

Carbonisation and Hot Stretching of a Phenolic Fibre

J. ECONOMY, RUEY-YUAN LIN

Research and Development Division, The Carborundum Company, Niagara Falls, NY, USA

A carbonisation study of a fibre derived from phenolic resin has been carried out. The carbon from this fibre is glassy in nature. The effect of both low and high temperature stretchings on the crystallite orientation has been investigated. Various degrees of preferential orientation could be observed in fibres prepared from the following treatments: (1) Carbonised under tension and heat-treated to 2750°C without tension, (2) Carbonised without tension but heat-treated to 2750°C under tension, and (3) Carbonised and heat-treated to 2750°C, both under tension. A significant increase in fibre modulus was observed in case 3. The mechanism by which preferential orientation is achieved and its relationship with increase in modulus are discussed.

1. Introduction

High strength, high modulus carbon fibres have been prepared from rayon [1] and polyacrylonitrile (PAN) [2] precursors by inducing preferential orientation of crystallites along the fibre axis. In the case of rayon precursor, orientation is achieved by stretching at temperatures in excess of 2500°C. With PAN precursor, orientation is induced by carrying out a low-temperature oxidative cross-linking under tension prior to carbonisation. Attempts to produce high modulus carbon fibre from a pitch precursor were, until recently, unsuccessful [3], but now it has been reported that high-temperature stretching over 2200°C results in fibres with modulus values of 30 to 70×10^6 psi (207 to 483 GNm⁻²) [4]. Recently a new precursor fibre, identified as KYNOL*, which consists of cross-linked phenol formaldehyde units, has become available [5]. This fibre would be particularly attractive as a carbon-fibre precursor since it gives a 60% carbon yield and its cross-linked structure permits a greatly simplified carbonisation process.

It was the purpose of this investigation to study the carbonisation of the phenolic fibre and to determine conditions necessary to induce preferential orientation of crystallites along the axis of the carbon fibre. The effects of applying tension at low temperature (room temperature to 800°C)

and high temperature (2500 to 2750°C) were studied.

2. Experimental

2.1. Description of Material

KYNOL fibre possesses a cross-linked phenolic structure and is prepared by curing of a precursor novolac fibre [6]. This fibre is made commercially available by The Carborundum Company in 5 to 46 cm staple lengths. The fibre is infusible, non-flammable and resistant to swelling in organic solvents such as acetone, benzene, xylene, trichlorethylene, etc. X-ray diffraction analysis shows that the fibre is amorphous. The cross-sectional shape of the fibre is nearly circular. The material used for this study was a 46 cm staple fibre with an average diameter of $\sim 12 \mu\text{m}$.

2.2 Low-Temperature Stretching

The low-temperature stretching, from room temperature to 800°C, was carried out in a vertical 30 cm-long Vycor tube heated in a "Hevi-Duty" furnace under a nitrogen atmosphere. The phenolic fibre in the form of a bundle of 4000 to 8000 filaments was suspended in the centre of the furnace with the upper part of the fibre bundle fastened to a metal clamp and the bottom portion attached to a variable weight. A calibrated scale was placed adjacent to the weight-holder in order to measure the length

variation of fibre during pyrolysis. The fibre bundle was carbonised under a load of 26.3 to 52.6 kg cm^{-2} . In most cases, the heating rate was maintained at $\sim 100^\circ\text{C h}^{-1}$. The fibre at this stage analysed at about 90% carbon.

2.3. High-Temperature Stretching

The 800°C carbon fibre was further heat-treated at elevated temperatures of 2500 to 2750°C in an induction-furnace. A graphite tube, $1.9 \times 1.3 \times 15.3 \text{ cm}$ (OD \times ID \times Length) was used as a susceptor. The length of hot zone was estimated to be about 3 cm. A tensile stress of about 105 kg cm^{-2} was applied by static loading and the degree of elongation was measured directly from the initial and final positions of the load. An elongation up to 1.3 cm was observed. Since the temperature distribution of the furnace was not uniform, the stretching could not be expressed in terms of "per cent elongation" at any given temperature. At all times an attempt was made to apply a load which approached the breaking stress of the fibre. The stretched portion of the filament bundle was identified from both the location in the furnace and the slightly reduced fibre diameter. The fibres collected after high temperature treatment were then evaluated by the techniques to be discussed.

2.4 Characterisation

2.4.1. Thermogravimetric analysis

A Cahn RG Electrobalance was used for thermogravimetric analysis. Nitrogen was used as the atmosphere and the heating rate was kept at 6°C min^{-1} .

2.4.2. X-ray study

The X-ray diffraction study of the carbonised KYNOL fibres was carried out on a Norelco X-ray Diffractometer using Cu-radiation (1.5405 \AA) scanning from 54 to 0° at about 1° min^{-1} . The crystallite dimension was estimated by the standard line-broadening technique.

2.4.3. Mechanical properties

The elastic modulus of filaments was determined on an Instron tensile machine, using 2.54 cm as the gauge length.

3. Results

3.1. Carbonisation of KYNOL Fibre

Initially, carbonisation of the phenolic fibre was studied in the absence of tension. The high carbon yield of phenolic fibre is shown in fig. 1

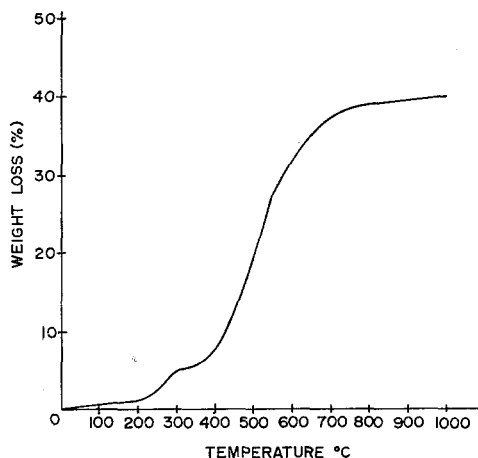


Figure 1 Thermogram of phenolic fibre.

where the weight loss of fibre from room temperature to 1000°C was determined by thermogravimetric analysis. The carbon obtained from the phenolic fibre is basically glassy; this results from the random cross-linking present in the precursor fibre [7, 8]. X-ray analysis showed that the crystallite dimensions of the carbonised fibre were insensitive to further heat-treatment up to 2750°C , which is a typical characteristic of glassy carbon (see fig. 2). The interlayer spacing (d_{002}) decreased from 3.95 \AA at 1000°C to 3.43 \AA at 2750°C as compared to 3.35 \AA for natural graphite.

The phenolic fibre can be carbonised at a very rapid rate owing to the low volume of volatiles evolved during pyrolysis. In fact, there is little difference in mechanical properties of phenolic

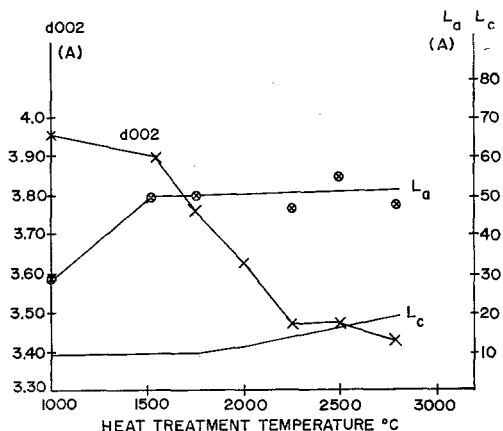


Figure 2 Changes of crystal dimension of carbonised kynol fibre with HTT.

fibre carbonised to 800°C over a wide range of heating rates of 10 to 200°C⁻¹. (table I). Hence, the ease of carbonisation combined with the high carbon yield make the phenolic fibre an attractive carbon fibre precursor.

TABLE I Effect of carbonisation rate on the properties of 800°C carbonised phenolic fibre

Sample	Heating rate (°C/h)	Tensile strength (10 ³ psi)	Modulus (10 ⁶ psi)
1	10	65.2	4.8
2	25	66.2	4.9
3	50	67.6	3.9
4	100	65.0	4.6
5	200	61.2	4.3

1 psi = 6.9 × 10⁴ dyn/cm².

3.2. Low-Temperature Stretching

An attempt was made to induce crystallisation and orientation during carbonisation of the phenolic fibre by applying tension from room-temperature to 800°C in a manner similar to that reported for PAN [9]. The phenolic structure undergoes a series of complicated degradation steps including ketonisation of methylene groups, etherification, thermal fragmentation and eventually ring opening and cyclisation reactions during pyrolysis. Under the influence of tensile stress these reactions might conceivably proceed in an ordered manner to yield a better crystallised and oriented carbon product. It was on this premise that the work to test the feasibility of inducing crystallisation and orientation by carbonising the phenolic fibre under tension was undertaken.

As the phenolic fibre was carbonised under a tension of 26.3 to 52.6 kg cm⁻² in a vertical furnace a length variation was observed as a function of temperature. The fibre elongated in the temperature range of 100 to 400°C and shrank thereafter. The degree of elongation and shrinkage depended upon the load applied to the fibre bundle. The temperature region where the shrinkage was observed coincided with a sharp increase in weight loss shown in fig. 1. Evaluation of fibres carbonised to 800°C with and without tension yielded the following results. Low temperature stretching did not induce crystallinity detectable by X-ray in the 800°C carbon fibre. Figs. 3a and b show the X-ray diffraction patterns of carbonised phenolic fibre processed without and with tension respectively. Both patterns indicate that the carbon at this stage is

TABLE II Properties of carbonised phenolic fibres under various conditions

Sample	Carbonisation conditions	Modulus (10 ⁶ psi)	Preferential orientation
1	Carbonised to 800°C without tension	4.5	Not detected, amorphous
2	Carbonised to 800°C under tension	8.4	Not detected, amorphous
3	Carbonised to 800°C without tension Further heat-treatment to 2750°C without tension	—	None, crystalline
4	Carbonised to 800°C without tension Further heat-treatment to 2750°C under tension	11.3	Slight
5	Carbonised to 800°C under tension Further heat-treatment to 2750°C without tension	5.6	Partial
6	Carbonised to 800°C under tension Further heat-treatment to 2750°C under tension	24.5	Medium

highly amorphous. Some orientation was induced in the fibre structure during low-temperature stretching but was detectable only after heat-treatment to 2750°C in the absence of tension (compare fig. 3b with 3c and d). A slight increase in elastic modulus was also observed as a result of low temperature stretching. This is illustrated in table II.

3.3. High-Temperature Stretching, 2500 to 2800°C

Since the low temperature stretching did not produce any significant crystallite orientation, effort was shifted to high temperature stretching, a technique used successfully for making high modulus carbon fibre from rayon precursor. As the 800°C carbon fibre was heated to 2750°C it underwent a slight additional weight loss.

The high temperature stretching was carried out in the temperature region of 2000 to 2750°C. Elongation could be detected at a temperature of 2200°C and continued up to ~ 2750°C. As expected the degree of elongation increased with higher loads. The X-ray pattern of the stretched fibre showed the typical unevenness of the (002) diffraction ring, indicating the presence of

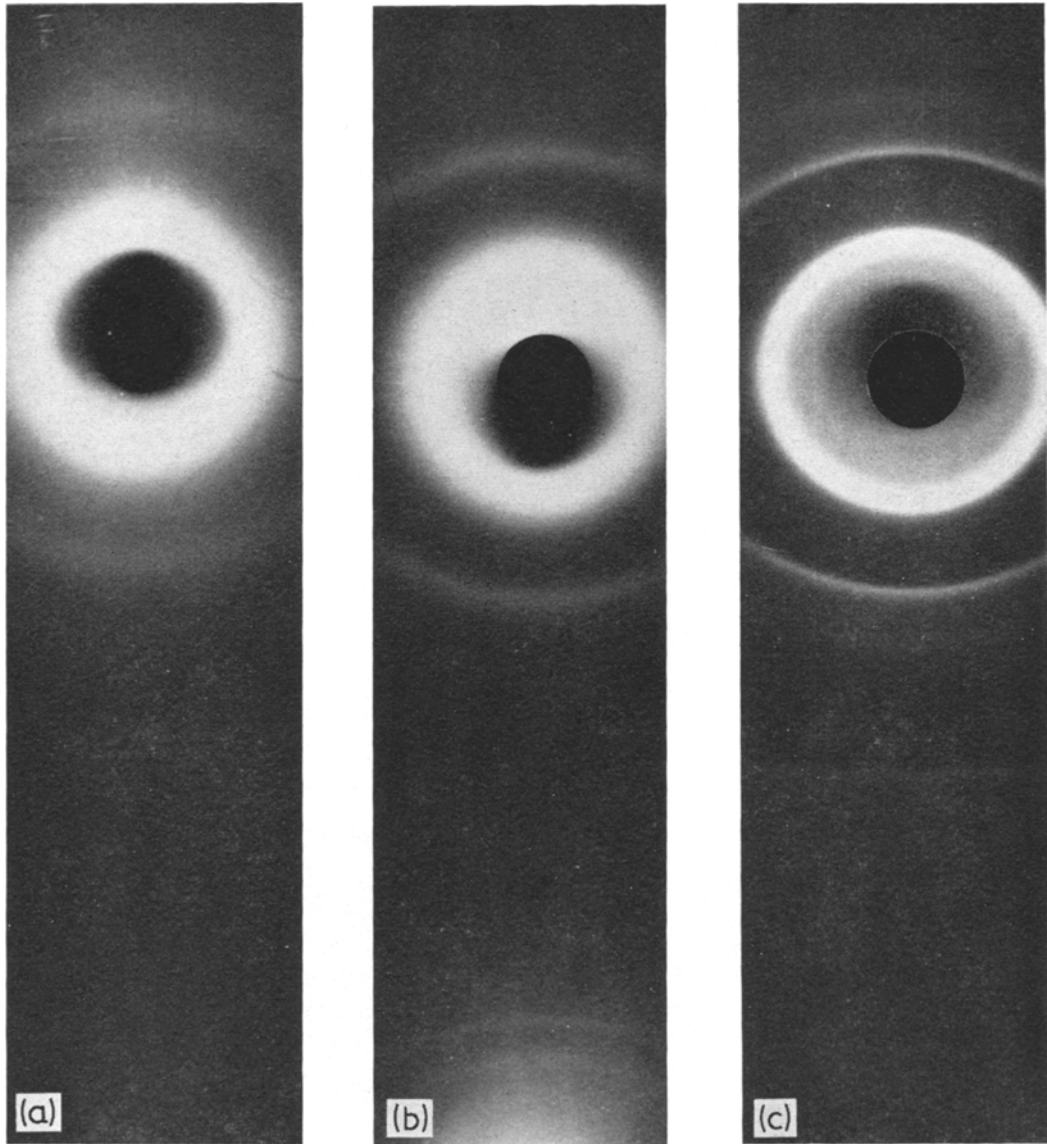


Figure 3

preferential orientation (fig. 3e). This was accompanied by an increase in elastic modulus. Although the stretching conditions remain to be optimised these results show that glassy carbon fibre can indeed be oriented to form high modulus carbon fibre. This observation has also been reported by Hawthorne and co-workers [4] working with a pitch carbon fibre. The effect of tension and temperature on the fibre structure and mechanical properties was examined under

six different conditions. The results are summarised in table II and discussed in the following section.

4. Discussion

It has been generally accepted that the increase in elastic modulus of carbon fibre is related primarily to the degree of preferential orientation of crystallites along the fibre axis. The method used to achieve high modulus depends upon the

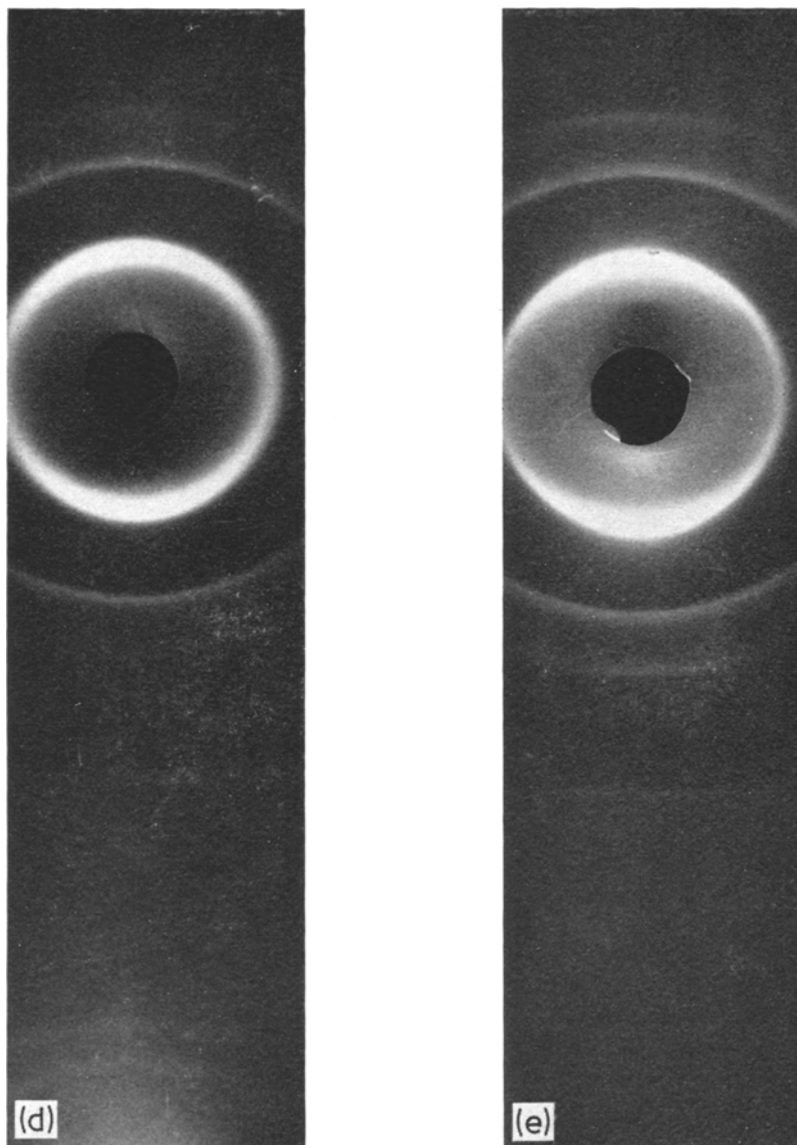


Figure 3 X-ray diffraction pattern of various carbonised phenolic fibres. (a) carbonised to 800°C without tension. (b) carbonised to 800°C under tension. (c) carbonised to 800°C without tension. Further heat-treated to 2750°C without tension. (d) carbonised to 800°C under tension. Further heat-treated to 2750°C without tension. (e) carbonised to 800°C under tension. Further heat-treated to 2750°C under tension.

nature of the precursor fibre. For PAN, ordering is induced in the early stages of carbonisation. It is important that the fibrillar structure formed during spinning of polyacrylonitrile be highly oriented. In addition, the cross-linking of polymer chains during oxidative heat treatment in air at 220°C must be carried out under a tensile stress to the fibre bundle. The ordered structure created at this stage can then be maintained during subsequent high-temperature treatment

without tension. The carbonisation of rayon involves the removal of oxygen from the cellulose chain as an essential step in the degradation mechanism. Low-temperature stretching techniques are not applicable to such a system due to the lack of fibre strength at this early stage. The orientation of carbon from rayon is induced by high-temperature stretching using a partially carbonised fibre (~80% in carbon content) as the starting material.

Graphitisation and preferential orientation occur almost simultaneously.

The first attempt to convert a glassy carbon fibre into a higher modulus carbon fibre was made by Otani [3] on a carbon fibre derived from molten pitch, generally designated as MP carbon fibre (molten pyrolysis). A slight increase in modulus, 20 to 25%, was obtained by applying a load to the fibres in low (1000°C) and high (1000 to 2200°C) temperature heat treatments. The carbon filaments still possessed an isotropic structure even after being heated up to 2600°C under stress. On the other hand, Fishbach [10,11] detected a deformation-induced anisotropy in bulk glassy carbon by magnetic susceptibility and X-ray measurements. This would suggest that preferential orientation can be induced in glassy carbon fibre under the proper process conditions. This has now been confirmed using glassy carbon fibres, obtained from either pitch or phenol-formaldehyde resin.

For carbon from phenolic fibre the increase in elastic modulus depends, not only upon the degree of preferential orientation, but also on the route used to achieve the orientation. For example, the fibre from carbonisation (800°C) under tension followed by high temperature heat treatment to ~ 2750°C without tension displayed some preferred orientation, but only a slight increase in modulus. On the other hand, the carbon fibre which was stretched up to 800°C and at 2750°C showed the presence of orientation and a sharp increase in modulus at the same time. This discrepancy may be explained on the basis of differences in intercrystallite bonding. As the highly strained carbonised fibre (due to carbonisation under tension) was heated to 2750°C without tension, the crystallites grew in an ordered pattern preset by the low-temperature stretching. However, in the absence of tension the partially deformed intercrystallite bondings tended to resume a normal configuration via a relaxation process. Thus, a carbon fibre with preferred orientation but without significant increase in modulus of elasticity results. Hot-stretching at 2750°C not only induces crystal growth and crystallite orientation, but also prevents the relaxation of the deformed intercrystallite bonds. Therefore, the modulus of elasticity increases.

In summary, the following observations can be made with respect to carbonisation and stretching of a phenolic fibre.

(1) Phenolic fibre can be carbonised to form a

glassy carbon fibre at very rapid heating rates up to 200°C/h.

(2) Crystallite orientation can be induced in carbon fibres derived from a cross-linked phenolic fibre.

(3) In order to increase the fibre modulus effectively, tensile stress must be applied at both low temperature (room temperature to ~ 800°C) and high temperature (up to 2750°C).

(4) Fibre modulus is determined not only by the degree of crystallite orientation but also by the nature of intercrystallite bonding.

Acknowledgement

We would like to express our appreciation to Mr. F. J. Frechette for his effort in liberisation of Novokic resin and Mr. H. H. Blakely for his work in mechanical tests of stress.

References

1. R. BACON, A. A. PALOZZI, and S. E. SLOSARIK, Proc. 21st Annual Meeting, Reinforced Plastics Div., Soc. Plastics Ind., Chicago, Ill., 8-10 Feb. (1966).
2. A. SHINDO, Studies on Graphite Fiber, 317 (Govt. Indus. Res. Inst. Osaka, 1961).
3. S. OTANI, A. YOKOYAMA, and A. NUKUI, *Appl. Polymer Symp.* No. 9, (1969) 325.
4. H. M. HAWTHORNE, C. BAKER, R. H. BENTALL, and K. R. LINGER, *Nature* 227 (1970) 946.
5. J. ECONOMY, L. C. WOHRER, and F. J. FRECHETTE, Reprints 39th Annual Meeting, Textile Res. Inst., New York, N.Y. 11 April 1969.
6. J. ECONOMY, L. C. WOHRER, F. J. FRECHETTE, and P. DIACHUN, U.S. Air Force Tech. Rep., AFML-TR-70-72, July 1970.
7. K. KAWAMURA and G. M. JENKINS, *J. Mater. Sci.* 5 (1970) 262.
8. E. FITZER, W. SHAEFER, and S. YAMADA, *Carbon* 7 (1969) 643.
9. W. WATT and W. JOHNSON, *Appl. Polymer Symp.* No. 9, (1969) 215.
10. D. B. FISHBACH, *Carbon* 7 (1969) 196.
11. *Idem*, Technical Report 32-1228, Jet Propulsion Laboratory, 1 March, 1968.

Received 8 March and accepted 16 May 1971.