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Review
Carbon fibers for composites

S. CHAND
Textile, Retail and Consumer Science, The University of Tennessee, Knoxville, USA
E-mail: subhash_chand@webtv.net

An attempt has been made to review and analyze the developments made during last few decades in the field of high performance carbon fibers. The focus is primarily on high technology sector, which includes aerospace and nuclear engineering or other areas, where the large scale use of carbon fibers is driven by maximum performance and not by cost factors. We have identified and suggested some specific areas for future research in order to minimize the gap between theoretical and practically realized tensile strengths and other mechanical properties of carbon fibers. © *2000 Kluwer Academic Publishers*

1. Introduction

Carbon fibers, which are a new breed of high-strength materials, are mainly used as reinforcements in composite materials such as carbon fiber reinforced plastics, carbon-carbon composite, carbon fiber reinforced materials, and carbon fiber reinforced cement. Carbon fibers offer the highest specific modulus and highest specific strength of all reinforcing fibers. Typical values of tensile properties of different carbon fibers are given in Table I [1]. The fibers do not suffer from stress corrosion or stress rupture failures at room temperatures, as glass and organic polymer fibers do. Especially at high temperatures, the strength and modulus are outstanding compared to other materials [1]. Carbon fiber composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They are also finding applications where high temperature, chemical inertness, and high damping are important. Carbon fibers also have good electrical conductivity, thermal conductivity, and low linear coefficient of thermal expansion [2].

The two main sectors of carbon fiber applications are high technology sector, which includes aerospace and nuclear engineering, and the general engineering and transportation sector, which includes engineering components such as bearings, gears, cams, fan blades, etc., and automobile bodies. However, the requirements of two sectors are fundamentally different. The large scale use of carbon fibers in aircraft and aerospace is driven by maximum performance and fuel efficiency, while the cost factor and the production requirements are not critical. The use of carbon fibers in general engineering and surface transportation is dominated by cost constraints, high production rate requirements, and generally less critical performance needs. This necessitates two different approaches in the areas of production as well as research for two sectors. A number of achievements have been made in the past in the area of cost reduction as well as fiber quality improvement. After all the developments, we have been able to achieve 90–95% of the modulus of perfect graphite ($\approx$1025 GPa), a material with highest absolute and specific modulus of all the materials known [1, 3]. However, carbon fiber in its current strength level range is 15–20 times below the theoretical strength limit. A common rule of thumb is that the strength of a fiber should be about 10% of the modulus of a single crystal. Thus, possible strength for carbon fiber is estimated to be about 100 Gpa. Though the theoretical tensile strength of single crystal of graphite is 150 Gpa [1], highest of all the materials known. Commercial high-strength carbon fibers have a maximum strength of 7 Gpa. Further, axial compressive strength of carbon fibers has been reported to be only 10–60% of their tensile strength [4] and transverse compressive strength 12–20% of axial compressive strength [5]. Compressive strength of carbon fibers is lower than of inorganic fibers but still higher than that of polymeric fibers [6].

Compressive properties dictate the use of carbon composites in many structural applications. Recently, a lot of research has been done on compressive properties and morphology of carbon fibers. Apparently, there still seems to be a lot of room for improvement in the properties of carbon fibers. In this paper, we have discussed the developments made in the past and suggested possibilities for further improvement in the future. Suggestions for future research focus on improvement in the mechanical properties of carbon fibers, as a challenge from the requirements of high technology sector. Increased oxidation resistance at high temperatures is also one of the critical requirements for some high-tech applications [3, 7], but has not been discussed here.

2. Developments in the past

2.1. Historical

Carbon fibers have been made inadvertently from natural cellulosic fibers such as cotton or linen for thousands of years. However, it was Thomas Edison who,

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TABLE I Axial tensile properties of carbon fibers [1]

Precursor	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at break (%)
PAN	2.5–7.0	250–400	0.6–2.5
Mesophase pitch	1.5–3.5	200–800	0.3–0.9
Rayon	≈1.0	≈50	≈2.5

in 1978, purposely took cotton fibers and later, bamboo, and converted them into carbon in his quest for incandescent lamp filaments [1, 8]. Interest in carbon fibers was renewed in late 1950s when synthetic rayons in textile forms were carbonized to produce carbon fibers for high temperature missile applications [9, 10]. The technical and commercial breakthrough for high-performance carbon fibers started in the late 1960s after introduction of the PAN process, which turned out to be more economical due to higher carbon yields, which is 50% against 30% for rayon, and simpler fabrication process [11]. PAN based fibers also had superior physical properties compared to rayon based fibers [3]. PAN fiber is today recognized as the most important and promising precursor for manufacture of high strength carbon fibers. Later carbon fibers were also prepared from pitch, a very cheap precursor. The most commonly used pitches are those obtained from petroleum, asphalt, coal tar, and PVC. The properties of pitch carbon fibers are generally inferior to PAN carbon fibers because, if not specially treated, the pitches are usually isotropic before pyrolysis, and the isotropy is maintained in the fibers unless the orientation of the larger planes is carried out under tension during the high temperature treatment, between 2000 and 3000 °C. Although this process gives the carbon fibers excellent performance properties, it is very expensive [2].

This expensive stretching treatment can be avoided by using mesophase pitches, which are liquid crystalline in nature. The high degree of molecular orientation of as-spun mesophase pitch fibers allows it, unlike PAN, to develop a truly graphitic crystalline structure during the carbonization/graphitization step [3]. Hence ultra high modulus carbon fibers are now produced from mesophase pitches.

2.2. Precursors

Numerous other precursors have been tried to produce carbon fibers. Cellulosic precursor fibers such as cotton, linen, ramie, sisal, heme, and flax, although of considerable historical significance, are no longer an important source of carbon fibers. Polynosic fibers have been suggested, but they do not provide any real advantage over regular rayon fibers [2]. More recent investigations into the production of carbon fibers from cellulosic fibers are concentrated toward modifying the degradation mechanism so that carbon yield can be enhanced. The possibility of converting nonheterocyclic aromatic polymers such as phenolic polymers [9, 10, 12–14], phenol formaldehyde resin [15–17], polyacenaphthalene [18, 19], polyacrylether [20], polyamides [21–24], and polyphenylene [25] into carbon fibers has also been investigated. These substances have several advantages, such as easy cyclization into a graphitic structure, easy elimination of non-carbon atoms, and a greater carbon yield, but no breakthrough in fiber properties has been observed. Some of heterocyclic high temperature-resistant organic polymers such as polyimides [26–28], polybenzimidazole [22, 26], polybenzimidazonium salt [29], polytriadiazoles [30] have been successfully converted into high modulus carbon fibers with unique mechanical properties and a carbon yield of as high as 90% in some cases [29]. The only drawback of these polymers is their high cost. Certain linear thermoplastic polymers such as polyethylene [31], polypropylene [31], polyvinyl chloride [32, 33], polyvinyl alcohol [34, 35], and polyvinylacetate [34] have also been well investigated for their conversion into carbon fibers, but have shown poor mechanical properties and very low carbon yields. Thus three precursors which are being used for large-scale production of carbon fibers are PAN, rayon, and pitches [2]. Other precursors are generally used where mechanical properties are not important.

Regular textile grade PAN contains 15% comonomers. However, the amount of comonomers in PAN used for carbon fibers should be lower than 8% [2]. Commercially available PAN precursors differ appreciably in several of their characteristics, such as molecular weight and its distribution, crystallinity, diameter, molecular orientation, and impurities level [36]. These characteristics can considerably vary the mechanical properties and other properties of the final carbon fibers. This is why many companies prefer to manufacture their own precursors using modified procedures, such as incorporation of certain additives to catalyze the cyclization reaction [37], resin coatings to suppress cylization exothermicity [38], and post-spinning stretching in superheated steam and nitrogen to improve the structure [39, 40]. The spinning and drawing of precursor fibers also play an important role. Modulus and strength of the final carbon fibers have been found to be directly related to stretch-ratio of the precursor [41, 42]. When glycerol was used as drawing medium, the tensile properties were further improved [43]. However, the properties of carbon fibers deteriorated when the draw-ratio was very high. This was attributed to the creation of defects due to over stretching. It has been strongly emphasized that all factors in processing that are bound to induce defects on the fiber surface (e.g. over stretching, the presence of dust etc.) should be avoided at all costs because they strongly influence fiber properties [2]. Based on the fact that carbon fiber properties depend upon precursor properties, efforts have been made to improve the properties of other precursor fibers also [35].

2.3. Processing

A limitation in the conversion of PAN into carbon fibers arises from slow oxidation, which is essential to stabilize the oriented structure and to stabilize the fiber against fusion during the high-temperature treatment. Though there is great uncertainty over pyrolysis and stabilization reactions, stabilization time has

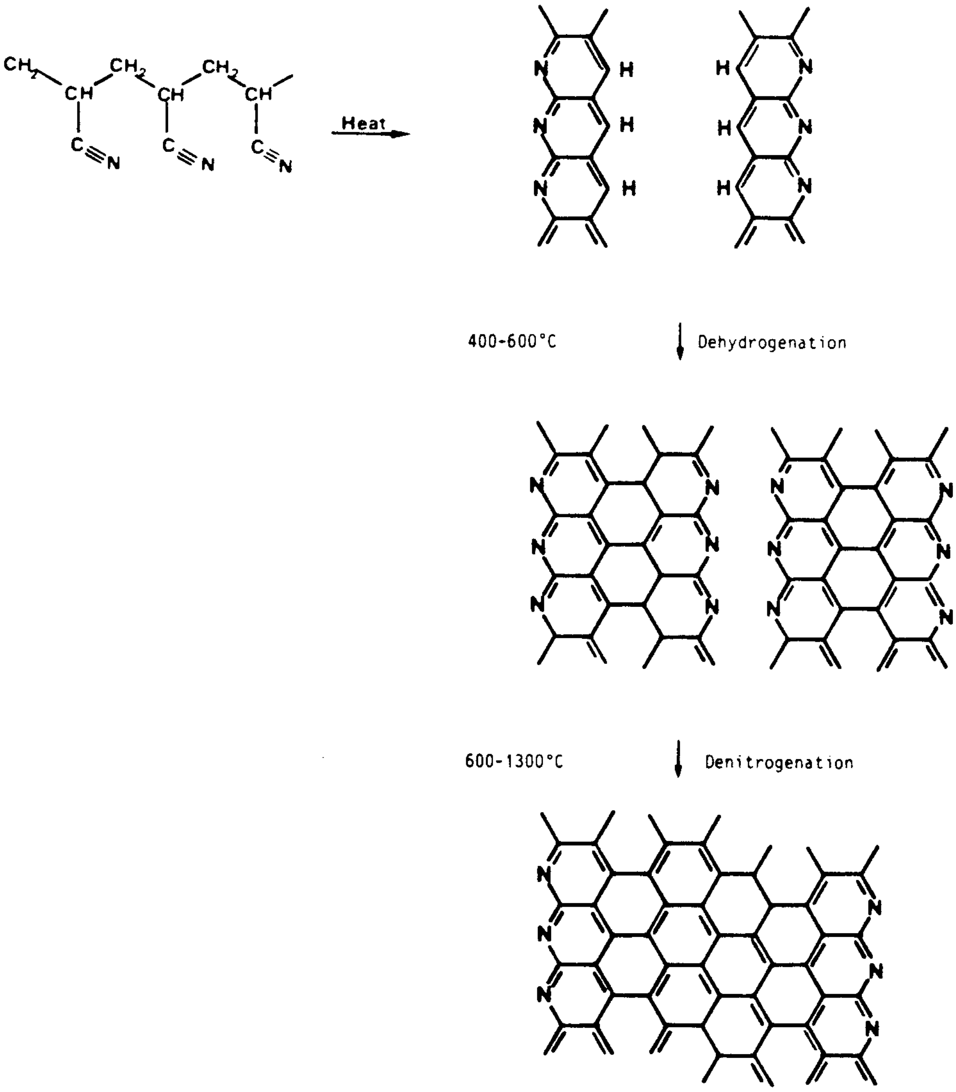

Figure 1 Schematic decomposition of PAN during carbon fiber preparation [2].

been drastically reduced from hours to minutes during last two decades. However, the decomposition of PAN during carbon fiber preparation cab be shown schematically as in Fig. 1 [2]. Grassie and McGuchan [44] observed that stabilization reaction can be initiated by the presence of electrophilic groups, such as acids, in comonomer. Inclusion of comonomers especially methacrylic acid, itaconic acid, and acrylamide into the PAN polymer chain enhanced the rate of degradation. The rate of degradation in the presence of vinyl acetate comonomer, although significantly faster than that of PAN homopolymer, was much slower than in the case of mathacrylic acid and acrylamide [45–47]. These comonomeric initiators also serve to lower the temperature required for stabilization. Lower temperatures result in reduced entropic relaxation of the molecules, which translates to improved tensile properties of the final carbon fibers [48]. When PAN is heated in oxidizing atmosphere, the rate of cyclization is faster and the final carbon product is produced in better yield and with improved mechanical properties. The use of oxidizing agents has also been suggested for the stabilization processes [49–52], but does not seem to be in industrial use. Raskovic and Marinkovic [53], and Raskovic *et al.* [54] investigated the stabilization of PAN fibers by oxidation with SO_2 instead of oxygen or air, and observed that considerable amounts of sulfur are incorporated into the fiber chemical structure, as bridges between the adjacent molecular chains, producing a rigid structure. Thus it has been observed that by combining low-temperature and high-temperature treatment with SO_2, fibers with more cross-linking and a higher initial carbon content can be obtained, which gives rise to carbon fibers with better mechanical properties. Incorporation of certain additives, such as aminosiloxane [55] or cuprous chloride [56, 57], into PAN fibers to catalyze the cyclization process has been reported [37]. Different temperature profiles have also been suggested for faster stabilization [58]. However, Fitzer and Muller [42] suggested that different fibers have different optimum stabilization parameters. Finer fibers are considered more suitable for stabilization [2].

Generally, carbonization is done above 1200 °C in an inert atmosphere. A nitrogen environment is generally used up to 2000 °C and argon is used as inert medium above this temperature because carbon reacts with nitrogen at this temperature to form cyanogen [48]. The carbon fiber yield can be enhanced by carbonizing oxidized PAN fibers in an atmosphere of HCl vapors [59]. Carbonization in HCl vapors decreases the amount of HCN by eliminating nitrogen as ammonia. It also has a marked dehydrating action and eliminates oxygen as water vapor. Consequently, carbon yield increases. There is an increase in the tensile modulus and strength with carbonization temperature. It has been observed that the strength values peak at carbonization temperatures of ≅1700 °C, whereas modulus continues to rise with carbonization/graphitization temperature. It has been felt that increased tension exposure during graphitization generally yields fibers with better mechanical properties using any PAN precursor material [60]. However, this approach has significant process implications and is generally avoided. An optimum tension during stabilization also leads to improvement in mechanical properties of the final fibers [61–63].

The reactions involved in the conversion of cellulose into carbon fibers are shown in Fig. 2 [2]. The yield of carbon fibers from rayon fibers is usualy very low, varying between 10 and 30%. A slow rate of heating results in a higher yield but is less economical. The carbon fiber yield and the processing rate can be markedly improved by carrying out the low-temperature pyrolysis of rayon in presence of reactive atmosphere, such as air or oxygen [64–66], chlorine [67–69], and HCl valor [70, 71]. The presence of a reactive atmosphere promotes dehydration of cellulose and inhibits the formation of tars [69, 70]. It has also been found that the decomposition of cellulose in the presence of flame-retardants occurs at lower temperature, at faster rate, and carbon yield is larger [72]. Rayon fibers are impregnated with flame-retardant substance from aqueous solution before heat treatment. Impregnation leads to more uniform and faster stabilization due to absence of diffusion related problems. The carbonization of rayon

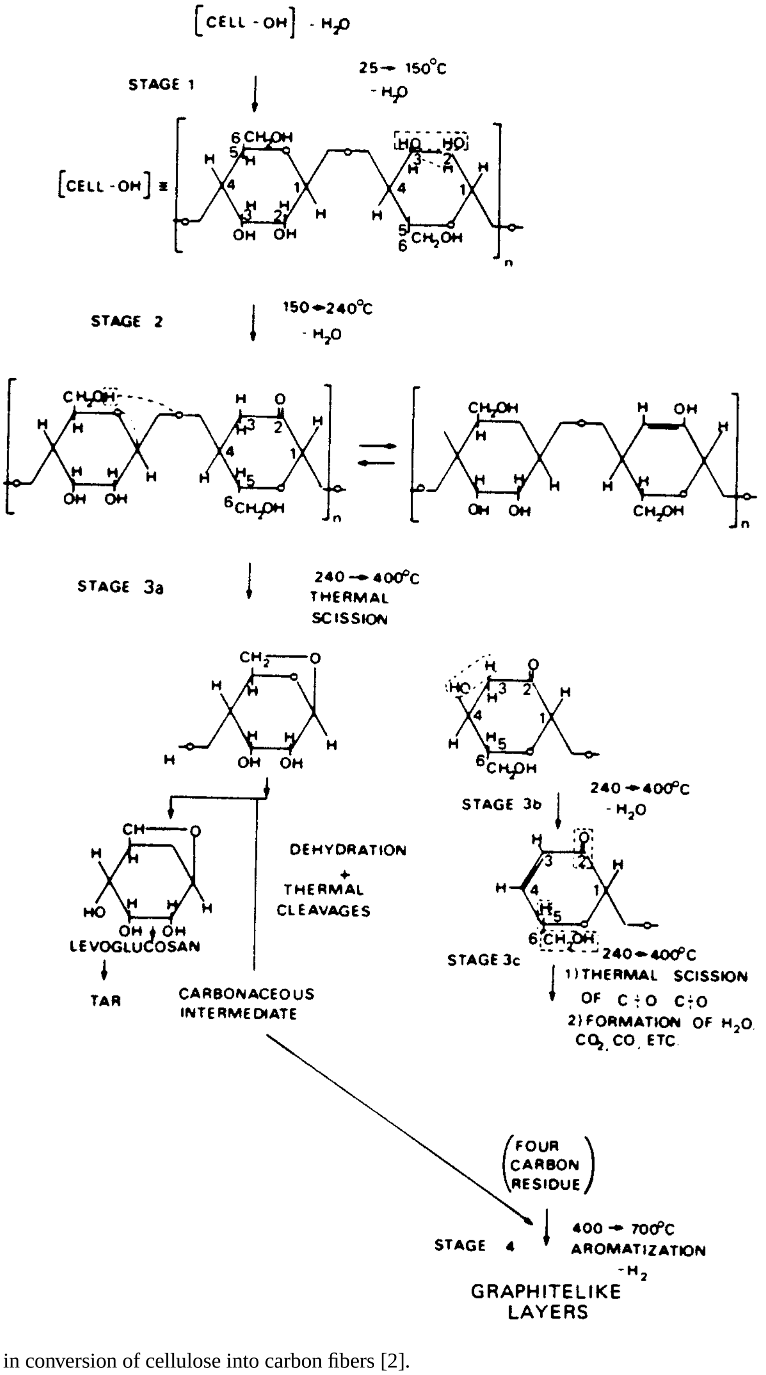

Figure 2 Reactions involved in conversion of cellulose into carbon fibers [2].

fibers is done usually in an inert atmosphere, although the use of reactive atmosphere has been suggested in the literature [70, 71]. Application of tension during carbonization and graphitization improves mechanical properties of the final carbon fibers [73].

Mesophase pitches are thermoplastic and are rendered infusible by a suitable oxidation treatment. As these pitches have higher softening points, the oxidation treatment can be carried out at a higher temperature, where diffusion and oxidation processes are faster. The oxidation is generally carried out in between 250 and 300 °C in electrically heated oven for about 40 minutes [2]. The stabilized mesophase pitch fibers are ready for carbonization and graphitization processes at any temperature, without need of high-temperature stretching. Increasing the final heat treatment temperature results in better mechanical properties of resulting carbon fibers [2].

Carbon fibers when used without surface treatment produce composites with low interlaminar shear strength (ILSS). This has been attributed to weak adhesion and poor bonding between the fiber and matrix [2]. All the carbon fibers are thus given a surface treatment, the exact nature of which is a trade secret. These treatments increase the surface area and surface acidic functional groups and thus improve bonding between the fiber and the resin matrix [74–79]. This tends to increase the wettability of the carbon fiber and enhances the ILSS. Surface treatments may be classified into oxidative and non-oxidative treatments. Oxidation treatments involve gas-phase oxidation, liquid-phase oxidation carried out chemically [80] or electrochemically [81], and catalytic oxidation. The non-oxidative treatments involve deposition of more active forms of carbon, such as the highly effective whiskerization, the deposition of pyrolytic carbon [82, 83], or the grafting of the polymers on the carbon fiber surface [84]. Carbon fibers can also be plasma treated to improve bonding between the fiber and matrix. Liquid phase oxidation treatments are milder, very effective and are preferred [2]. Although whiskerization treatment gives excellent results, it is not commercially used because it is expensive and difficult to carry out precisely. It also needs to be understood that many times a weak interface is desired between fiber and a brittle matrix to improve toughness of the composite [84]. A weak and elastic interface provides better crack resistance [85, 87]. Though, a strong interface between fiber and a ductile matrix results in improvement in tensile strength, compressive strength, and yield strength of the composite [80, 88–90]. Zhu *et al.* [85] overcame this limitation of interface by using bone-shaped fibers with enlarged ends in conjunction with weak interface, in short fiber composites.

2.4. Fiber morphology and mechanical properties

Perfect graphite has three-dimensional periodicity and belongs to the hexagonal crystal system. However, Johnson [91] reported that face centered cubic sequence is also observed. In carbon fibers, within each basal plane of aromatic rings, the carbon atoms are placed on a hexagonal lattice, but the corresponding atoms on an adjacent plane may be translated by an arbitrary displacement. Hence carbon fibers generally have only two-dimensional order referred to as ‘turbostratic’ structure [48]. Inter-plane spacing in carbon fibers, processed even at higher temperatures, is significantly higher than that of perfect graphite. However, many researchers [6, 92–94] have reported evidence of three-dimensional order in certain carbon fibers. Kumar *et al.* [6] have reported that most of PAN based carbon fibers have particulate morphology, whereas pitch based carbon fibers have sheet-like morphology. They also reported that a sheet-like morphology does not necessarily imply a three-dimensional order and, on the other hand, a fiber with particulate morphology can display three-dimensional order. Rayon based fibers show particulate morphology and may have three-dimensional order. Typical scanning electron micrographs of PAN-based, pitch-based, and rayon-based carbon fibers are shown in Figs 3–5 [6], respectively. It has been observed that extensive graphitized small areas do exist even in those fibers which had never been exposed to temperatures beyond 1100 °C [2]. Preferential orientation of graphitic sheets in fiber axial direction increases with heat treatment temperature. Orientation and size of these sheets is greater on the surface than in the interior of a carbon fiber [2, 6]. Modulus of the fibers increases with increase in orientation [2]. Carbon fibers are supposed to have up to 20% voids elongated in fiber axial direction [48]. There is a transition from many small pores to fewer larger pores as heat treatment temperature is increased [2].

PAN based carbon fibers have higher tensile and compressive strength than pitch based carbon fibers, because PAN based fibers have particle-like structure and smaller crystals as compared to sheet-like structure and larger crystals in pitch based fibers [5, 95–98]. The cross-sectional structure of carbon fibers also plays an important role in determining compressive properties of carbon fibers. Endo [99] and Hayes *et al.* [95] studied compressive behavior of two different pitch-based carbon fibers and proposed that fibers with a folded-radial texture show higher compressive strength than fibers with flat-layer structure. The two structures have been reproduced in Fig. 6 [95]. Knibbs [100] identified three different types of structures for PAN carbon fibers prepared under different processing conditions. The three structures are schematically represented in Fig. 7 [2]. Transverse structure of the final carbon fibers depends very much upon the type of spinning process used, temperature of spinning, the shape of spinneret, the use of stirrer and its shape [2, 101]. However, the structure is independent of heat treatment temperature [2].

It has been found that compressive strength increase with decrease in crystallite size, orientation, density, and with increase in inter-planar spacing and void content [102–105]. Crystal anisotropy, as measured by $L_c L_b / L_a$, where L_a, L_b, L_c are crystal sizes parallel to fiber axis in graphitic plane, perpendicular to fiber axis in graphitic plane, and perpendicular to graphitic plane,

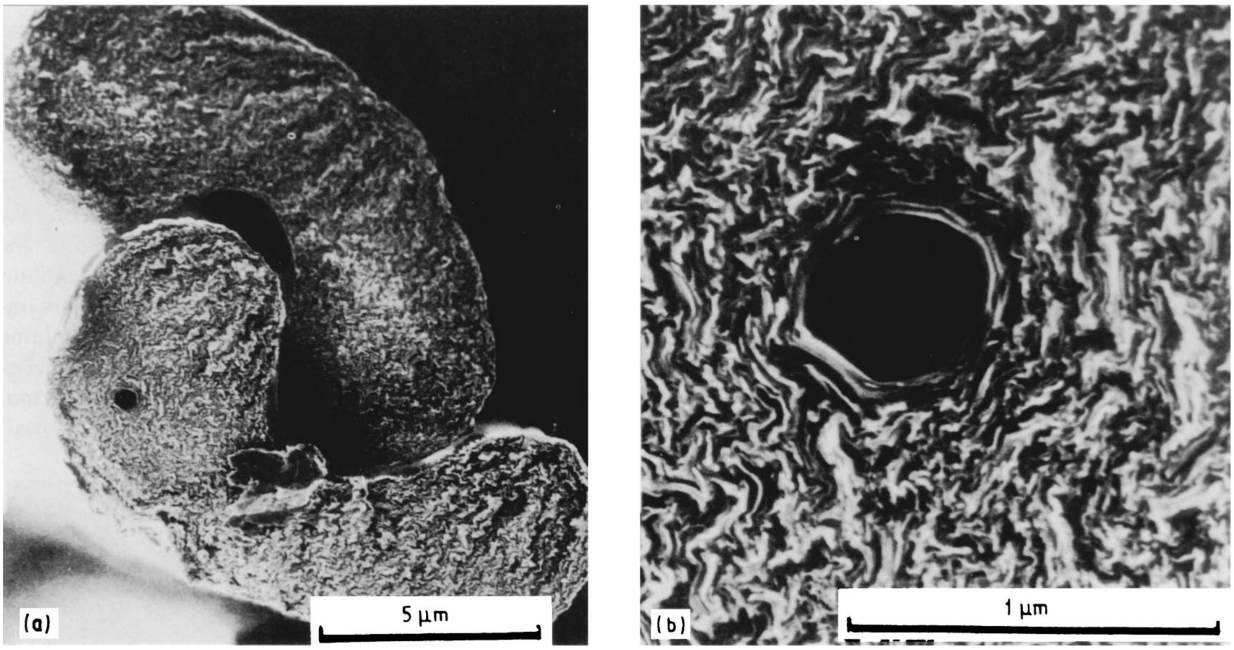

Figure 3 Scanning electron micrographs of PAN-based carbon fibers [6]: (a) low and (b) high magnification.

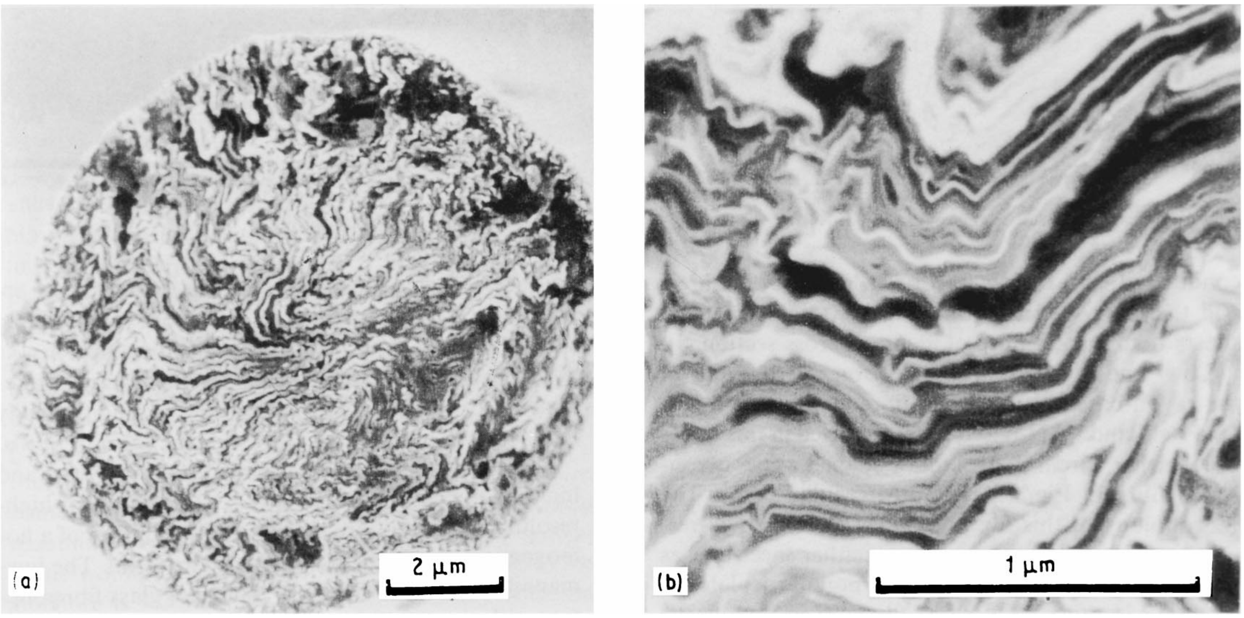

Figure 4 Scanning electron micrographs of pitch-based carbon fibers [6]: (a) low and (b) high magnification.

respectively, provides the best correlation so far with carbon fiber compressive strength [6]. Compressive strength of the fibers has been found to decrease with increase in modulus for both pitch and PAN based fibers [6, 95]. Though, up to a carbonization temperature of 1500 °C, compressive strength, tensile strength, and tensile modulus show similar tendency [106]. For both pitch and PAN based fibers, the same modulus fibers can have different compressive strengths [6]. For a given modulus compressive strength may be improved if desired orientation may be achieved along with smaller crystal size. High-modulus fibers fail in shear mode while low-modulus fibers fail in buckling mode [6, 95]. With boron-ion implantation, the carbon fiber compressive strength and torsional modulus increased by up to 25% and 50%, respectively, while the crystal size decreased [107]. Compressive strength is considered to be well related to shear modulus between the basal planes [97, 98]. Surface and sizing treatments are usually necessary to realize higher compressive strengths in carbon fiber composites [108, 109]. However, it has been observed that surface and sizing treatments are more effective in tension than in compression, whereas the effect of fiber morphology is more prominent in compression than in tension [110, 111]. Miwa *et al.* [112] studied the effect of fiber diameter on compressive strength of the fibers and reported that compressive strength increases with decreasing diameter but remains almost unchanged at a diameter range smaller than 10 μm. This improvement may be due to statistically less number of flaws and more uniform structure in smaller diameter fibers [87].

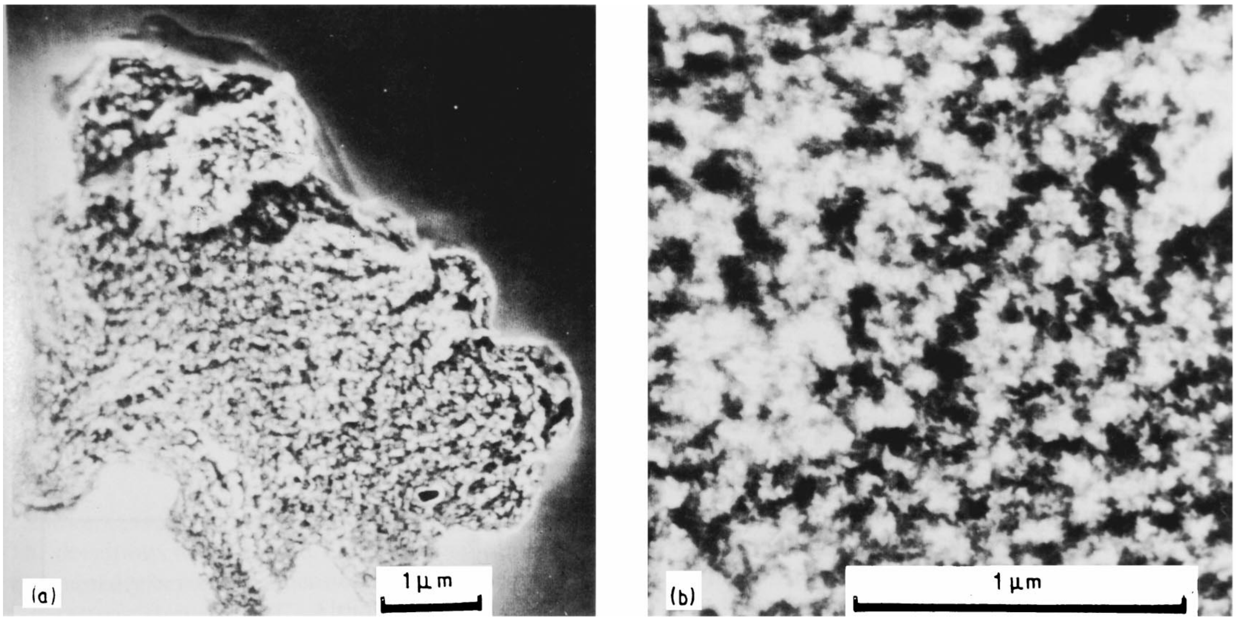

Figure 5 Scanning electron micrographs of rayon-based carbon fibers [6]: (a) low and (b) high magnification.

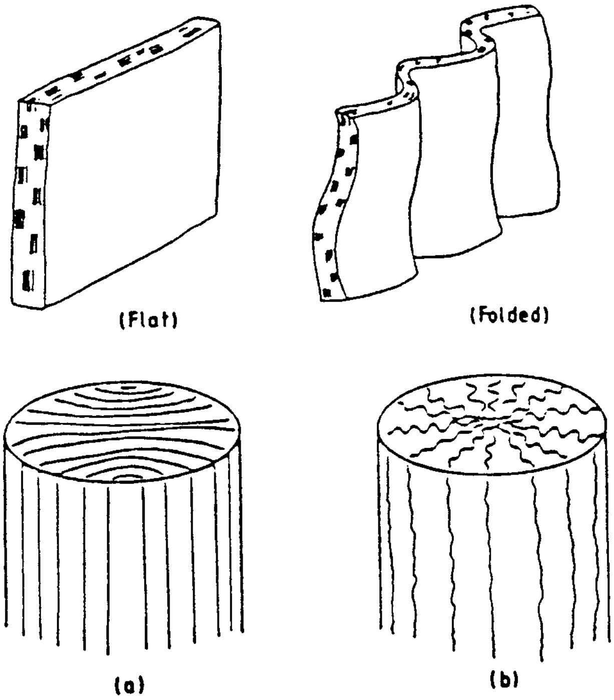

Figure 6 Endo's proposed structure for two different pitch-based carbon fibres [95].

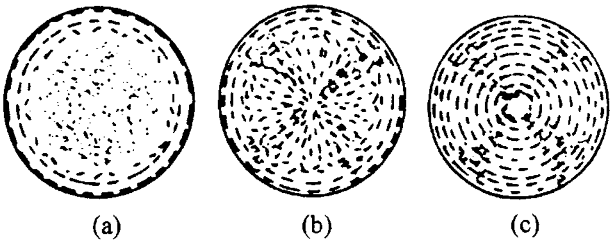

Figure 7 Knibbs' identified three different types of structures for PAN-based carbon fibers prepared under different processing conditions [2].

3. Possibilities for the future

Several mechanisms have been proposed to explain the tensile failure of carbon fibers [48]. Cooper and Mayer [113] proposed that dislocations accumulate at the crystallite boundaries and eventually form a crack. Williams *et al.* [114] suggested a similar scheme of build-up of dislocations followed by plastic yielding. Stresses on the curved surfaces of the ribbons of graphite planes [115], the presence of three dimensional graphite [116], and plastic deformation at crystallite boundaries [117] are other explanations that have been offered for the fracture for the fracture of carbon fibers. Elongated micro-voids may not be that detrimental because they also act as a buffer preventing propagation of a crack [118]. Poor compressive properties of carbon fibers have been attributed to ease of shear between basal planes. Immaterial of failure mechanisms, now it is almost certain that only a carbon fiber having minimal defects, high connectivity between the graphitic planes, and high connectivity between the crystallites could bridge the gap between theoretical and practically realized tensile strengths and also improve compressive strength of carbon fibers. The removal of surface flaws by oxidative etching [119, 120], acid etching [121], and electrolytic etching [122]; filling of holes and pits by pyrolysing a hydrocarbon [48]; and pinning of the dislocations by neutron irradiation [123, 124] have been tried and have led to some improvement in strength. But no breakthrough has been observed so far.

It has been felt that atacticity of PAN [125] is one of the important factors contributing to the defects in carbon fiber [48, 126, 127]. So far no efforts have been on this aspect in manufacture of carbon fibers. PAN with high degree of isotacticity was first prepared by canal polymerization of acrylonitrile with urea through γ irradiation [128–130]. Anionic polymerization also affords a possible and not so expensive route for the production of stereoregular polymers by nature of counter ion structure forming in its propagating end. Very recently anionic synthesis method using organomagnesium compounds has proved to give PAN with high degree of isotacticity [126, 131–135]. However, in order to obtain high molecular weight PAN with high yield, it is necessary to polymerize under strictly limited conditions [132]. This may be one reason why the anionic polymerization of acrylonitrile has not been utilized commercially. Another possible reason is that the need for isotactic PAN has not been strongly realized. However, there was also a recent patent stating the preparation of isotactic polymer using compounds of metal and sulfur as catalyst [136]. The polymer was subsequently solution spun into fibers. Fiber formation from isotactic PAN should not be a problem because Isotactic PAN has been found to dissolve in DMF and other polar solvents, though at relatively higher temperatures [128]. Thus, it seems essential to explore this possibility of production of carbon fibers from isotactic PAN and go further to improve the whole process of polymerization and fiber formation, if any encouraging results are observed.

Many researchers [11, 97, 137] have reported the presence of presence of sp^3 bonding (–C–C–) in carbon fibers. According to some researchers [97, 137], sp^3 crosslinks between the basal planes are one of the important factors governing compressive properties of carbon fibers. There is no doubt in that improved connectivity between the planes and crystallites would lead to improvement in mechanical properties of carbon fibers. Introduction of diamond-like sp^3 bonding sequences in to fiber structure may be one of good ways to improve desired connectivity in the structure. Both graphite and diamond are two very stable forms of carbon [138]. Graphite is thermodynamically more stable than diamond at room temperature and pressure, whereas diamond is thermodynamically more stable at very high pressure [101, 139]. Large activation energies are required to disrupt either of these crystalline forms after they are established. Unsuccessful early attempts for direct graphite-to-diamond transformation by heat and pressure alone emphasized this point. In 1983, Fedoseev and Derjaguin [140, 141] reported a radically different and incredibly simple method of diamond synthesis. This technique involved exposure of carbon black, in air, to a modest carbon dioxide laser flux in a continuous wave mode. This technique was later confirmed by Alam *et al*. [142]. The basic structure of carbon black is not far different from carbon fibers, only difference being in order and inter-plane spacing [143]. Thus, this method may be explored to partly introduce diamond-like structure in to carbon fibers by converting non-graphitized parts of carbon fibers to diamond. Proportion of graphitic and diamond-like structure may be optimized by proper sequencing of carbonization, graphitization, and diamond forming step. A well-connected composite-like structure, thus achieved, of graphite and diamond should provide excellent mechanical properties to carbon fibers. Diamond has much higher compressive strength (14 GPa) than graphite (105 MPa) and tensile modulus second to graphite [1, 6]. However, It needs to be added here that ‘pure’ diamond fibers, which can be produced by chemical vapor deposition (CVD), may not be of much interest in terms of their mechanical properties due to much lower modulus of diamond ($\approx$20 GPa) as compared to that of graphite ($\approx$1000 GPa) [1].

The presence of highly oriented and larger crystals on the fiber surface makes the fibers more prone to propagation of a crack. Therefore, it is desirable to have a thin isotropic layer having smaller crystals on the fiber surface. This may be possibly achieved in the case of pitch based fibers by making use of bicomponent technology in melt spinning. Core will be spun from mesophase pitch, and sheath from isotropic pitch. However, it needs to be emphasized that melt spinning of mesophase pitch is itself a difficult process [2] and, therefore, further addition of bicomponent technology would make it even a more complex process.

It has been well understood in all branches of materials science that needle-like crystals [6, 144, 145] provide high strength and toughness to the material. The crystal size, shape, and their distribution in a carbon fiber may depend on precursor composition, precursor morphology and processing conditions. Not enough work has been done to understand the relationship between these. Among few important things to be explored are effect of comonomer type and its percentage, stereoregularity of the polymer, and impurities on both structure and properties of carbon fibers. So far role of comonomer has been focussed mainly as to reduce stabilization time [2]. However, distribution of comonomer units in the fiber, which work as initiating species for ladder structure, will depend on reactivity ratios of monomers [146] and concentration of the comonomer. Concentration and distribution of these initiating species may play an important role in governing the structure of the final carbon fibers. There also exists a critical comonomer level, which is very much different for different comonomers, above which the characteristic PAN morphology begins to rapidly disappear [146]. The level of comonomer should be below this critical level, for PAN precursor fibers. Stereoregularity of the polymer and level of impurities must greatly affect the level of perfection achieved in the structure of carbon fibers. The level of perfection in the structure may be further improved by controlling diffusion of pyrolysis gases, especially keeping in mind that these gases have enough solubility in the polymer [147] and thus may impair cyclization process. Uniformity of the structure, which demands more uniform stabilization and use of smaller diameter or hollow fibers, has also been emphasized by many researchers [3, 148].

There is need of renewed focus on development of new precursors for carbon fibers. Although chemistry of pyrolysis is very complex, but still some clues about a possible good precursor have been established in the past. These may be summarized as under:

1. Precursor should have a higher carbon content [3], such as polyphenylene.
2. Precursor should be high temperature resistant [2], and therefore preferably an aromatic heterocyclic polymer.
3. There should be no more than one carbon atom between aromatic rings [33].

4. Precursor molecules should have high degree of order, orientation and flatness [149, 150].

5. Simple release of non-carbon atoms and easy cyclization [48, 149]; e.g., nitrogen and oxygen atoms should be a part of side groups rather than of main chain.

6. Precursor should have a high molecular weight [33].

It has been emphasized that any significant improvement is most likely to be led by synthesis of new precursor materials that can cause increase in lateral –C–C– bonding sequences while maintaining a high axial orientational order in the carbon fibers [151].

4. Concluding remarks

A considerable progress has been made in the past in establishing the fundamental material-process interactions in the field of high performance carbon fibers. However, a significant degree of discrepancy still exists especially with regard to tensile and compressive strengths of carbon fibers. There is need of a different and more comprehensive approach for the development of carbon fibers used in high technology sector. Based upon our current knowledge of the process and related topics, suggestions made in the paper for future research seem to be very much plausible. Therefore, integrated efforts may be made in these and other possible directions in order to reduce the existing gap between theoretical and practically realized tensile strengths, and also improve compressive behavior of carbon fibers.

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