3D PRINTED CARBON FIBER REINFORCED COMPOSITE-ADVANCED AND EFFICIENT AUTOMOTIVE MATERIAL

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Abstract. Automakers are always in search of novel materials that suit the critical requisite characteristics of a material to be applied in automobile applications viz., high strength to weight ratio, high yield strength to ultimate tensile strength ratio, and optimum ductility. Several metallic materials that meet these requirements are being applied directly or treated to obtain the said characteristics. However, chemical reactivity, sensitive to oxidation, and undertaking post weld heat treatment processes to enhance the applicability have always been some of the challenges thrown to auto manufacturers. Of late, some of the research outcomes indicated that the carbon fibers are the best suited automobile materials that would pose minimal constraints to the auto engineers. The current paper critically insights the synthesis and manufacture of carbon fibers, and bottlenecks encountered while fabricating these fiber reinforced composites. A critical solution of 3D Printing technology of manufacturing carbon fibers to produce low cost carbon fibers is also discussed in detail.

Keywords: Carbon Fibers, Flexural strength, Fused Deposition Modeling, Impact energy, Light material, Tensile strength, 3D printing

I. INTRODUCTION

Carbon fiber is a synthetic fiber which consists of at least 92 wt% of carbon in composition. It is a thin strip of carbon atoms bound together in a rigid crystal formation. The diameter of a carbon fiber is typically a few microns and it has a micro graphite crystal structure [1]. The carbon fibers are strong, light and stiff and are used in many sectors like aerospace, marine applications, buildings and automobile applications. They are manufactured from three precursors: polyacrylonitrile (PAN), rayon and coal-based pitch. Industrial production of carbon fibers started with rayon-based carbon fiber since 1950's and in 1960's, the method of making carbon fiber from PAN and pitch was developed. The pitch based carbon fibers are grouped in two classes: 1) Isotropic pitch-based carbon fibers 2) Mesophase pitch-based carbon fibers.

1.1 Background

Joseph Swan produced carbon fibers for the first time in 1860, for use in light bulbs. In 1879, Thomas Edison baked cotton threads or bamboo slivers at high temperatures carbonizing them into an all-carbon fiber filament used in one of the first incandescent light bulbs to be heated by electricity [2]. Lewis Latimer developed a reliable carbon wire filament for the incandescent light bulb in 1880, heated by electricity. In the 1950s, carbon fibers were first developed as reinforcement for high-temperature components on missiles. These initial fibers were produced by heating strands of rayon until they were carbonized. In the 1960s, as the carbon yield was only around 20%, and the resulting fibers had low stiffness and strength properties polyacrylonitrile (PAN) was designed as a precursor for carbon fiber. This raw material had substantially improved mechanical properties than fiber derived from Rayon and was yielding about 55% carbon.

During the 1970s work continued to find other raw materials which resulted in the introduction of carbon fibers made from a petroleum pitch, derived from oil processing. Yielding about 85% carbon, these precursors had modulus and strength that was regarded as acceptable for many applications. Due to the outstanding flexural modulus and ability to be easily graphitized, pitch fibers were considered an exceptional choice for specialty applications.

1.2 Structure, Properties, and Applications

The atomic structure of carbon fiber resembles the structure of graphite, which consists of carbon layers arranged in regular hexagonal pattern. The microstructure of carbon fiber depends on precursors and processes conditions. Carbon fibers are black in color and have a smooth surface with silky luster. The cross-section of carbon fibers is round with flattened sides sometimes. Because of its close packed structure, the carbon fiber is very strong and has a high modulus. Carbon fiber is the second heaviest textile fiber because its specific gravity is in the range 1.77 to 1.96. Carbon fibers have zero percent moisture regain. These fibers have excellent resistance to acids and alkalis even at high temperatures, but strong oxidizing agents will degrade the fiber. They are inert to all common solvents, but sensitive to hypochlorite. These fibers have excellent resistance to microbiological organisms, aging and sunlight. They do not melt and oxidizes slowly at temperatures above 3000°C. The high strength and specific toughness make these fibers being applied in aerospace. Good amount of dimensional stability and low coefficient of thermal expansion facilitate their applications in missile applications. Substantial vibration damping and toughness aid their use as the robot arm materials. Apart from these applications, the biological inertness of these carbon fibers finds their inclusion in some of the critical medical equipment. Despite having enhanced strength, stiffness, dimensional stability and lighter in weight, these carbon fibers suffer from tendency of clogging, brittleness and being highly abrasive.

II. MANUFACTURING CARBON FIBERS

2.1 PAN type carbon fiber

The precursor for producing PAN type carbon fiber is polyacrylonitrile (PAN). PAN is copolymerized with another monomer to control its oxidation rate and to lower its glass transition temperature. The list of monomers is show in the Figure1 below.

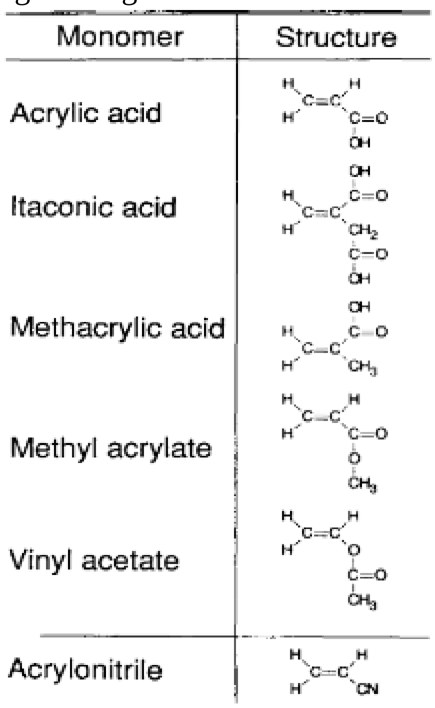

Fig.1 Monomers copolymerized with acrylonitrile to form PAN-based carbon fiber precursor [3]

2.1.1 Solution Spinning of PAN Precursor Fibers:

In this process, the copolymer is first dissolved in a suitable solvent and loaded into a storage tank. The solution is filtered when it is pumped through a die head where the impurities are removed before being extruded through a large number of small capillary holes of approximately 100-μm. Then the solution immediately enters a coagulating bath as it exits the capillary. This process is called as wet spinning. In another type of solution spinning, the polymer solution is extruded into a hot gas environment. This is called as dry spinning, which produces an as –spun fiber with a dog-bone-shaped cross section. These both wet and dry-spun fibers are washed to remove final traces of solvent after fiber formation. Then these fibers are passed through one or two stages in which they are stretched to further align the molecules parallel to the fiber axis.

2.1.2 Oxidation of PAN Precursor Fibers

This oxidation step is carried in large furnace were in the rolls are used to pull the PAN precursor fiber slowly to the oven under a control attention. The PAN stabilization reactions generate CO_2, water and HCN. Therefore the exit air must be properly exhausted from these furnaces.

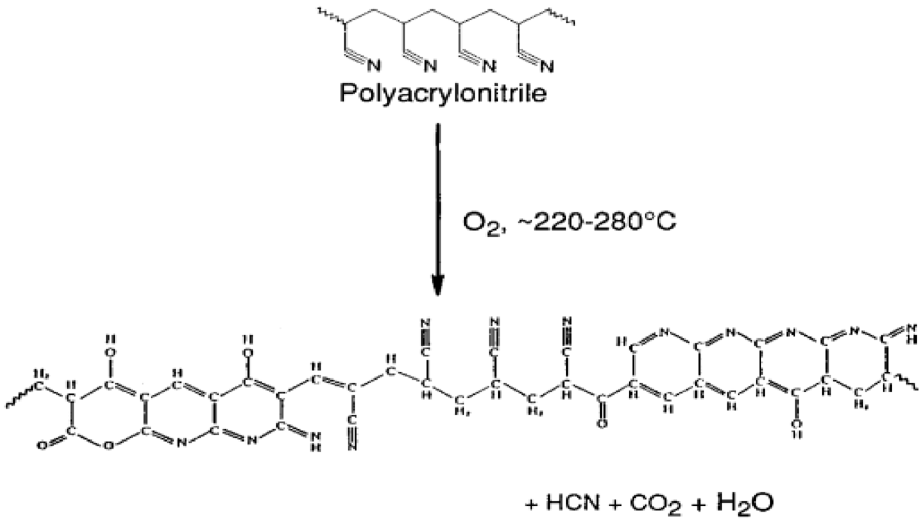

Fig.2 Stabilization PAN Precursor summarizing the most frequently observed functional groups [3]

After stabilization process the fiber is carbonized and sometimes graphitized by heating it in an inert atmosphere from 1000°C to 2800°C. Almost all non-carbon elements are driven from the fiber during the final heat treatment. Thus, the carbon content of the final fiber varies from 80% to 99% depending upon the carbonization temperature. After this final heat treatment, most of the PAN-based carbon fibers are given surface treatments to improve their bonding with polymeric matrix. After surface heat treatments, in order to remove the wettability of the fiber epoxy-sized fiber is coated with a low molecular weight epoxy.

The flowchart of manufacturing of PAN precursor fibers is as show in the Figure 3.

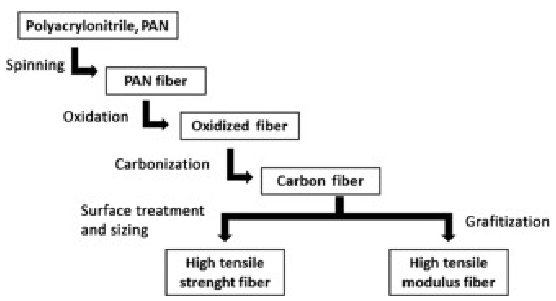

Fig.3. Manufacturing process of PAN type carbon fibers [4]

2.2 Rayon-Based Carbon Fiber

The precursor for producing Rayon-based carbon fiber is Rayon or cellulose. A wet spinning process is to produce the cellulose fibers. In this process raw cellulose is dissolved in a basic solution and treated with CS_2 to form cellulose xanthate. This derivative is then dissolved in NaOH and extruded into a coagulation bath containing 10%-15% sulfuric acid. As it enters the acidic bath, cellulose xanthate is hydrolyzed and filaments are precipitated. Thus formed cellulose precursor fibers are oxidized by heating it in air to a temperature above 400°C. The cellulose polymer decomposes as it is stabilized. Therefore CO, CO_2 and water are given off as decomposition begins. After stabilization of cellulose precursor fibers, they are carbonized and graphitized in an inert atmosphere. Upon converting cellulose precursor fiber into a carbon fiber, it results in 10%-30% of yielding. This low yield is due to extensive decomposition during stabilization.

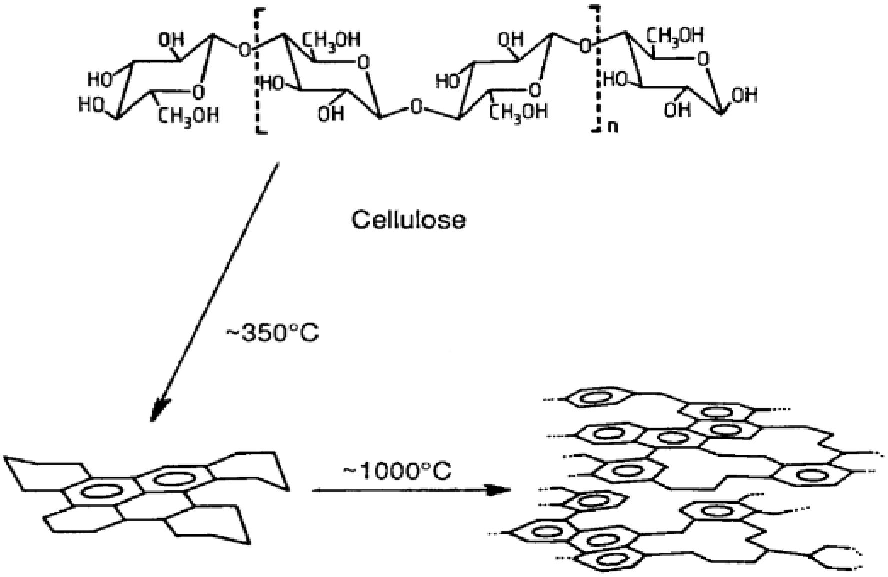

Fig.4 Molecular structure of cellulose and approximate structure during thermal degradation to carbon [3]

2.3 Pitch-Based Carbon Fiber

The precursor for producing Pitch-based carbon fiber is raw pitch (coal or petroleum). These are grouped in two categories:

A) Mesophase Pitch-Based Carbon Fiber

B) Isotropic Pitch-Based Carbon Fiber

These two carbon fibers are different not only in precursors but also in their structure and properties. The production processes of these two fibers are shown in the Figure 5.

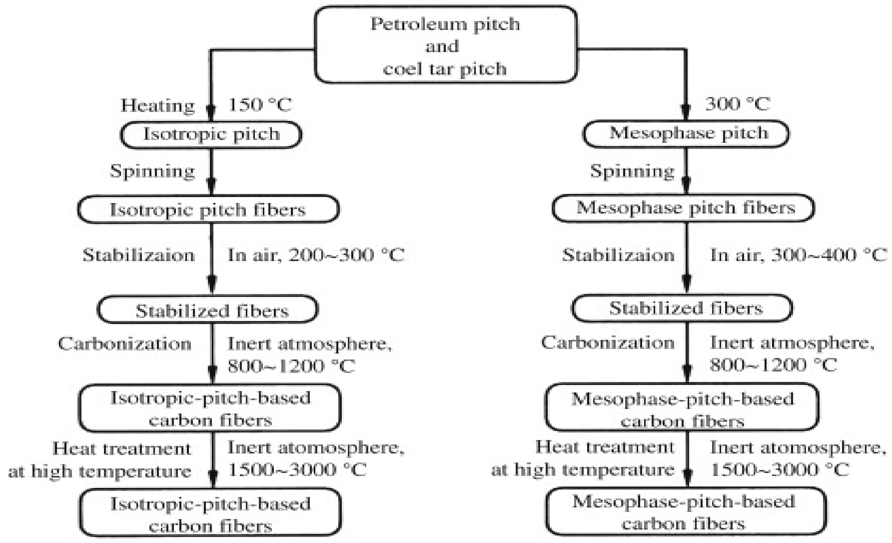

Fig.5 Production processes for pitch-based carbon fibers [5]

III. CHARACTERIZATION

As PAN-based carbon fibers are more expensive, research is going on to lower the manufacturing cost and to produce high quality carbon fiber. The solution for this problem is to produce pitch based carbon fibers. The carbon fibers spun from pitch have different properties compared to PAN precursor. Pitch carbon fibers have high tensile strength and high tensile modulus and are good conductors of heat. Characterization of fiber is important to improve fiber properties.

3.1 Scanning Electron Microscopy (SEM):

SEM uses an electron beam to create detailed images of the sample fibers. A single fiber is placed length-wise on a metal bar where in the ends are secured by press-on glue tabs. A scanning beam of electrons in a vacuum is directed at the sample. The sample must be conductive otherwise it will charge and this charging causes the sample image to blur. Most of the carbon fiber products are conductive. The ISI Super III SEM was used to make detailed images of fibers [6]. At different locations the images were taken along the fiber length. As the sample cannot be rotated because of its attached nature only top view for each fiber was imaged. As a result, a circular cross section is assumed when measuring the diameter of the image. A micro function in the SEM software measures the diameter from the images [6].

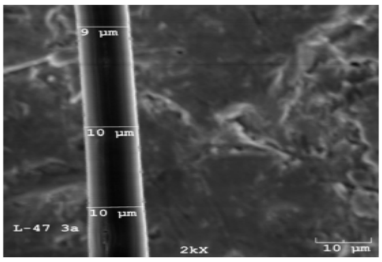

Fig. 6 Carbon fiber sample image produced by the SEM [6]

3.2 Mechanical characteristics evaluation

The samples of Carbon Fiber Reinforced Composites are subjected to tensile, flexural, and impact tests. Fig. 7 illustrates the images of the samples prepared according to ASTM standards for these characterizations.

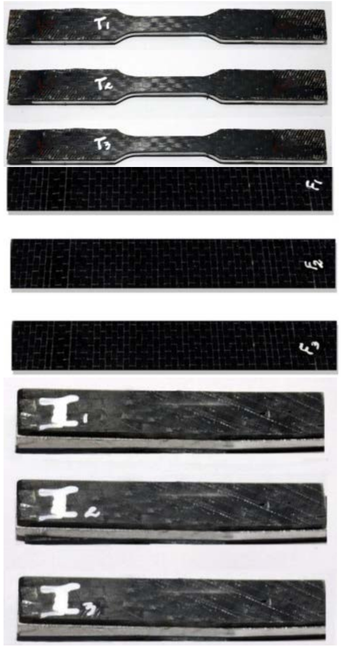

Fig. 7. The ASTM standard samples for (a) tensile (b) flexural and (c) impact test [7]

The results of these tests are tabulated and indicated in table 1.

Sample No.	Tensile Strength (MPa)	Flexural Strength (KN)	Impact Energy Absorbed (Joules)
1	310.75	2.41	10
2	301.35	2.05	9.4
3	290.15	2.22	10

IV. CARBON FIBER REINFORCED COMPOSITES IN AUTOMOBILE INDUSTRY

BMW, Mercedes-Benz, Lamborghini and other high end automakers have committed to increase the use of CFRP components to reduce the weight of the vehicle [8]. Of roughly 100 million vehicles are made each year, carbon fiber is used in less than 100,000. The barrier is carbon fiber's high cost. We need to drive the price of the coal-based precursor beneath the "tipping-point." Carbon fiber then becomes an affordable alternative to steel. Carbon fiber cars then move from a niche market to mass market. The solution to this major problem is to reduce the cost of carbon fibers and this is possible by manufacturing coal-pitch precursor carbon fiber. Coal is the cheapest source of carbon. But most carbon products are expensive as they come from petroleum [9]. Making carbon fibers from coal is not new. Since the 1960s, production processes for these pitch-based carbon fibers have been investigated, developed and commercialized by numerous entities, including Mitsubishi Chemical Carbon Fiber & Composites Inc. (Tokyo, Japan) and Nippon Graphite Fiber Corp [10]. (Hyogo, Japan). Mitsubishi's high-performance DIALEAD fiber, for example, is considered by many as essential to the success of many zero-CTE- and stiffness-critical aerospace and space projects. What is new is that, within the past year, several projects have sprung up, with two purposes: 1) find new uses for coal that don't involve power generation, thereby reducing carbon emissions while preserving miners' jobs, and 2) convert this low-cost, carbon-rich precursor into useful, low-cost fibers suitable for non-aerospace applications [10]. The most recent cutting edge researches have indicated that the 3D printing technology is the best candidate process for manufacturing of carbon fibers at relatively low cost.

V. 3D PRINTING OF CARBON FIBER REINFORCED COMPOSITES

Carbon fiber is one of the most popular types of fibers used in 3D printing. Carbon fibers have very high strength to weight ratio and thus, it is very valuable for creating light weight strong parts. Most 3D printers capable of processing composite materials are based on the polymer-extrusion process, known as fused filament fabrication (FFF). In 3D printing of carbon fibers, the fiber can take two different forms:

5.1 Chopped fibers 3D printing

These are short-length fibers copped into segments less than a mm in length, were in these segments are mixed with traditional 3D printing plastics like nylon, ABS to form filled plastic. Chopped composite 3D printing materials takes normal plastic that may be lacking in certain properties and improves it [11]. In case of carbon fiber the fibers boost the strength, dimensional stability and stiffness than its base plastic. The length of the chopped segments and the quantity of fibers impacts the quality and the strength of the part. The 3D printing of filaments containing chopped fibers requires only a hardened steel nozzle to resist abrasive fiber strands.

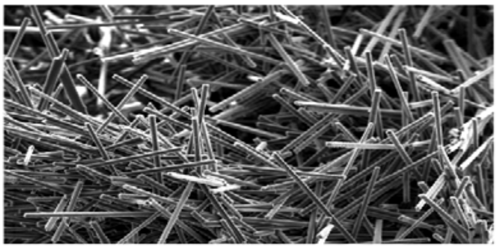

Fig.8 A close up of Chopped carbon fibers used in 3D printing, taken on an SEM [11]

5.2 Continuous Fiber 3D Printing

It adds continuous strands of fiber to achieve metal-strength properties at the fraction of the weight. This method consists of two steps: First, a traditional thermoplastic is extruded to form the infill and shells which serves as the matrix. Next, the continuous fiber is ironed into the matrix bonding with the thermoplastic by using a compatible resin coating. This process is called Continuous Fiber Fabrication (CFF).

VI. SUMMARY AND CONCLUSION

An overview of carbon fiber and the emerging technology leading to cost reduction were illustrated in this paper. The need for mass usage of carbon fibers in automobile applications was discussed. The characteristics and applications of carbon fibers were elucidated. The 3D technology used to print carbon fiber filaments with the advantages and disadvantages were discussed. The mechanical properties of CFRPs were evaluated. It can be concluded that the 3D printing technology of manufacturing of CFRP would revolutionize the automotive sector as it involves lesser cost yet retention of requisite mechanical characteristics of an automobile component.

VII. REFERENCES

1. Pierson H.O., Handbook of Carbon, Graphite, Diamond and Fullerenes - Properties, Processing and Applications (1993)
2. Roger Bacon and Charles T. Moses., High Performance Carbon Fibers. National Historic Chemical Landmarks, Program of the American Chemical Society in 2003, acs.org.
3. John D. Buckley and Dan D. Edie, Carbon-Carbon Materials and Composites (1993)
4. “Carbon Fiber Production- An Overview”, sciencedirect.com
5. “Pitch Based Carbon Fiber- An Overview”, sciencedirect.com
6. Cochran, Heather Darlene, Analysis of Carbon Fiber Characterization Techniques (2008)
7. Uthirapathy Tamilarasan, Loganathan Karunamoorthy and Kayaroganam Palanikumar., “Mechanical Properties Evaluation of The Carbon Fiber Reinforced Aluminum Sandwich Composites”, Materials Research, 2015, 18, pp.1029-1037.
8. Amanda Jacob, Carbon Fiber Use Increasing in The Automotive Industry, Materials today.com (2011)
9. “Carbon from coal”- The National Council (Atkins-NCC-Spring-2018), nationalcouncil.org
10. “Coal as an avenue to low-cost carbon fibers”, Composite World.com, 2017.
11. Alex Crease., “3D Carbon Fiber and Other Composites”, Markforged.com