orientation. As the heat-treatment temperature is increased, there is a progressive increase in the anisotropy in the diffraction pattern.

The oxygen process has usually been conducted with an initial processing temperature of approximately 260°C in oxygen or 230°C in air, and we have been obtaining a process yield of approximately 20%. Under these pyrolysis conditions, the X-ray diffraction pattern of the original cellulose structure gradually diminishes and ceases to be evident at approximately 50% weight loss. When the initial heat-treatment temperature is in excess of 300° C, a different type of pyrolysis occurs. At these temperatures, the simple diminution of the crystalline rayon diffraction pattern is replaced by a change in the relative intensity of the diffraction peaks because of the transformation of the normal Cellulose II crystalline structure into the Cellulose IV structure. This crystalline transformation takes place without degradation of yarn properties in the presence of saturated steam [4]. However, in the oxygen heat-treatment process there is a decrease in the process yield associated with the formation of the Cellulose IV. When the initial pyrolysis was performed at temperatures in excess of 400° C, the crystalline fraction of the rayon became almost pure Cellulose IV at approximately 50% weight loss. For this experiment, the weight loss associated with the complete disappearance of the crystalline structure was 75%, rather than the normal 50%, and there was an accompanying reduction of the total yield of the process.

Shrinkage occurs in rayon during heat-treatment at a fairly uniform rate. However, we have observed that, during normal processing in air, there is a tendency for accelerated shrinkage to occur at approximately 25 and 45% weight loss. These points of accelerated shrinkage are associated with a tendency for the yarn filaments to kink if there is no tension on the yarn. Largely as a result of this tendency of the yarn to kink, the batch air pre-treatment was terminated at 40% weight loss, thus allowing the second shrinkage point to be passed during the subsequent continuous process during which the yarn was under sufficient tension to prevent the kinking of the filaments.

In the interest of speed, the highest possible processing temperature would be desirable; however, there are two limiting factors. First, as mentioned earlier, if the temperature of processing reaches approximately 300° C before the Cellulose II structure has been degraded, there is a conversion of the structure to Cellulose IV, with an accompanying loss in process yield. Second, owing to the exothermic nature of the pyrolysis of rayon in an oxidizing atmosphere, ignition of the yarn will occur if the temperature is raised too rapidly at any point in the process. When 1650 and 3300 denier material is processed in pure oxygen, the temperature limiting factor is the ignition of the yarn rather than the formation of Cellulose IV. Allowing a margin of between 10 and 15° C between the processing and ignition temperature it is possible to use 260° C initially and 285° C near the completion of the process in pure oxygen atmosphere (see the first three examples in Table III).

Having chosen a convenient temperature schedule for the heat-treatment, we still had to ascertain when to terminate the processing in oxygen. Trials which were conducted to establish the termination point demonstrated that, although there was consideragle allowable variation, oxygen processing should be carried to approximately 50 to 55% weight loss. This weight loss corresponds with the point at which X-ray fibre diffraction pictures no longer show any evidence of the cellulose structure.

At the conclusion of the oxidative heat-treatment stage (50 to 55% weight loss), the yarn is quite weak and cannot sustain the stress necessary for carbonization and graphitization to high modulus. However, a short residence time of 1.5 min at 350° C in an inert atmosphere is adequate to increase the strength sufficiently to permit stress-carbonization [2].

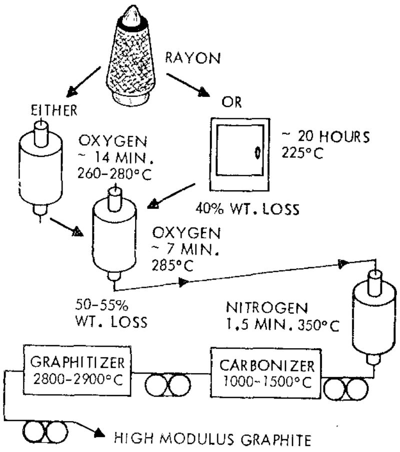


Figure 1 Schematic representation of the oxygen heat-treatment process.

The complete process from rayon to graphite is schematically represented in Fig. 1. The figure is divided into five processing stages.

1. Oxidation of the precursor either in air or in pure oxygen to approximately 40% weight loss. Although tension can be applied during this step, completely free shrinkage is satisfactory.

TABLE I Manufacturers' specifications for trial series of rayons

Designation	Manufacturer	Denier	No. of filaments	Filament denier
Fortisan	Celanese	800	720	2.3
Beaunit Tyrex	Beaunit	1650	1100	1.5
Amvis Tyrex	American Viscose	1650	1500	1.1
Suprenka	American Enka	1650	1644	1.0
Villwyte	Industrial Rayon	1650	720	2.3
Briglo 2610	American Enka	2200	960	2.3
Spin Twist	Industrial Rayon	900	150	6.0
Briglo	American Enka	1650	950	1.7
Skenandoa	Beaunit	900	150	6.0
Bemberg	Beaunit	900	744	1.2

TABLE II Physical properties of precursor rayon samples

Designation	Yarn tenacity ($g\ cm^{-3}$)	Elongation (%)	Wet/dry strength	% regain at 58% r.h.
Fortisan	7.59	13.0	0.50	12.58
Beaunit Tyrex	4.03	10.0	0.68	13.04
Amvis Tyrex	4.60	11.5	0.72	13.17
Suprenka	4.34	15.5	0.71	12.40
Villwyte	3.03	13.0	0.50	12.58
Briglo 2610	3.18	10.8	0.58	12.44
Spin Twist	3.10	13.5	0.48	12.51
Briglo 2699	3.18	9.8	0.51	12.31
Skenandoa	2.30	19.5	0.43	12.40
Bemberg	1.77	12.5	0.43	11.63

2. Completion of the oxidative degradation of the rayon crystalline structure in pure oxygen with slight tension. At the completion of this stage, the weight loss is 50 to 55% and there is no crystalline structure evident in the X-ray diffraction picture.

3. Final heat-treatment stage for 1.5 min in inert atmosphere at 350°C to start the development of the final carbon structure and to strengthen the yarn sufficiently to allow stress-carbonization. If the heat-treatment in stage 2 has been adequate, a 3300 denier yarn will sustain 50 g tension in this stage without appreciable elongation. Inadequate heat-treatment in stage 2 will result in elongations in this stage of as much as 15% at the 50 g tension level. The expected weight loss at the completion of this step is 60 to 65%.

4. Carbonization at temperatures between 1000 and 1500°C. Temperatures outside this normal range, namely, 900 to 2000°C have also been employed.

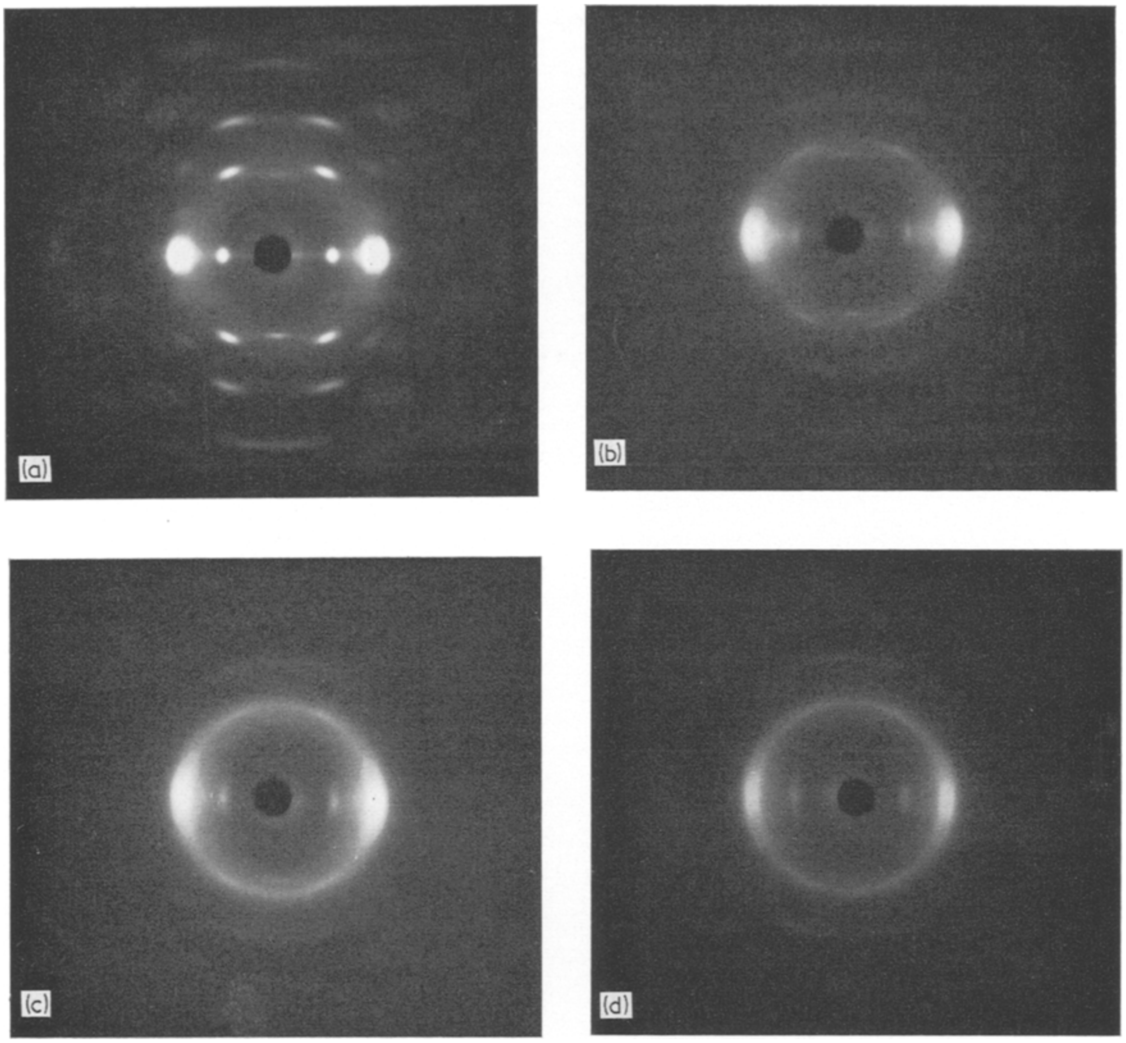
5. Graphitization at temperatures in the 2800 to 2900°C range.

In these experiments, the goal was to process all of the samples to approximately the same modulus (50×10^6 psi) for comparison purposes. Therefore, the total elongation through carbonization and graphitization was adjusted to yield this value of modulus.

3. Rayon precursor characterization

Ten rayons listed in Table I have been chosen for these studies as representative types of rayons which are commercially produced. These rayons were produced by five different manufacturers and, through reference to the physical properties given in Table II, can be classified into the following five different types of rayons: (1) very high strength (Fortisan); (2) tire rayon (Beaunit Tyrex and Amvis Tyrex), (3) high strength textile rayon (Suprenka); (4) textile rayon (Villwyte, Briglo 2610, Spin Twist, Briglo 2699, and Skenandoa); (5) cuprammonium (Bemberg).

The crystalline structure and the microstructure of these rayons have been studied by X-rays in the small-angle and wide-angle domains, and by optical and electron microscopy. The characteristic X-ray diffraction patterns of these rayons are shown in Figs. 2 and 3. The high angle transmission patterns (Fig. 2) were made



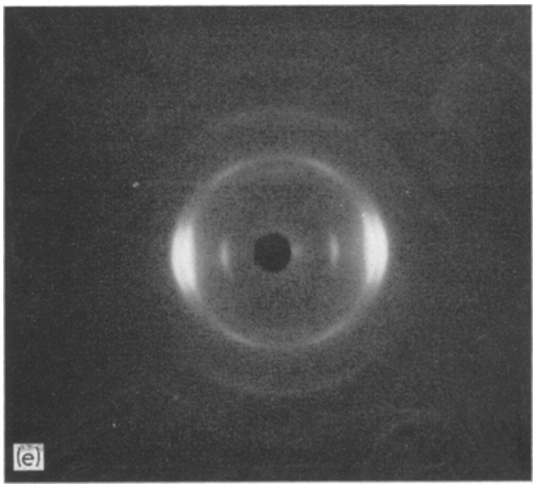


Figure 2 Flat plate transmission wide-angle X-ray diffraction pictures on ten selected rayons. (a) Fortisan, (b) Beaunit Tyrex, Amvis Tyrex, Suprenka, (c) Villwyte, (d) Briglo 2610, Spin Twist, Briglo 2699, Skenandoa, (e) Bemberg.

with a sample-to-film distance of 5 cm and monochromatic Cu radiation. The small-angle pictures (Fig. 3) were obtained with a point geometry small-angle diffraction camera of the Kiesig design and a sample-to-film distance of 40 cm with filtered Cu radiation; the prints shown in the figure represent exposure times of 47 h. Although ten different rayons have been studied by X-ray diffraction, only five diffraction patterns are presented in Figs. 2 and 3, because only five distinct types of patterns were obtained.

The rayons represented by each pattern are indicated in the figures.

The prints in Fig. 2 show clearly the well-oriented crystalline structure of the high strength rayons. The diffraction patterns also reflect the well-crystallized structure of Fortisan as compared with the poorly crystallized structure of the tire rayons. The textile rayons have diffraction patterns characteristic of an intermediate level of crystallinity.

The small-angle diffraction prints shown in Fig. 3 illustrate the relation between the magnitude of the small-angle scattering and the strength of the rayon. However, other experimental results indicate that this correlation is fortuitous in that the observed scattering arises from the presence of voids in the precursor rayon structure. The small-angle diffraction demonstrates that the production techniques used for the manufacture of high strength rayons have a tendency to produce voids in the structure as a side effect. The presence of these voids makes it impossible to study the changes in the microstructure of the rayon material phase by small-angle scattering, since any scattering from inhomogeneities arising from variations in crystallinity in the constituent Cellulose II is masked by the scattering form of the voids.

Rayon samples were prepared for microscopic examination by mounting and polishing the rayon in standard metallographic mounts and then removing the disturbed surface of the rayon by ion bombardment etching. Micrographs of two rayon yarns (Villwyte and Fortisan) prepared in this manner are reproduced in Fig. 4. Subsequent to the optical microscopy two-stage replicas were obtained from the rayon yarn samples and high resolution micrographs were obtained. The electron micrographs of the textile rayons are shown in Figs. 5 to 9. The electron micrographs for the high strength rayons have not been included. Those micrographs would show that high strength rayons have a high density of pores, as mentioned in the discussion of the small-angle scattering results. Therefore, the rough appearing surface in the optical micrograph of the Fortisan yarn in Fig. 4b is associated with the pores that are present in the rayon. The texture that appears in the optical micrograph of the textile rayon (Villwyte, Fig. 4a), on the other hand, is shown by the electron micrograph to be associated with the formation of etch pits in the rayon surface rather than with pre-existing pores.

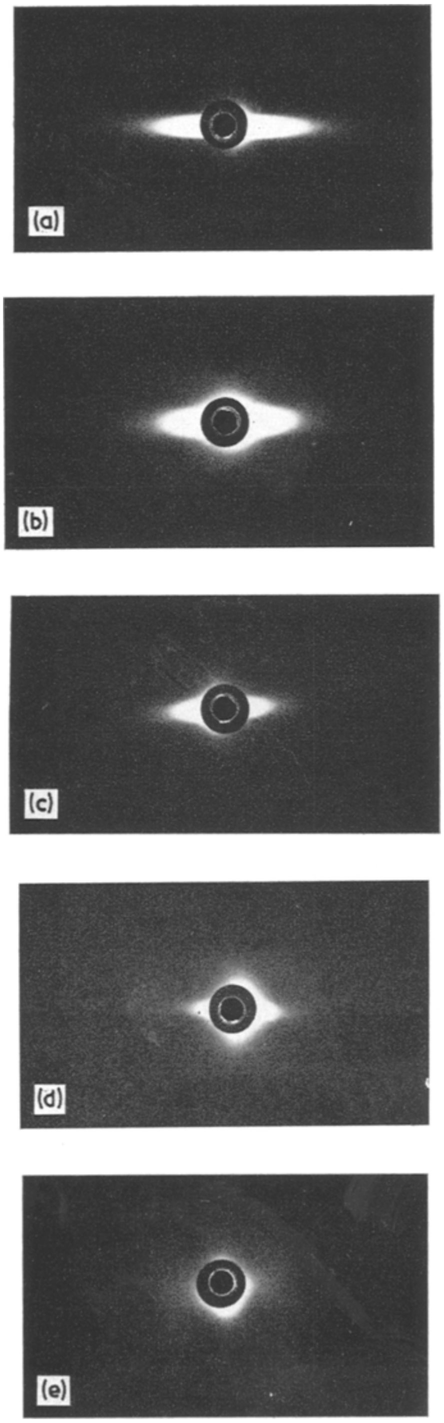


Figure 3 Low-angle X-ray diffraction pictures of ten selected rayons. Sample-to-film distance 40 cm. (a) Fortisan, (b) Beaunit Tyrex, Amvis Tyrex, (c) Suprenka (d) Villwyte, Briglo 2610, Spin Twist, Briglo 2699, Skenandoa, (e) Bemberg.

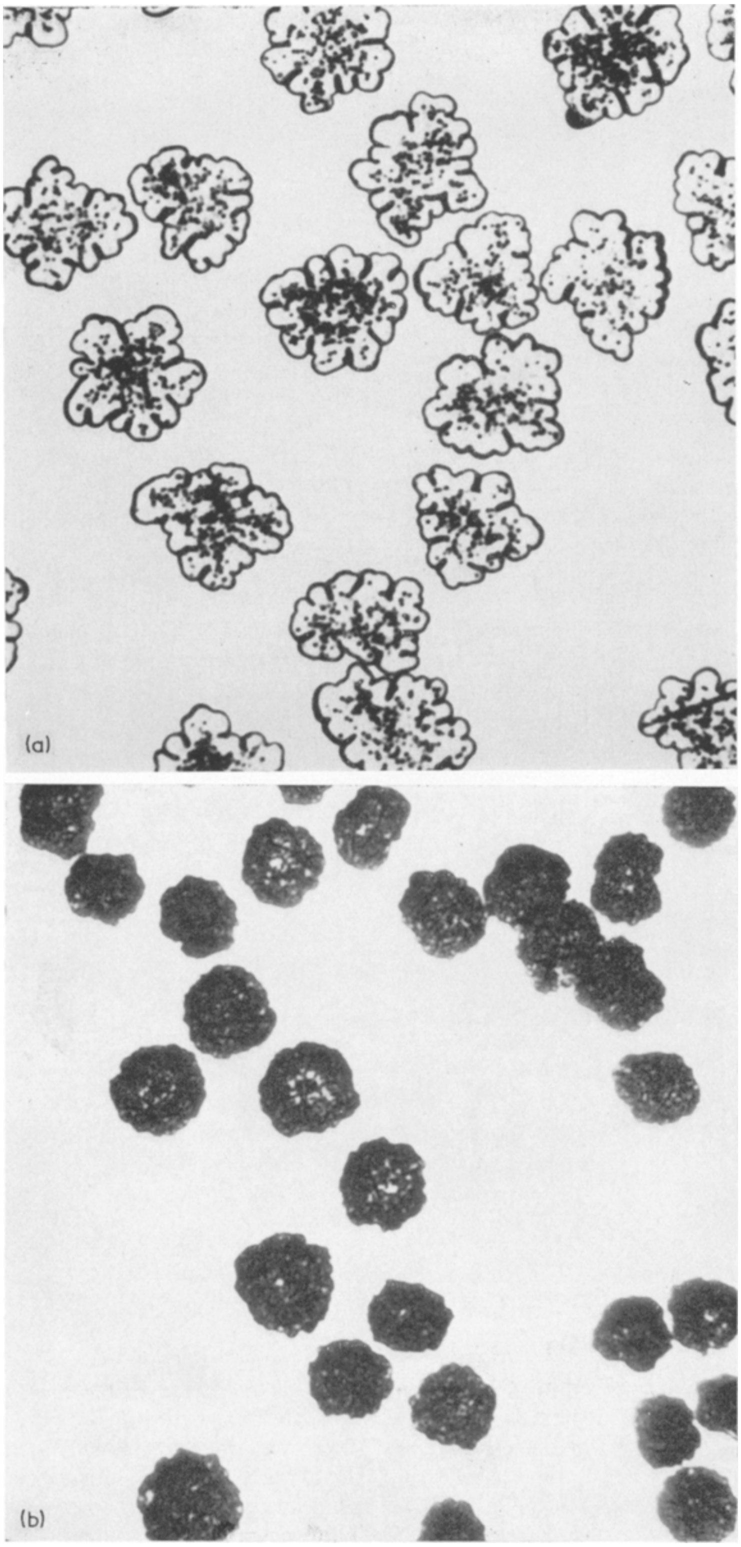


Figure 4 Photographs of Villwyte and Fortisan rayons etched by ion bombardment. (a) Villwyte, (b) Fortisan.

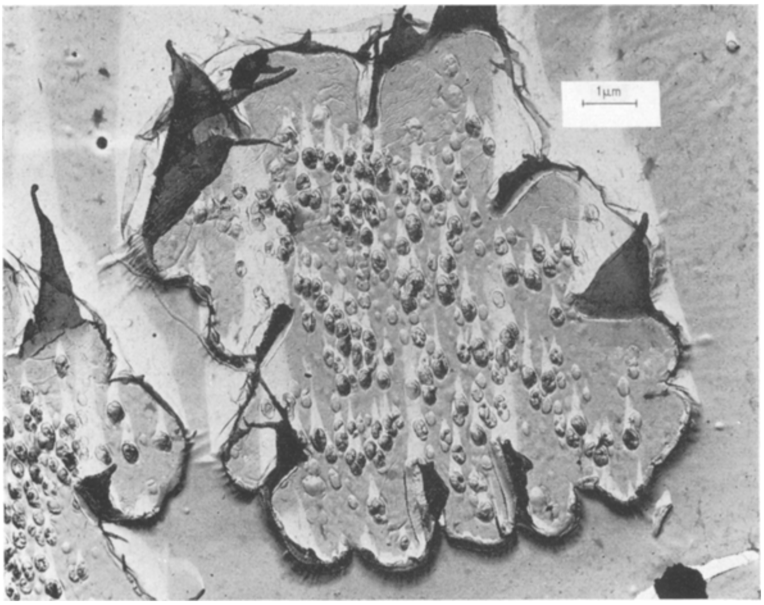


Figure 5 Electron micrograph of Villwyte etched by ion bombardment.

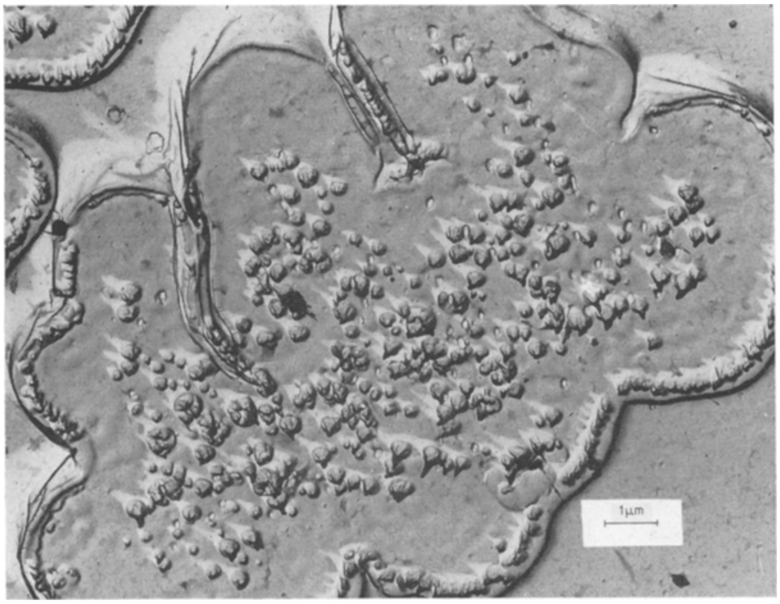


Figure 6 Electron micrograph of Birglo 2610 etched by ion bombardment.

The etching pattern observed in the micrographs (Figs. 5 to 9) indicate a fibrilar structure for the textile rayons with a fibril size of about 0.2 μm.

4. Processing results

Although all ten of the rayons listed in Table I have been subjected to processing, in some cases it had to be discontinued owing to stiffness which developed in the yarns. When stiffness was a problem, it could be observed very early in the processing (at weight losses of less than 10%). The occurrence of stiffness at this low weight loss, a point at which one would not expect to

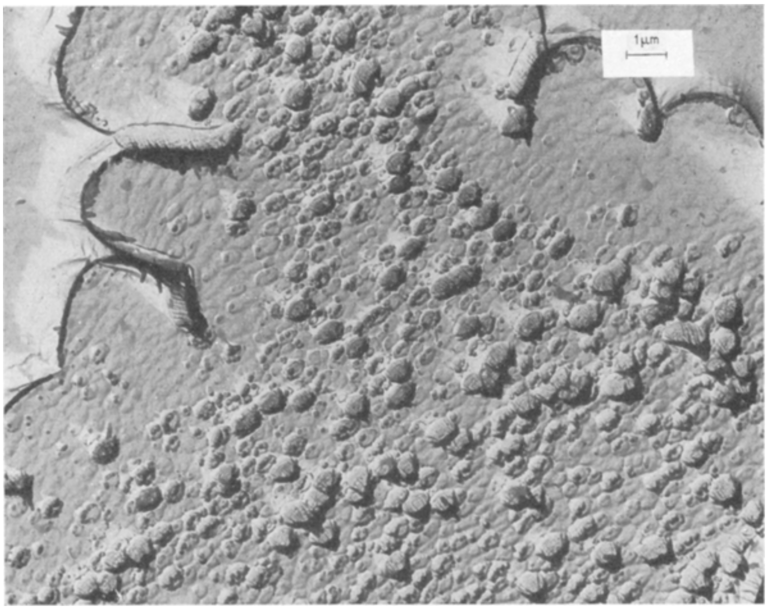


Figure 7 Electron micrograph of Spin Twist etched by ion bombardment.

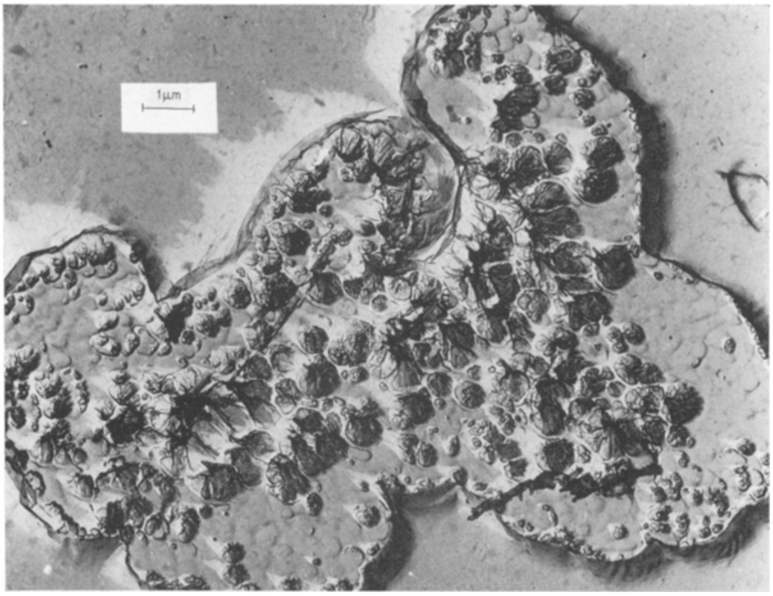


Figure 8 Electron micrograph of Briglo 2699 etched by ion bombardment.

obtain pyrolysis products from cellulose decomposition which could cement the filaments together, combined with the fact that only the high strength viscose rayons were stiff, suggested that the modifier employed during the spinning of these rayons caused the stiffness. This conclusion was later verified by washing one sample of "Tyrex" yarn in boiling water to extract the Carbowax modifier. After the sample was washed it was successfully processed. The cuprammonium rayon, which does not contain modifier, was also too stiff to process. However, with this type of rayon, the filaments are normally somewhat adhering. This interfilament

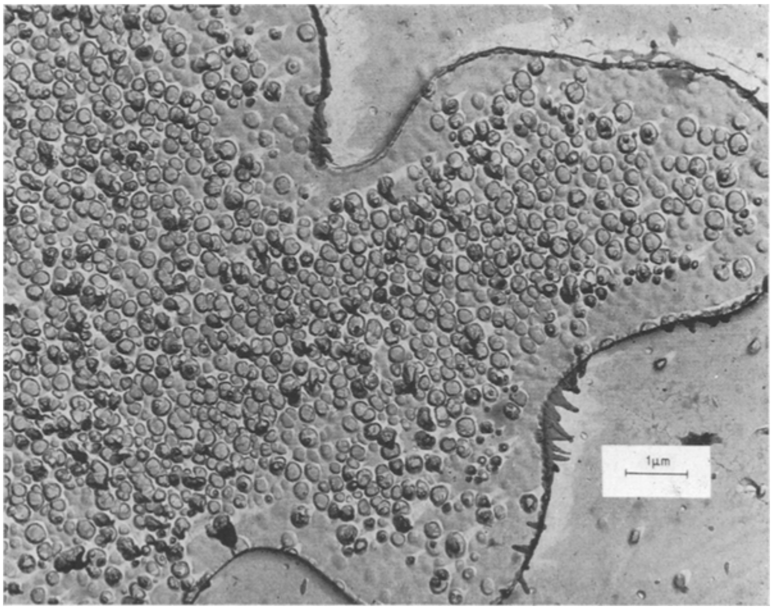


Figure 9 Electron micrograph of Skenandoa etched by ion bombardment.

bonding precludes any possibility of processing unless the filament can be separated during or before processing. The stiffness displayed by this yarn demonstrates that the interfilament bonding is not eliminated during processing.

The single-filament tensile properties which were obtained for the samples successfully processed are listed in Table III together with the times and temperatures employed during heat-treatment. The first three samples listed were processed continuously with the entire heat-treatment process taking place in pure oxygen. The last seven samples, the parameters of which are shown in the table, were batch pre-treated in air and the heat-treatment completed in a pure oxygen environment.

The repeated entries in Table III for Villwyte occur because every modification made in the process was tested by processing a length of the standard precursor. These trials with Villwyte demonstrate that all modifications of the process produce equivalent final products. Experiment no. 6 suggests that the pure oxygen (in stage 2 of the process) can be dispensed with and the entire oxygen requirements met by an air atmosphere.

All the textile rayons could be processed; however, it was not possible to obtain the target of 50 × 10^6 psi modulus with all of the samples. Both of the high tenacity yarns resulted in graphite yarns possessing lower strength-to-modulus ratios than the textile yarns. The spinning methods which are normally employed to produce a high tenacity yarn result in filaments which have high void content. It is expected that these small voids would act as weak points in the filaments, causing failure at reduced strain levels.

5. Conclusions

1. The oxygen heat-treatment of rayon in quantities suitable for the fabrication of small composite test specimens has been demonstrated with readily available laboratory equipment.

2. The heat-treatment process is easily controlled by measurements of weight loss.

3. The heat-treatment process is independent of the heating schedule employed within broad limits; provided the proper weight loss is achieved at the end of each processing stage.

4. Unmodified (textile) rayons as a general class are suitable precursors for the production of high modulus graphite yarn.

5. Modified (tire cord) rayons can be processed to high modulus if the modifiers are extracted from the rayon before processing.

6. Crystalline structure and preferred orientation in the precursor rayon are not a major factor in the final graphite yarn properties.

7. Gross physical characteristics, such as

TABLE III Summary of oxygen heat-treatment experiments

Exp. no.	Rayon sample designation	Batch pre-treatment in air		Continuous heat-treatment in O_2*		Final weight yield (%)	Graphitized fibre properties	
		Time (h)	Temperature (°C)	Time (min)	Temperature (°C)		Young's modulus (10^6 psi)	Tensile strength (10^3 psi)
1	Villwyte	—	—	6.0	260			
		—	—	3.0	275	18.9	45.9	236
		—	—	12.0	285			
2	Fortisan	—	—	6.0	260			
		—	—	3.0	270	15.3	54.2	224
		—	—	12.0	285			
3	Skenandoa	—	—	6.0	260			
		—	—	3.0	275	19.4	29.4	116
		—	—	21.0	285			
4	Villwyte	6.0	230	5.0	395	20.2	53.4	256
5	Villwyte	19.5	225	6.0	275	19.6	53.6	266
6	Villwyte	19.5	225	1.5	300‡	20.2	50.4	256
7	Spin Twist	7.0	230	7.0	295	21.0	52.3	246
8	Briglo 2699	6.0	230	13.5	275	20.0	41.1	184
9	Briglo 2610	6.0	230	7.0	285	20.6	36.3	187
10	Amvis Tyrex†	20.0	225	3.0	280	17.5	47.0	210

*All samples subjected to additional heat-treatment at 350° C for 1.5 min in nitrogen atmosphere before carbonization.
†This tire yarn was washed in boiling water prior to processing.
‡Air was substituted for O_2 atmosphere.

voids or adhering filaments, are carried through the process. Therefore, a uniform flaw-free end-product requires a uniform flaw-free precursor.

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