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Chapter

Vapor-Grown Carbon Fiber Synthesis, Properties, and Applications

J. Manivannan, S. Kalaiselvan and R. Padmavathi

Abstract

Carbon nanofibers are promising to revolutionize several fields in material science and are suggested to open the way into nanotechnology. Carbon fiber has become an important reinforcement material in composite materials and battery technology because of its low density, high strength, and tensile modulus. Furthermore, high electrical conductivity, thermal conductivity, and mechanical properties of carbon fiber make it useful in a wide variety of products. This chapter highlighting the synthesis and growth pattern of vapor grown carbon fiber (VGCFs). This chapter work reported here includes the application of VGCFs in composite and battery technology.

Keywords: VGCFs, composites, PAN, epoxy, polycarbonate, floating reactor

1. Introduction

Carbon nanofibers are linear filaments with diameter of 100 nm that are characterized by flexibility and their aspect ratio above 100. Materials as fiber are of extraordinary viable and scientific significance. The blend of high specific area, flexibility and high mechanical strength permit nanofibers to be utilized in our everyday life in addition creating arduous composites for vehicles and aviation. Be that as it may, they ought to be discriminated from conventional carbon fibers [1–3] in their small diameter (**Figure 1**). Conventional carbon fibers have a few micrometer-sized diameters.

Likewise, they are not quite the same as notable carbon nanotubes [5–9]. Carbon nanofibers could be developed by passing carbon feedstock nanosize estimated metal particles at high temperature [5, 10–15], which is fundamentally the same as the development state of carbon nanotubes.

Such a unique structure renders them to show semi-conducting behavior [16] and to have chemically active end planes on both the inner and outer surfaces of the nanofibers, thereby making them useful as supporting materials for catalysts [17], reinforcing fillers in polymeric composites [18], hybrid type filler in carbon fiber reinforced plastics [19–21], and photocurrent generators in photochemical cells [22, 23].

Though, their geometry is not quite the same as concentric carbon nanotubes containing a whole empty core, since they can be pictured as normally stacked shortened conical or planar layers along the filament length [24–27]. Such a one of a kind
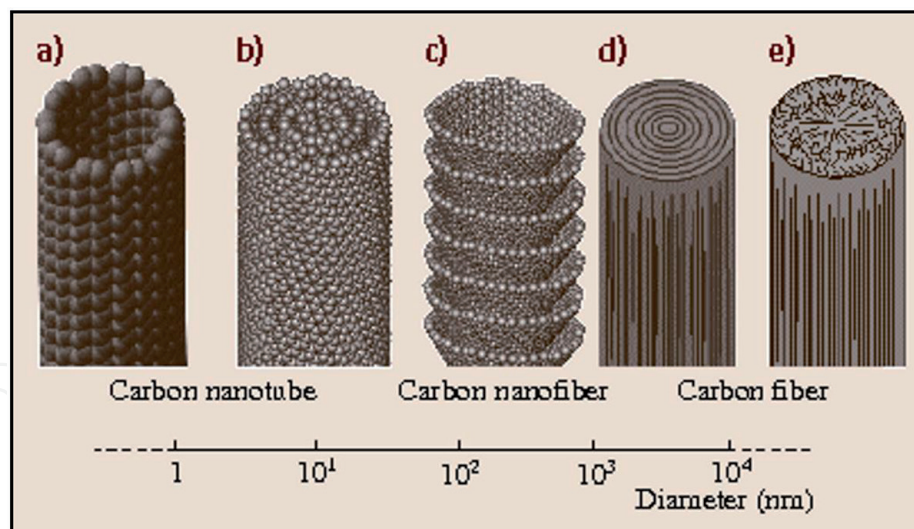
Figure 1.
Schematic comparison of the diameter dimensions for various types of fibrous carbons [4].

structure renders them to show semi- conducting behavior [16] and to have synthetically dynamic end planes on both the inner and outer surfaces of the nanofibers, in this way making them helpful as supporting materials for catalysts [17], reinforcing fillers in polymeric composites [18], hybrid type filler in carbon fiber reinforced plastics [19–21], and photocurrent generators in photochemical cells [22, 23].

2. Synthesis and properties of carbon fibers

Since the temperature and pressure essential to synthesize a carbon fiber from the fluid stage is at the triple point (Temperature—4100 K, Pressure—123 kbar), it would be practically difficult to get ready carbon fibers from the liquefy under modern preparing conditions. As a result, carbon fibers are arranged from organic precursors. This preparation is commonly done in three stages, including stabilization of a precursor fiber in air (at 300°C), carbonization at 1100°C, and subsequent graphitization (> 2500°C). Fibers undergoing only the first two steps are commonly called carbon fibers, while fibers undergoing all three steps are called graphite fibers.

Carbon fibers are commonly utilized for their high strength, while graphite fibers are utilized for their high modulus. Graphitic whiskers were developed under conditions close to the triple point of graphite. At that point, the structural model was proposed, in which the layers comprising of graphene sheets are twisted around the axis like as in rolling up a carpet. These whiskers were utilized as the presentation focus in the beginning times of carbon fiber technology, despite the fact that they have never been manufactured on a large scale.

Carbon fibers are

1. High-strength polyacrylonitrile (PAN)-based fiber

2. A high-modulus PAN-based fiber

3. A mesophase pitch-based carbon fiber (MPCF).

The PAN-based fibers comprise of little sp^2-carbon structural units specially lined up with the carbon hexagonal portions corresponding to the fiber axis. This orientation is liable for the tensile strength of PAN-based carbon fibers [28].

By shifting the preparing conditions (e.g., oxidation conditions, choosing of precursor material, and particularly by increasing the heat treatment temperature) of PAN fibers, a better arrangement of the graphene layers can be accomplished, thus leading to stiffer, higher-modulus PAN fibers, however with lower strength [29]. PAN-based fibers are one of the distinctive hard carbons.

MPCFs comprise of perfectly-aligned graphitic layers equivalent to the corresponding fiber axis, and this high level of favored direction is liable for their high modulus or stiffness just as their high graphitizability. The structures depicted above suggest ascent to various physical properties, although each kind of fiber highlights carbon hexagonal systems, having the sturdiest covalent bonds in nature (C—C bonds). These sturdy interatomic bonds lie in sheets basically corresponding to the fiber axis, and are liable for the high mechanical performance of these carbon fibers.

3. Vapor-grown carbon fibers

PAN- based fibers have high strength and MPCFs have high modulus, while VGCFs afford fundamentally ultra-high modulus materials. VGCFs have an extremely unique structure like annular-rings and are prepared by something diverse arrangement process than that used to prepare PAN-based and MPCFs. Specifically, VGCFs are not prepared from a fibrous precursor, but instead from hydrocarbon gas, utilizing a catalytic growth process [5, 11–15]. Ultrafine transition metal particles, for example, iron particles with diameter under 10 nm, are scattered on a ceramic substrate, and a hydrocarbon, for example, benzene diluted with hydrogen gas is introduced at temperatures of around 1100°C. Hydrocarbon decomposition happens on the catalytic particle, showing a ceaseless carbon take-up by the catalytic particle and a persistent output by the particle of efficient tubular filaments of hexagonal sp^2 carbon. The swift development rate which is 106 times quicker than that analyzed for the development of normal metal whiskers [30], permits the production of commercially suitable amounts of VGCFs.

4. Vapor grown carbon Fiber growth

While portraying the production of VGCF, two distinct strategies can be discriminated. In the primary strategy, the fibers are manufactured on catalyst-seeded substrates, in two independent consecutive stages. In the first stage, the impetus molecule, for the most part with iron being the prevalent constituent, starts a long, thin, somewhat graphitic fiber when presented to a hydrocarbon gas close or more 1000°C.

A petite fraction of these fibers grows to macroscopic lengths when exhibited to a low carburizing potential gas, while keeping up the outside diameter of the initial catalytic particle. The sizes of these particles, and subsequently the filament diameter, have been considered from 10 to 200 nm [31–33]. The development of the filament may extend as quickly as 1 mm/min and persevering for a few minutes until the catalytic particle is deactivated [33]. At this stage filament lengths of a few centimeters might be acquired.

In the second stage, when the gas potential is increased, the filament thickens because of the deposition of pyrolytic carbon. Fibers with diameters up to 100 nm have been produced in batch conditions by this method. Pyrolytic carbon is deposited with the basal planes specially arranged corresponding to the surface, the properties of the fiber are moderately graphitic [34].

Methane, hydrogen and an inert gas are utilized to develop the fibers at atmospheric pressures on nesting cylindrical substrates inside a growth tube. Lower centralizations of the methane-hydrogen blends are utilized for fiber extending, though higher concentrations are utilized for thickening. As methane is an economical feedstock in certain parts of the world, the production of VGCFs can turn out to be exceptionally financial contrasted with other carbon filaments.

5. Mass production of vapor-grown carbon nanofibers (VGCFs)

On account of their unique properties, for example, high strength and electric conductivity and special functional properties, researchers have indicated a lot of consideration for the large scale manufacturing of these materials.

1. The physical properties of vapor grown carbon fibers, with littler diameters across ought to be more grounded than those with larger diameters fume developed carbon filaments and exploratory outcomes demonstrated this expectation.

2. Furthermore, it was accounted for that the distance across of the nanofibers is represented by the size of the impetus particles.

3. For the large scale manufacturing of VGCFs the key procedure is the seeding of the impetus particles. VGCFs with distances across of 50–100 nm was created effectively utilizing a blend of ferrocene and fluid hydrocarbon in a vertical heater. The outcomes show that this strategy gives the chance of large scale manufacturing. Be that as it may, in view of the trouble of proficiently scattering little Fe particles in showering impetus arrangement, vague blends of filaments and residue were constantly gotten.

Carbon nanofibers were manufactured with diameters of 50–80 nm from catalytic decomposition of hydrocarbon gas with catalyst metal powder utilizing the support catalyst method. In spite of the fact that the support catalyst technique can create high quality fibers, the preparation and defined scattering of ultrafine catalyst particles are very difficult and are exceptionally troublesome, the yield of this strategy is spendthrift to be in any way marketed. So as to tackle the above issues the floating catalyst technique was created with the help of support catalyst to deliver carbon nanofibers with diameter of 50–100 nm.

6. Vapor grown carbon nanofiber by floating reactor method

Vapor-grown carbon fibers (VGCFs) have been developed by the deterioration of hydrocarbons, for example, benzene and methane, utilizing transition metal particles as a catalyst at a development temperature of 1000–1300°C [31–35]. These fibers have been portrayed regarding the profoundly favored orientation of their graphitic basal planes corresponding to the fiber pivot, with an annular ring surface in the cross segment. This structure offers ascend to amazing mechanical properties, high electrical and thermal conductivity, and a high graphitizability of the fibers [32, 33]. In this way, numerous scientists have attempted to arrive at the last objective of large scale manufacturing of these fibers filaments with ease.

Among the different preparing techniques, the most significant one has been the advancement of the floating reactant technique [36, 37], which permits a

three-dimensional scattering of the hydrocarbon together with the catalytic particles got from the pyrolysis of organometallic compounds, for example, ferrocene, in a reaction chamber, ensuing about a high yield and a fairly uniform diameter across of the resulting fibers. Thus, the floating reactant strategy is believed to be a promising method for the large scale manufacturing of carbon fibers at generally economical.

7. Fiber morphology

Because of their production method, VGCFs arrive in an assortment of morphologies that are fundamental to understand their properties. A few unique morphologies have been accounted in the literature [38]. Somewhat, these morphologies emulate the internal structure of the fiber. The structure of VGCFs looks like that of a tree trunk, with concentric annular rings. The original filament lies in the middle of axis of symmetry. The layers are in part aligned turbostratic carbon, with the average basal plane skewed from the fiber axis by around 10–15° [30]. In thinner fibers, or in fibers submitted to high temperature heat-treatments, cracks are observed between consecutive rings, and the external surfaces are often crenulated. Cracks are seen between consecutive rings when thinner fibers, or in fibers exposed to high temperature, and the external surfaces are frequently crenulated.

When the pyrolytic carbon is subjected to cooling, it shrinks more quickly in the radial than in the tangential direction. The ensuing radial stress (tension) will be reduced if circumferential cracking between the rings happens. Then again, the contraction in the tangential direction prompts a high compressive pressure that can be halfway eased by the formation of the crenulations.

The uniform geometry and the basically carbon structure of the VGCFs makes the fibers very graphitizable. Swift graphitization increased with increased temperatures [28]. Above 2600°C, VGCFs structure moves toward like a single crystal graphite structure. Evidently, this property will let improvement to a specific level, tailoring of the fiber properties to preferred values. In recent years, a widen interest has been appeared in the surface properties of VGCFs, as this can be identified with the interfacial properties of the fiber in composites. It was pointed out that the surface reactivity of VGCFs is lower than that of ex-pitch or ex-PAN carbon fibers [39]. On the other hand, the surface reactivity can be increased by oxidation treatment to be nearer to that of the other carbon fibers.

The effect of diverse oxidative surface treatments (nitric acid, plasma, air and carbon dioxide) on the fibers surface reactivity has been studied [30].

It was observed that, surface oxidation of carbon fibers is the standard innovation to increase adhesion between fiber and matrix, air and carbon dioxide treatments do not fundamentally expand the fiber's surface reactivity, in spite of extensive weight reduction. This was ascribed to the presence of traces of iron left on the VGCF from the growth stages, that may have catalyzed carbon gasification by a pitting mechanism [40].

Cleansing of the VGCFs with HCl to remove the iron can prevent this behavior. Although nitric acid and plasma treatments were found to increase surface reactivity without altering significantly the morphology of the fibers, the latter appeared to be more favorable in improving the adhesion of VGCFs to a matrix.

To expel the iron, VGCFs is cleaned with HCl can obviate this behavior. Though nitric acid and plasma treatments were found to increase surface reactivity without changing fundamentally the morphology of the fibers, the latter gave off an impression of being progressively great in improving the adhesion of VGCFs to a network.

8. Properties of VGCFs

8.1 Mechanical properties

The modulus and the elasticity of VGCFs can be found easily [34]. The calculated modulus value varies from 100 to over 1000 GPa. The stiffness of VGCF depends upon their diameters. Even though the fibers are produced in the same experiment the diameters increased from 6 to 32 nm, the modulus decreases 300–1200GPa [33, 34].

The degree of favored orientation of graphitic basal planes is related to the stiffness of pyrolytic carbon. The stiffness of a graphite fiber is connected as a component of the orientation point of the graphitic plane. This model was fitted to the stiffness-data of VGCFs by measuring their orientation parameter. This model was fitted to the solidness information of VGCFs by estimating their direction parameter. As the main fitting parameter utilized in the model is free of fiber diameter, the dwindle in the solidness of thicker fibers was assigned to the decrease in their graphitic requesting.

This again is because of a swifter deposition of pyrolytic carbon during the thickening period. This is as per the finding that that increasing the graphitization of VGCF by heat-treatment also additionally increases their modulus considerably. In one example, the modulus of vapor grown fibers more than doubled to about 500 GPa when they were heated at 2200°C [30].

Heat-treated fibers are unsuccessful more commonly in the "sword-in-sheath" mode and in this mode; grouping of circumferential breaks along the internal rings permits continuous cylinders to slide telescopically inside one another, slowly diminishing the load bearing limit of the fiber. It is obvious from these outcomes that the modulus and the disappointment method of vapor grown carbon fibers are connected to their structure.

The values of the tensile strength of VGCF are progressively reliable, changing from 2.5 to 3.5 GPa for fibers with diameters across just beneath 10 µm. The reliance on the diameter however is strong [33, 34, 41]. This was clarified by accepting that thicker fibers have a larger flaws population, and a more prominent likelihood of failure, than thinner ones.

8.2 Electrical properties

The carbon structure and potential graphitization of VGCFs by heat-treatment makes them a fascinating possibility for thermal and electrical applications. VGCFs are known to have the most noteworthy electrical and thermal conductivities among carbon fibers because of their conceivable high structural perfection [42].

It was verified that VGCFs heat-treated at lower temperature have a resistivity that is practically constant with temperature. The resistivity of fibers heat-treated at higher temperatures decreases with the operating temperature. At the most elevated temperatures, the resistivity of the VGCFs approaches that of single crystal graphite, with a resistivity of about 5×10^{-7} ohm cm at 300 K. Besides, the decrease in resistivity with fiber diameter across is ascribed to the expanded arranged graphite regions as the diameter increases.

8.3 Thermal properties

The thermal conductivity of VGCFs is astoundingly high [31]. The thermal conductivity of both s-grown VGCFs and the other VGCFs heat-treated to 3000°C were evaluated through a temperature range of 10–300 K. It was demonstrated that

the heat treatment expands the fiber conductivity by a factor of 50. The heat-treated fibers rank among the best thermal conductors available, at room temperature.

Besides, it was demonstrated an immediate connection between electrical resistivity, thermal conductivity and tensile modulus of carbon fibers. The strong correlation between thermal conductivity and electrical resistivity was elucidated by comparative fiber structural effects dominating these properties. This, in blend with the recently pointed out connection between fiber structure and tensile modulus [34], could prompt the expectation of the properties legitimately from fiber structural considerations.

9. Applications of VGCFs

9.1 In composites

In recent times, there has been a developing enthusiasm for the utilizations of VGCF in carbon and polymer matrix composites. The primary thermoplastic submicron-size VGCF composites, utilizing polycarbonate and nylon as a matrix was reported [36]. The growing mechanical and thermal properties were calculated with fiber volume fraction, despite the fact that this increase is less than could be theoretically expected. The composites were compression molded utilizing a straightforward set-up bringing about a fiber arrangement that was believed to be irregular in three dimensions. It was anticipated higher properties if a process like injection molding was utilized to stimulate fiber alignment.

The process ability of submicron VGCFs in thermoplastic matrices was analyzed by extruding polycarbonate-VGCF composites in a single screw extruder and sub-sequently melt-drew the composites to induce fiber orientation. It was concluded that the dispersion of the fibers in the matrix was very poor at 2 vol% fiber fraction and turned out to be much less fortunate when the fiber content was expanded to 5 vol%. It was recommended that grinding or melt-blending the fiber with the polymer before extrusion may bring better result in better dispersion.

The utilization of submicron VGCFs as arbitrary layers between layers of ceaseless carbon fibers in an epoxy matrix was studied [43] and it was found that the VGCFs improve appreciably the damping capacity of the composites at fiber fractions as low as 0.6 vol%.

The utilization of VGCFs for fabricating thin paper was made effectively by supplanting the generally utilized commercial chopped ex-PAN and ex-pitch fibers to acquire planar isotropy [44].

Submicron VGCFs were used in cement-matrix composites, an application wherein they could be amazingly valuable, because of the relative minimum cost and simple process ability [41]. With a fiber heap of just 1.5 vol%, they accomplished the most noteworthy electromagnetic interference (EMI) shielding effectiveness ever achieved for a cement-matrix composite.

Composites based on VGCF-mats were made and heat-treated at 2800°C and their thermal conductivity was studied [45]. It was acquired that the 36 vol% composite exhibited a room-temperature thermal conductivity of 564 W/mK. This value is some extent higher than that of copper (+/− 450 W/mK) and it was ascribed to the greatly graphitic nature of the VGCF mats.

Aluminum matrix and carbon-carbon composites based on VGCFs were fabricated and compared [46]. For the aluminum-VGCF composites at 36.5 vol% the thermal conductivity of 642 W/mK was found. An outstanding value of 910 W/mK was observed for a 70 vol% carbon-VGCF composite which is double the value of copper.

S.No	Properties	Carbonized s-VGCFs[a]	Graphitized s-VGCFs[b]	Method needed for characterization
1	Lattice constant	6.900 A	6.775 A	XRD
2	Diameter of fiber	0.2 mm	0.2 mm	SEM
3	Length of fiber	10–20 mm	10–20 mm	SEM
4	Volume density	0.02–0.07 g/cm^3	0.02–0.07 g/cm^3	Tapping
5	Real density	1.9 g/cm^3	2.1 g/cm^3	Pycnometer
6	Surface area (BET)	37 m^2/g	15 m^2/g	N absorption
7	Ash content	1.5%	0.03%	SDK
8	pH	5	7	PH Meter
9	Starting temperature of oxidation	550°C	650°C	TGA

[a]*Carbonized s-VGCFs indicate the sample heat treated at 1200°C.*
[b]*Graphitized s-VGCFs indicate the sample heat treated at 2800°C.*

Table 1.
Basic properties of submicron VGCFs [48].

The mechanical properties of VGCF-carbon composites was studied and arrived the result that the tensile properties of these composites are lower than anticipated It was concluded that the thermal properties of VGCFs are preferred and converted into composites.

9.2 Application in batteries

The fibers acquired by the floating reactant method have a thin diameter distribution (from 0.1 to 0.2 mm), indicating nearly a similar morphology when contrasted with that of normal VGCFs (10–20 mm), which comprise of a central filament and an external deposit of pyrolytic carbon with the annular structure of a tree. Moreover, these fibers have a high possibility for application as filler in composites and as an anode material in lithium ion batteries, including additives to anode materials, because of incredible conductivity and high surface to volume ratio.

For s-VGCFs acquired by a floating reactant technique, the fundamental properties and micro structural development of these fibers with Heat Treatment Temperature (HTT), the physical properties of a solitary fiber and in the massive state were assessed to apply this material as the filler in electrodes of lead acid batteries and in the Li-ion battery system. Graphitized s-VGCFs showed attractive desirable properties when utilized as filler in electrodes, for example, genuinely high mechanical strength and electrical conductivity in a single fiber, a high degree of resiliency and good volume conductivity in the bulky state. These desirable properties should yield improved execution performance in actual batteries (**Table 1**) [47, 49–51].

10. Conclusion

Vapor grown carbon fiber composites for batteries and supercapacitors have been extensively studied worldwide. The CNFs and their composites can be utilized in numerous fields; they have unique mechanical, electrical and thermal properties that may be useful in making composite materials like polycarbonate-VGCF, epoxy-VGCF, PAN-VGCF and aluminum-VGCF and filler in electrodes of lead-acid batteries and the Li-ion battery system.

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