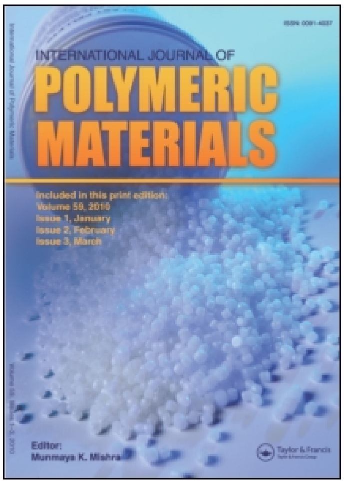

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Daniel J. O'neil[a]
[a] Georgia Institute of Technology, Engineering Experiment Station, Atlanta, Georgia

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Precursors for Carbon and Graphite Fibers

DANIEL J. O'NEIL

Georgia Institute of Technology, Engineering Experiment Station
Atlanta, Georgia

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Commercial production of carbon and graphite fiber products has been dominated by technology based on the thermal conversion of rayon and polyacrylonitrile fibers. In fact, a wide range of potentially useful and low-cost precursors exist. Most recently, pitch-based fibers have materialized as strong contenders for carbon fiber production. This study is a comprehensive analysis of carbon fiber precursors. It presents a data base for the development of a generalized theory for the prediction of formation of carbon fibers with high mechanical properties.

1 INTRODUCTION

From the laboratory curiosity of the mid-'60s, carbon and graphite fibers have emerged to a stage where they are on the threshold of widespread commercial usage. From a limited usage reinforcement, confined to strategic aerospace applications and to specialty products such as high-performance sporting goods, carbon or graphite fibers are now about to make a significant impact on mass markets. With U.S. governmental pressure for higher-mileage automobiles, the industry is responding by seeking weight reductions in the vehicles. Not unsurprisingly, the commercially available carbon fibers have been developed from commercially available, fibrous precursors. However, with the possible exception of pitch-based carbon fibers there appears to be a lower limit of cost which has retarded the widespread use of these materials as reinforcing agents in composites. Consequently, a developing need can be perceived for further research and development of low-cost fiber precursors.

Additionally, we have viewed the withdrawal of rayon-based carbon fibers from the market place by Union Carbide Corporation. The significant role played by these fibers, as specified materials for strategic defense applications, has led to the need to define additional, reliable sources of raw materials for production of carbon and graphite fibers.

Another objective in investigating non-commercial fiber precursors for carbon fibers is the need ultimately to tailor the properties of fibers to the application. At this stage of materials development, our efforts are dedicated—confined to the manipulation of existent products of existent processes. One cannot expect the development of carbon fibers to cease with rayon, polyacrylonitrile, or pitch. If for no other reason than that specialty markets will develop (wherein, for example, the surface properties rather than the gross mechanical properties of a fiber will dominate), additional and continued study of new precursors is warranted by both the industrial and government sectors.

Finally, the work of Hawthorne[1] and others has demonstrated that structural anisotropy may be induced in any type of carbonaceous fiber, irrespective of the nature of the precursor fiber, by axial plastic strain at graphitization temperatures.

In this paper, an attempt is made to survey the field of available and potential precursors and to begin to draw some conclusions about the typology of the precursors in relation to the resultant properties of the carbon and graphite fibers.

2 COMMERCIAL FIBERS

Tables I, II, and III summarize the commercial fibers which have been or are available today. It must be noted that the values given for mechanical properties are not necessarily comparable since different test methods have been used. The data derives from the literature, including the product literature of manufacturers.

Historically, bamboo was decomposed to make weak fibers for the original carbon filament incandescent lamps. Carbonized rayon fibers were introduced for thermal insulation and were used in ablative reinforced plastics during the late 1950s. Their competitive position *vis-á-vis* glass fibers could not be direct since the basic cost of the cheapest staple rayon monofilament was about twice the price. However, very significant increases in the mechanical properties of rayon-based carbon fibers were achieved by Union Carbide. Using stress graphitization[2] the random microcrystalline structure of rayon-based carbon fiber was converted to an oriented turbostratic-graphite structure. Small-scale production of high modulus, high strength carbon fibers began at Union Carbide and was followed by HITCO, Inc. and, later, other organizations.

It appears that at about the same time (1964) British researchers[3] were experimenting independently with the conversion of polyacrylonitrile to carbon fiber. Shindo[4] in Japan, had achieved success in producing PAN-based carbon fibers with relatively high modulus, but low strength. The British investigators discovered results similar to those of the investigators of rayon. High strength and high modulus carbon fibers could be produced from oriented polyacrylonitrile polymers and copolymers by constraining or elongating the fibers during oxidation. While PAN fiber was more expensive than rayon, it produced about twice the carbon yield. Fiber was produced in hanks or tows of a few feet by batch processing. Capital equipment requirements, at this stage of low production, was not costly. Inevitably, demand for reproducible properties in quantity led to the development of continuous operations with substantial investment requirements. The commercial potential for PAN-based fibers is probably best expressed by the number of manufacturers who are actively competitive in the market place, as evident in Table II.

In the mid-'60s, Kureha Chemical Industry Co. Ltd. in Japan[5] were investigating asphaltic or pitch materials for carbon or graphite filaments. Distillation and isolation of specific fractions was followed by heating, extrusion, and spinning. Stabilization by oxidation of the fibers, followed by carbonization and graphitization led to comparatively low-to-intermediate strength, intermediate-modulus carbon fibers (4-38 × 10^6 psi). This work and others with pitch-type materials, including lignins and lignosulfonates,[6] was motivated by the necessity to reduce the selling price of carbon fibers to a

TABLE I

Commercial rayon-based carbon fibers

Manufacturer	Type	Tensile strength		Tensile modulus	
		psi × 10^{-3}	MPA	psi × 10^{-6}	GPA
Union Carbide (U.S.)	T-25	180	1241	25	172
	T-40	250	1724	40	276
	T-50	300	2069	50	345
	T-75	365	2517	75	517
	VYB-70 1/2	120	827	6	41
	WYB-85 1/2	90	621	5	34
HITCO (U.S.)	HMG-25	150	1034	25	172
	HMG-40	250	1724	40	276
	HMG-50	300	2069	50	345
	GY2-1	200	1379	4	28
Poly Carbon (U.S.)	CX5/CX2	175	1207	4	28
Carborundum (U.S.)	GSCY-2-5	140	965	4	28

TABLE II

Commercial polyacrylonitrile-based carbon fibers
(Mechanical properties primarily based on manufacturers' claims)

		Tensile strength		Tensile modulus	
Manufacturer	Type	psi × 10^{-3}	MPA	psi × 10^{-6}	GPA
Celanese (U.S.)	Celion GY-70	270	1860	75	517
	1000	360	2482	34	234
	3000	400	2758	34	234
	6000	400	2758	34	234
Courtaulds (U.K.)	Grafil A	390	2689	31	214
	HM	340	2344	52	359
	HT	400	2758	36	248
Great Lakes (U.S.)	Fortafil 3U	360	2482	27	186
	3	360	2482	30	207
	5	400	2758	48	331
Hercules (U.S.)	Magnamite AS	450	3102	32	221
	HTS	400	2758	36	248
	HMS	340	2344	50	345
Le Carbonne—Lorraine (France)	Rigilor 250	250	1724	55	379
	350	350	2413	45	310
Morganite Modmor (U.S. and U.K.)	*Modmor*				
	Type I	300	2069	60	414
	Type II	360	2482	42	290
	Type III	350	2413	34	234
Polycarbon (U.S.)	A	300	2069	35	241
	T	350	2413	40	276
	M	300	2069	60	414
Sigri (Germany)	Sigrafil	215	1482	70	483
		355	2448	28	193
Stackpole (U.S.)	Panex 30A	440	3034	32	221
	30C	335	2310	32	221
	30Y	260	1793	32	221
	20	470	3241	21	145
Tokai Electrode (Japan)	Thermalon T-3	230	1586	70	483
Toray (Japan)	Torayca T-300A	360	2482	35	241
	T-200A	300	2069	—	—
	M-40A	—	—	50	345
Union Carbide (U.S.)	Thornel T-400	450	3102	30	207
	T-300	365	2517	34	234
	T-300A	360	2482	35	241

TABLE III

Other commercially available carbon fibers

		Tensile strength		Tensile modulus	
Manufacturer	Type	psi × 10^{-3}	MPA	psi × 10^{-6}	GPA
Kureha (Japan)	Pitch-based	75	517	38	262
		250	1724	4	28
Nippon (Japan)	"Kayacarbon", lignin-based	85	586	—	—
Union Carbide (U.S.)	"Type P", pitch-based	250–350 300–400	1724–2413 2069–2758	50–70 28–35	345–483 193–241

level where they can be employed in composite products for mass markets. It is generally recognized that the cost components of carbon fibers can be divided between precursor material costs and processing costs. While the latter cost can be reduced substantially on a unit basis as production volume increases, raw material costs are not as volume-sensitive, and, in fact, precursor costs are continually increasing. Consequently, lower cost precursors are needed for volume markets.

Union Carbide is developing its Type P pitch-based carbon fiber on the basis that these types of carbon fibers alone can currently achieve a cost structure which will allow acceptable pricing of carbon fiber for widespread commercial applications.[7]

3 CARBON FIBER PRECURSORS

In this section, a review of materials which have been employed for production of carbon fibers is undertaken.

3.1 Polyacrylonitrile

The carbon fibers produced according to the British (NRDC) patent, and under licence, employ "Courtelle," which is understood to be a terpolymer of acrylonitrile, methyl acrylate (6%) and another vinyl monomer which acts as a dye site. A limitation in the PAN-conversion process is the slow preliminary oxidation of the fiber at 220°C which is necessary to stabilize both the oriented structure and the thermal integrity of the fiber. To minimize this factor, finer filaments are preferred which increases the cost of textile versions. Evidently, "Courtelle" is a superior starting material both because of its chemical composition and its physical dimensions. However, unlicensed manufacturers of PAN-based fibers have produced competitive carbon fibers using conventional precursor fibers, e.g., orlon. Ezekiel[8] has provided laboratory evidence that low-tenacity homopolymers can be successfully graphitized directly to high modulus graphite fibers while fairly high, but erratic, tensile strengths were reported. The suggestion is inferred that neither high tenacity nor a high degree of yarn orientation is obligatory in a precursor yarn but that increased tension and exposure during graphitization yield very large increases in modulus and tensile strength.

The literature, particularly patents, is replete with numerous variations of the polyacrylonitrile starting material. The range of comonomers which have been used with acrylonitrile cannot possibly be reviewed in this paper. However, in general, a typical composition contains a minimum of 85% acrylonitrile and a maximum 15 mole % of comonomers such as methyl methacrylate, methyl acrylate, vinyl acetate, vinyl chloride, other monovinylic compounds. Ross[9] has recently summarized the use of PAN-based precursor yarns for carbon fiber reinforcement.

3.2 Cellulosics

Cellulose-based precursor fibers include rayon, cotton, linen, wood, straw, bamboo, ramie, sisal, hemp, and flax. Regenerated cellulose, or rayon, has been the most used, of course. Polynosic fibers were not found to provide any advantages to conventional rayon in the production of high strength fibers. Perhaps the predominant area of study with regard to cellulosic raw materials since the classic patent of Ford and Mitchell[10] has been in modifying the degradative mechanism to increase carbon yields by addition of inorganic compounds, by modification of the cellulose, or by varying the reactive environment. Russian investigators[11] converted cellulose by oxidation to poly (anhydrouronic acid), reacted this with various metal salts (Al, Ba) to metal content of 15%. Subsequent carbonization resulted in a 30% yield of C-metal fiber in contrast to conventional carbon yields as low as 10%.

As with polyacrylonitrile, a compendious amount of published work exists on methods of making carbon fibers and textiles from cellulose or rayon precursor materials, and there are hundreds of patents, some of which describe variations in the methods or conditions of heating. Gill[12] summarizes some of the patents. More recently, Schmidt[13] has critically assessed the historical development and decline of rayon-based carbon fibers.

3.3 Pitch

Union Carbide researchers[14] have recently outlined the development of high modulus carbon fibers from pitch precursors. Until recently, high carbon-content polynuclear aromatic pitches had achieved relatively high modulus values, but poor tensile strengths (Table III). The Union Carbide researchers have dramatically increased the properties of pitch-based carbon fibers giving them the potential of possessing properties equivalent to PAN and rayon-based carbon fibers. Their limitations at present include relatively low strength (175–250,000 psi) and uniformity or reproducibility problems—essentially the same problems which occurred in the developmental stages of rayon-and PAN-carbon fibers. One major difference is reflected in a much wider variation in fiber shapes and in a broader distribution of average diameter.

From a raw materials standpoint, special composition of aromatic pitches have been recommended for the development of anisotropy in melt-spun fibers and the derivative carbon fibers.[15] The suitability of commercial pitches appears to be limited to by-products of specific thermal cracking operations for petroleum fractions.

Union Carbide claims its successes are achieved by preparation of highly oriented fibers of "mesophase" pitches, i.e., pitches which incorporate a substantial liquid crystalline phase. The viscoelastic properties of the pitch raw material is one of the most significant parameters in processing.

The Japanese have taken pitch-based carbon fibers to commercial development stages (Table III). Otani and coworkers[16] have conducted studies on carbon fibers produced from pitches which are derived from polyvinyl chloride. Using tension during heat treatment they were able to improve mechanical properties. However, the carbon fibers, unlike those produced by Union Carbide and Hawthorne at the University of British Columbia,[17] were isotropic and, hence, possessed low modulus values.

3.4 Non-heterocyclic aromatic polymers

It would appear that non-heterocyclic aromatic polymers would be the most promising precursors for carbon or graphite fibers. They offer a high capacity for cyclization to form graphitic structures, they have the advantage of high carbon content (so, high carbon yield), they facilitate electron delocalization during free radical rearrangements, and unlike heterocyclic compounds the elimination of non-carbon atoms is not as great a problem. We have seen already that polynuclear aromatic pitches can be formed into graphitic-type high-strength, high-modulus carbon fibers. Table IV lists non-heterocyclic aromatic polymers which have been used as carbon fiber precursors.

Phenolic polymers have been studied rather extensively. "Kynol," the flexible phenolic textile fiber produced by Carborundum, can be treated to produced glassy carbon fibers with little shrinkage and a carbon yield of

TABLE IV

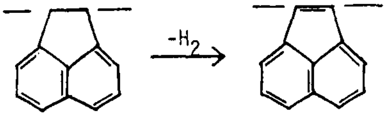
Non-heterocyclic aromatic polymer precursors

Phenolic polymers
Polyacenaphthylene
Polyindene
Poly(2,6-diphenyl-1, 4-phenylene oxide)
Polyamides, aromatic
Polyphenylenes
Polyacetylenes

60%.[18,19] Kawamura and Jenkins[20] produced glassy carbon fibers with an isotropic core surrounded by a highly-oriented sheath, starting with phenolic-hexamine polymers.

Tokai Electrode has also patented a carbon fiber prepared from phenol-formaldehyde resins,[21] as have Haveg Industries,[22] Carborundum,[23] and Coal Industries Ltd.[24] The properties of these fibers are much lower than those required for critical structural composite applications. They are finding use as adsorptive fibers, particularly when surfaces are activated.[25]

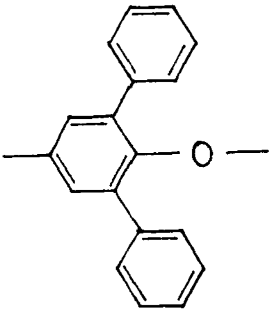
Polyacenaphthylene is a potential precursor for carbon and graphite fibers.



Dehydrogenation can yield a fully aromatic polymer. A general study of the decomposition of this polymer was made in the U.S.S.R.[26] Sumitomo Chemical Co., Ltd. received a patent for the product'on of carbonized films and fibers based on this polymer.[27] The same patent covers the use of *polyindene*, as well. Singer at Union Carbide[28] used acenaphythylene-containing tars to produce pitch-based carbon fibers.

The highly aromatic *polyarylether*, namely poly(2,6-diphenyl-1,4-phenylene oxide), which is produced by General Electric and AKZO, has yielded a carbon fiber after carbonization at over 480°C, and after controlled oxidation in the range, 300–480°C.[29] Good carbon yields are reported.

Ezekiel[30] reported that an experimental, high temperature-resistant *aromatic polyamide* yarn formed graphite fibers after a three-stage process. However, the resultant fibers were of large diameter and were hollow due to insufficient oxidative stabilization stage. He[31] subsequently reported that well-stabilized yarns could undergo direct graphitization at high tension to yield high modulus and high strength yarns. The polyamides were derived



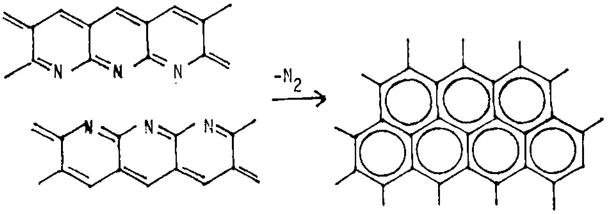
from condensation of arylene diamines and dicarboxylic acids. Structurally, the polyamide had three meta-substituted nuclei per para unit.[32] Hirsch[33] also patented a process for conversion of aromatic polyamides to carbon fibers by reaction of oxidizing vapors from metallic halides and oxyhalides of Group IV, V, VI. Santangelo[34] patented a process for graphitization of fibrous polyamide materials. "Nomex," the first commercially heat-resistant fiber, an aromatic polyamide, was converted to carbon fibers after oxidative stabilization.[35,36] None of these carbon fibers have achieved the mechanical properties of pitch, rayon, or PAN-based products.

Although fibrous precursors can be produced by extrusion of *polyphenylenes*,[37] the low molecular weight, branched nature of these polymers, in addition to residual catalysts, leads to brittle products, albeit of high carbon yield.

Greater success with conjugated hydrocarbon polymers has been achieved by White, Sliva, and other researchers at General Electric. In a series of recent patents, they have described processes for the production of *polyacetylene*, copolymers and terpolymers and plasticized polyacetylene blends, which incorporate arylene substituents, by oxidative coupling polymerization of diethynyl arylene monomers.[38,39] A very interesting continuous method for making polyacetylene fibers which are convertible to high strength carbon fibers is patented.[40,41,42,43] The fiber is heat stabilized at temperatures below 1000°C, resulting in a modulus of $1\text{–}3 \times 10^6$ psi. This stage can be accomplished in air or without oxygen. Subsequent carbonization and graphitization, under tension and in an inert atmosphere, has resulted in carbon fibers with tensile strength of 225,000 to 311,000 psi and a modulus range of $50\text{–}70 \times 10^6$ psi. A strong patent position has been established with the precursor, as well as the resultant carbon products. No public indication has been noted of G.E.'s plans for exploitation of these inventions. Undoubtedly, raw material costs is a dominant factor in the market decision.

3.5 Aromatic heterocyclic polymers

Considerable interest has developed in determining the possible utility of novel high-temperature resistant organic polymers based on aromatic heterocyclic structures as fibrous precursors for carbon fibers. One obvious reason was the structural similarity of many of these polymers to the naphthyridine-type intermediate structure which has been postulated to explain the mechanism of degradation of polyacrylonitrile fibers,[44] e.g.



These polymers which have been used to a fair degree of success in producing carbon fibers are typically comprised of large, relatively inflexible or "stiff," often nearly planar, repeating units. In many cases these units are linked by a single bond, about which rotational isomerization may be possible, or are linked by multiple bonds so that no rotational isomerization is predicted. In the latter case, the overall molecular conformation may be rodlike, as in poly(*p*-phenylene) polymer, or an inflexible coil. While they possess relatively high aromatic contents, they represent essentially linear rather than densely crosslinked polymers like the phenolics, for example. Effectively, they are a variety of linear, double-chain "ladder"-type polymer structure. Like phenolics, and other highly crosslinked polymers, they provide the potential for high carbon yields but without the restriction of highly mitigated molecular motion during pyrolysis. Consequently, more dense, low porosity, less isotropic, potentially anisotropic carbon fibers may be expected. The major obstacle to widespread use has been their high cost and in the case of some aromatic polyheterocycles, they have unique mechanical properties and practical application in their own right without modification. Table V lists such polymers which have been used as carbon precursors.

Ezekiel and Spain[45] first mention that an aromatic *polyimide* may be a useful precursor based on thermal analyses. Later, Ezekiel,[46] without providing an example, makes the claim that polypyromellitimides are represen-

TABLE V

Aromatic heterocyclic polymer precursors

Polyimides, aromatic (PI)
Polybenzimidazoles (PBI)
Polybenzimidazonium salt
Polyoxadiazoles (PODA)
Polythiadiazoles (PTDA)
Polyphenylquinoxaline (PPQ)

tative of nitrogen-containing polycyclic polymers which can be used to manufacture carbon fibers of relatively high modulus and strength. More recently, Bourdeau and Galasso[47] have reported the preparation of carbon ribbon from a polimide precursor. Bruck has discussed the thermal degradation of aromatic polyimides in terms of the production of organic semiconductors.[48]

Polybenzimidazoles were also screened at a relatively early stage.[45] Very high modulus of elasticity carbon fiber was reported to have been produced from direct graphitization of oxidatively stabilized PBI yarn.[31] Stuetz converted PBI fiber in a two stage process: (a) air preoxidation and (b) graphitization in an oxyacetylene flame.[49] Good physical properties were achieved. Another Celanese invention[50] describes the production of large denier carbon fibers from a *polybenzimidazonium salt* which resulted from acid treatment of PBI yarn. Oxidative stabilization, followed by non-oxidative heating to 1000°C gave a fiber containing 90% carbon by weight. Claims for production of high modulus graphite fibers from poly [2,2′-(*m*-phenylene)-5,5′-bibenzimidazole)] are made.[46] In the same patent, it is asserted that *polyoxadiazoles* and *polythiadiazoles* are also convertible to high modulus carbon fibers.

Augl[50] has evaluated *polypheny quinoxaline* fiber as a percursor for high modulus carbon fiber. And in 1972, a patent was issued for a fiber forming graphitic polymer prepared from *tetramino anthraquinone* and *naphtalene*-1, 8,4,5-*diindandione*.[51]

3.6 Linear thermoplastic-type polymers

Polymers which fall in this class had been largely discounted as valid candidates for production of high modulus, high strength carbon fibers since, if they did not depolymerize largely to monomer and low molecular weight volatiles, they were expected to form, at best, isotropic cokes which could not achieve the degree of orientation necessary for high performance in fibers treated to graphitization temperatures. There were exceptions, of course—notably polyacrylonitrile. And there exist related polymers which undergo degradation according to mechanisms similar to that of PAN-fibers. Also, since the discovery that isotropic pitch-based carbon fibers could be converted to high-strength, high-modulus fibers, renewed interest must follow in those polymeric precursors which are capable of mesophase formation. Table VI lists linear thermoplastic-type polymers which have been used as carbon fiber precursors.

TABLE VI

Linear thermoplastic precursors

Polybutadiene (syndiotactic), homo- and copolymers
Polyethylene
Polypropylene
Polyethylene, chlorinated
Polyvinyl chloride
Plyvinyl alcohol
Vinyl chloride-vinyl alcohol copolymers
Polyvinylidene chloride
Polyvinylidine fluoride
Polyvinyl acetate, homo- and copolymers
Polymethyl vinyl ketone
Polyacrylonitrile and derivatives polyvinylamidoxime
Polyacrylacylamidrazones
Polyamides, linear
Polyurethanes

Quite recently, patents have been issued for the production of carbon fibers from fibers composed of polymers and copolymers of *syndiotactic polybutadiene*.[52,53] Moduli of 9×10^6 psi and tensile strength of 125,000 psi have resulted after heating to 1500°C.

Even *polyethylene* fiber has been converted to carbon fibers by heating under oxidative conditions after radiation crosslinking from a Co-60 source. Full carbonization was accomplished in an inert atmosphere.[54] In a pitch-type process, mixtures of hydrocarbon polymers, such as polyethylene and *polypropylene*, and aromatic distillation residues were melt spun after heat treatment to 420°C, oxidized, and carbonized to carbon fibers.[55] A variation of this process used mixtures of polyolefins with non-spinnable, but carbonizable, materials such as starch.[56] *Chlorinated polyethylene* fibers have also been pyrolyzed and graphitized.[57]

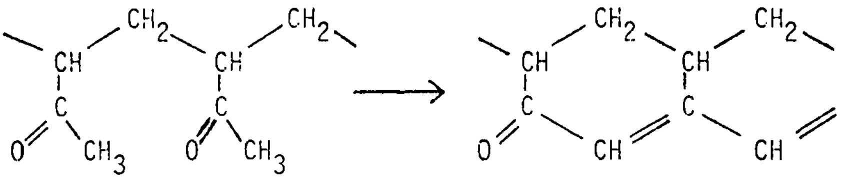
Polyvinyl chloride (PVC) may be pyrolyzed directly under controlled conditions, or, as we have seen, converted to a pitch, melt-spun, and subsequently carbonized and graphitized. *Copolymers* of *polyvinyl chloride* and *vinyl alcohol* have been treated with concentrated sulfuric acid to render the fiber infusible, and then heated to produce carbon fibers.[58] Russian authors describe a process for cyclization and graphitization of polyvinyl chloride fibers.[59]

Oriented *polyvinylidine chloride* fibers have been used to produce carbon fibers after alkylamine dehydrochlorination.[60] Radiative crosslinking and carbonization has also been used.[51]

Polyvinylidine fluoride homopolymers and copolymers have been treated below its melting point with nucleophilic agents such as amines, alkali metals, hydroxides, etc. to induce dehydrofluorination.[61] Catalytic agents are vital since PVDF, unlike PVC or PVDC, is extremely stable at its melting point. The fibers may subsequently be pyrolyzed to yield carbon fibers.

Polyvinyl alcohol and *polyvinyl acetate* were examined quite early in the development of carbon fiber technology. Shindo[62] produced low tensile strength (75,000 psi) carbon fibers with carbon yields of 34%. In recent work, copolymers of polyvinyl alcohol and the ammonium salts of polyphosphoric acid have increased carbon yields dramatically but the resultant carbon fibers are not used for structural applications.[63,64]

Polymethyl vinyl ketone has been spun into fibers, oriented by stretching, cyclized by dehydration, and carbonized in an inert atmosphere.[65] The mechanism is analogous to PAN conversion but resultant properties are low.



Various nitrogen-containing precursors have been used, other than polyacrylonitrile. One variation of polyacrylonitrile has been the chemical conversion of PAN to a *polyvinyl amidoxime* derivative, which is postulated to result in a shorter carbonization time for production of PAN-type carbon fibers.[66] Magre has employed *polyacrylacylamidrazones* as precursors.[67] *Aliphatic polyamides* have also been used.[68] *Polyurethane* resin has been impregnated with furan resin and the composite has been carbonized to give a carbon structure.[69]

4 CONCLUSION

Certain generalities may be drawn, at this stage of study, concerning the potential of various precursors for production of carbon fibers. It appears that the chemical structure of the precursor is quite important. A capacity for cyclization, for ring fusion, and chain coalescense are significant factors in obtaining high carbon yields, whether or not a polymer is thermoplastic or thermosetting. The nature of the degradation mechanism is critical. Internal cyclization type mechanisms (e.g., PAN, polymethylvinyl ketone, etc.) or mesophase-type mechanisms are required.

The initial types of degradative chemical reactions seem to be critical. One looks for, (a) bond cleavage at the most reactive molecular site to produce a free radical intermediate without gross chain scission or "unzipping," (b) rearrangement of radicals to more stable intermediate structures, preferably with induced orientation, (c) polymerization, cyclization, graphite-layer formation with elimination of non-carbon atoms from the structure. Chemical and physical means may be used to control the initial chemical reactions (nucleophilic agents with PVDF, oxidative stabilization of PAN, etc.)

It does appear that orientation during pyrolysis might be more important than the initial orientation of the precursor fiber, contrary to many reports. The uniformity and purity of polymer precursors greatly affects the final properties of the carbon fibers, as well as influencing the mode of degradation and degree of graphitizability. Little work has been done to determine the influence of microstructure of polymeric precursors on the final properties. This factor will certainly influence the rate of intramolecular and intermolecular rearrangements. Similarly, the glass transition temperature of the precursor or its stabilized intermediate form can be a critical parameter in carbonization and graphitization.

In attempting to predict the potential for carbon fiber formation with high mechanical properties, the use of the pyrolysis activation energy, since it relates to the degree of graphitizability, may be a most valuable tool in developing a general theory.[70]

Carbon yields obtained by thermogravimetric analysis is not a reliable predictor of graphite fiber formation.[71] Since aromatic compounds, particularly because of their planarity and electron resonance stabilization, have been shown to be desirable moieties in polymeric precursors, fundamental parameters, such as ionization potential, may be used to correlate thermal reactivity and graphite fiber formation. Flexible chain-type structures, which can adopt "boat" or "chair" configurations, appear to hinder mesophase formation, as do bulky pendant groups except as they may aid in the development of stiff backbones, e.g., poly(2,6-diphenyl-1, 4-phenylene oxide).

In conclusion, it does appear that a substantial body of data exists which is amenable to the development of a general theory for carbon and graphite formation. Research towards this goal could have significant impact on the rapidity with which carbon fibers are produced with wide ranges of engineering applications.

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