

## Producing high-quality precursor polymer and fibers to achieve theoretical strength in carbon fibers: A review

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**ABSTRACT:** The precursor fiber quality has a large impact on carbon fiber processing in terms of its performance, production yield, and cost. Polyacrylonitrile precursor fibers have been used commercially to produce strong carbon fibers with average tensile strength of 6.6 GPa. There is a scope to improve the average tensile strength of carbon fibers, since only 10% of their theoretical strength has been achieved thus far. Most attempts to increase the tensile strength of carbon fibers have been made during the conversion of precursor fiber to carbon fiber. This review highlights the potential opportunities to enhance the quality of the polyacrylonitrile-based precursor fiber during polymer synthesis, spinning, and postspinning. These high-quality precursor fibers can lead to new generation carbon fibers with improved tensile strength for high-performance applications. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43963.

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### INTRODUCTION

Carbon fiber-reinforced composite materials are used for applications where high strength and light weight are required. These include aerospace, automotive, civil engineering, energy generation, and military applications. At present, the carbon fibers with high average tensile strength (6.6 GPa) and high modulus (324 GPa) are T1100G, produced by Toray.<sup>1</sup> Carbon fibers produced with highest average modulus are from Toray (M60J) with 590 GPa but these have intermediate average tensile strength of 3.9 GPa.<sup>2</sup> This reflects that when the fibers are graphitized at >2500 °C as occurs for the Toray M60J, the modulus increases but strength reduces. Carbon fiber obtained without sacrificing strength are T1100G from Toray. These carbon fibers are polyacrylonitrile (PAN) based.<sup>2</sup> PAN-based carbon fibers have attained 70% of their theoretical modulus but only 10% of their theoretical strength.<sup>3</sup> While pitch-based carbon fibers have obtained 85% of their theoretical modulus but only 3.3% of their theoretical strength.<sup>4,5</sup>

Carbon fibers strength and modulus are related to the fiber crystalline structure. Carbon fibers are made of regularly stacked graphite crystallites but randomly arranged adjacent planes (called a turbostratic graphite structure). The perfect graphite crystal has a theoretical modulus and theoretical strength of 1000 GPa and 100 GPa, respectively.<sup>6</sup> As the carbon fiber structure is close to that of graphite, there is a scope for improving the strength of the carbon fibers for high-performance

applications. Such high-performance carbon fibers may also reduce cost, as a lower quantity of these stronger fibers will be required to provide composite materials of the same strength.

Manufacturing of carbon fibers can be categorized into four stages—polymer production, spinning, postspinning, and thermal conversion (which involves oxidation and carbonization). Figure 1 outlines the four stages in the manufacturing of carbon fibers.

In polymer production, the polymer can be synthesized using many different polymerization techniques which will be discussed later. During spinning, the polymer solution coagulates into precursor fiber by dual diffusion process. Different types of spinning techniques can be used, such as wet, dry, melt, and electrospinning.

Wet spinning is the traditional spinning method used in the industry. It is also a preferred method for making high-strength PAN-based fibers because other spinning techniques such as melt, dry, and electrospinning produce fibers with voids and surface defects.<sup>7</sup> Spinning involves mechanical stretching of the fibers to retain orientation of PAN molecular chains but there are certain limitations on stretching the fibers during spinning. Very high stretching can cause fiber break as the fiber is still in the process of formation. Alternatively, incomplete stretching can reduce orientation in fibers. This occurs due to limited quantity of comonomers added during polymerization. Lower

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comonomer limits (0.5–8 wt %) are set to improve carbon yield during thermal conversion.<sup>8</sup> These comonomers are added all together, therefore do not get distributed well. This uneven distribution can cause nonuniform stretching leading to skin-core fiber structures. Such incompletely stretched fibers after spinning can be stretched further to improve their strength and orientation. This process is called postspinning.<sup>9,10</sup> This involves coating or impregnating the spun fibers with chemicals or catalysts to either stretch them further or to indirectly catalyze the oxidation reaction during thermal conversion.

Stage four is thermal conversion of PAN precursor fiber into carbon fiber.<sup>11</sup> Here the precursor fiber is passed through oxidation oven at a temperature between 230 °C and 300 °C in the presence of oxygen along with mechanical stretching. Then the fiber enters the carbonization oven at 400 °C up to 1700 °C in an inert atmosphere. The fibers are always kept under tension throughout the process. This step provides high strength to the fibers. To obtain high modulus fibers, the carbonized PAN fiber is further heated up to 2800 °C, but this process results in a loss of strength as the size of the flaws increases at high temperature.

The commercial manufacturers keep the polymer recipes and processing parameters for producing different grades of carbon

fibers as secrets. They focus mainly on improving the oxidation and carbonization stages of production to enhance the tensile strength of the carbon fibers. This is because making any changes while the fiber is being formed (during spinning) has certain limitations and also is complex. Moreover, the structure–property relationship is also most often studied in carbon fibers<sup>2,6,12,13</sup> rather than the precursor fiber. The carbon fiber properties are influenced by the PAN precursor fiber properties. Therefore opportunities to enhance strength in carbon fibers need to be explored prior to thermal conversion during polymer synthesis, spinning, and postspinning.

The oxidation and carbonization processes for production of PAN-based carbon fiber have been widely studied.<sup>14–16</sup> By changing the heat treatment temperatures (HTT), carbon fibers of different average tensile strength are obtained.<sup>17–19</sup> For instance, a HTT of 1000 °C produces carbon fibers with average tensile strength of ~2.5 GPa while an HTT of 1500 °C produces carbon fibers with average tensile strength of ~4 GPa. Furthermore, preoxidation treatments are used to make the fibers thermally stable so that they can withstand higher carbonization temperatures resulting in higher strength.<sup>20</sup> Preoxidation treatments also help in inter fiber cohesion, enhance drawing, and reduce the heat liberated during oxidation.<sup>21</sup> Sizing treatments



**Figure 1.** Stages of carbon fiber manufacturing. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Comparison of Different Carbon Fiber Precursors, Their Source, and Achieved Average Strength

Precursors	Source	Average tensile strength (GPa)	Spinning method (preferred)	Yield (%)
PAN <sup>1</sup>	Propylene from crude oil	6.6	Wet	>50
Rayon <sup>25</sup>	Cellulose (wood pulp)	0.4	Wet	10
Pitch, <sup>29</sup> mesophase pitch <sup>30</sup>	Petroleum, coal tar	0.6	Melt	6080
		3.5		
Sulfonated polyethylene <sup>31</sup>	Natural gas, petroleum	2.5	Melt	60-80
Lignin, <sup>32</sup> lignin blend with PAN <sup>33-35</sup>	Cellulose (wood pulp)	1.2	Electro, wet	10
		2.5		28

are used on the carbon fiber surface to enhance bonding of carbon fibers with the matrix. These treatments affect the mechanical strength of the carbon fiber or carbon fiber composites.<sup>22</sup> Introduction of higher drawing ratios or performing drawing in several steps during the oxidation and carbonization stage has resulted in high average tensile strength of carbon fibers (548 kg/mm<sup>2</sup> or 5.37 GPa).<sup>23</sup> Any defects in the fiber caused *via* stretching or due to high HTT can result in decrease in tensile strength of carbon fibers.<sup>3</sup> Smaller diameter carbon fibers produce high tensile strength fibers as there are fewer defects.<sup>24</sup> A clean room environment is applied to carbon fiber production to eliminate impurities and defects as far as possible from the manufacturing process.<sup>17</sup>

This review begins with the selection of the right precursor for producing strong carbon fibers. Then leads into the advanced polymerization techniques used for making the desired characteristics in precursor polymers. Following into the spinning methods that will produce high-quality precursor fibers. This review will identify gaps in the correlation of the structure of the precursor fiber and the final carbon fiber properties. It will also unravel the complexity of turning polymer into a precursor fiber.

## PRECURSOR SELECTION

The first step in the carbon fiber production process is selecting the precursor. The choice of precursor will determine the properties and applications of carbon fibers produced from them.

Many different precursors are explored in the literature such as polyacrylonitrile (PAN), rayon, pitch, polyolefins, and bio-based precursor polymer. Not all of these precursor polymers have the necessary characteristics to produce high-strength carbon fibers. In general, the requirements for a precursor polymer for producing a strong carbon fiber are high carbon content/yield, high melting point, high molecular weight (HMW), high crystallinity, and ease of stretching.<sup>25-28</sup> Table I shows a comparison of different carbon fiber precursors, their source, and achieved average strength values.

### Polyacrylonitrile (PAN)

Over the last five decades, the most suitable precursor polymer for producing high strength carbon fibers has proven to be PAN.<sup>36</sup> The molecular properties of PAN determine its end-use. PAN polymer used for textile applications has a molecular

weight (MW) in the range of 70 to 200 kDa.<sup>37</sup> A precursor fiber made from PAN precursor polymer for carbon fiber production should have high MW (at least >200 kDa) and comonomers should be added to achieve high drawability and better oxygen permeability during spinning and oxidation, respectively.

Despite its high cost, 90% of world's carbon fiber production relies on PAN as a precursor polymer because it produces carbon fibers with excellent properties as depicted in Table I, and is therefore preferred over other precursor polymers such as rayon,<sup>25</sup> pitch,<sup>29</sup> and polyolefin.<sup>38</sup> Such characteristics are found in PAN due to its molecular structure containing highly polar nitrile groups, which results in strong interactions and which maintain the orientation of polymer chains at high temperature.<sup>39</sup> Generally, HMW PAN (at least >200 kDa) will result in high crystallinity and high strength PAN precursor fibers. However, MWs of <200 kDa are used for the practical reason that high MW PAN is difficult to dissolve due to its high polydispersity (PDI). PDI refers to mass average molar mass of polymer divided by number average molar mass of polymer.

The high PDI results from conventional free radical solution polymerization, although alternative polymerization methods can be used to obtain HMW polymers with low PDI to make dissolution easier.<sup>40</sup> This will be discussed later.

PAN precursor fibers were produced by DuPont in the 1940s.<sup>41</sup> PAN filaments were first made into carbon fibers at a Japanese Government Industrial Research Institute in 1964<sup>42</sup> and the technology was licensed to Toray Industries in 1970, now the largest global manufacturer of carbon fiber.<sup>43</sup> PAN polymer is the most suitable precursor for carbon fiber production due to its molecular properties, high carbon yield, and its ability to decompose to form a char prior to melting.

### Rayon

Union Carbide Corporation in 1963 obtained a patent on using rayon (a cellulosic material derived from wood pulp) as a precursor for carbon fiber at large scale due to its ability to decompose prior to melting.<sup>44</sup> Rayon shows very low carbon fiber yield which makes the process expensive. Therefore these precursors are chemically modified to improve their yield using chlorosilanes and boron-phosphorous compounds. These treatments improved the carbon fiber yield by up to 28%.<sup>45</sup> Further, the strength achieved using cellulosic-based precursors is poor,

so these are not used for high-performance applications in industry.<sup>25</sup>

### Pitch

Pitch is a byproduct from coal and petroleum industry.<sup>46</sup> It produces high modulus but low strength carbon fibers, with a sheet-like structure that allows easy formation and propagation of cracks, resulting in low strain to failure. In order to obtain high average tensile strength carbon fibers from pitch, it has to be converted into a mesophase pitch<sup>30</sup> by stretching fibers at high temperature, which involves high cost. Carbon fibers produced from pitch have a broad distribution of mean fiber diameter.<sup>29</sup> Nevertheless, pitch contributes 10% of carbon fiber production because of their high carbon yield.<sup>4</sup> So pitch-based carbon fibers are used for high modulus applications, such as premium sporting goods, producing industrial rollers, and in spacecrafts.<sup>47</sup>

### Other Synthetic Polymers

Synthetic polymers such as polyethylene, polystyrene, and polyacetylene have been used as potential carbon fiber precursors. Polyethylene<sup>31,38</sup> and polystyrene<sup>48</sup> have been modified using fuming sulfuric acid to improve their yield at lab scale; however, this process is not feasible for industry. Sulfonation is done to obtain better carbonization yield (60–80%) and to increase the melting point.<sup>31</sup> Polyvinylacetylene has been modified by exposing it to UV light source in nitrogen atmosphere but the yield was not found to increase, using the simple thermogravimetric analysis.<sup>49</sup> Although these polymers have a high carbon yield, the carbon fibers produced from them have low average tensile strength (as seen in Table I).

### Bio-Based

Bio-based carbon fiber precursors such as lignin have been used.<sup>32,34,50,51</sup> Although these precursors are cheap and eco-friendly, they do not satisfy the requirement for high strength in the precursor fiber. Lignin is a HMW aromatic biopolymer with a complex structure which encounters problems with conversion into a carbon fiber structure during initiation of oxidation, carbonization, and graphitization.<sup>32</sup> Lignin has been blended with other polymers such as polyethylene, polypropylene, and melt spun to obtain carbon fibers with improved average tensile strength.<sup>33–35</sup>

Nanocellulose (NC) whiskers have been used to form PAN/NC precursor hybrids. The NC whiskers were derived from wood pulp by acid hydrolysis and then blended with PAN.<sup>52</sup> These were found to effectively increase the crystallite size and tensile properties of carbon fibers.<sup>52</sup> Australian spinifex grass has been considered as a source of NC to produce NC hybrid precursor with PAN for carbon fiber production by University of Queensland.<sup>53</sup> The spinifex grass is deconstructed to obtain NC that is used to make hybrid precursors with PAN.<sup>53</sup> These bio-based precursors offer the advantages of using renewable resources to produce carbon fibers; however, the fibers produced are of low quality.

### Summary

PAN is the only precursor with the potential to produce carbon fibers with high average tensile strength in the foreseeable

future, and so the remainder of this review will focus on PAN-based precursor polymers, their synthesis, and spinning. There are several polymer synthesis methods that are used to produce PAN, and these are discussed in the next section.

## PAN POLYMER SYNTHESIS

### Polymerization Methods

The polymerization conditions used strongly influence the MW, PDI, and molecular defects occurring in the produced polymers. Solution, aqueous suspension, and solvent-water suspension methods are all used for PAN polymer synthesis.<sup>54,55</sup>

In solution polymerization, a monomer is dissolved in a non-reactive solvent that contains a catalyst. The reaction results in a polymer which is also soluble in the chosen solvent. Generally in solution polymerization, once the polymer is formed the excess solvent must be removed. However, in PAN fiber production, the polymer dissolved in excess solvent can be used directly as the dope to spin to precursor fiber in a one-step process. As this involves the use of organic solvents, it is an expensive process. Solution polymerization has been considered to be the most advantageous as the precursor polymer obtained stabilizes at lower temperature during oxidation and also has fewer molecular defects.<sup>7</sup> Recently an efficient aqueous phase precipitation polymerization has been used, which is low at cost as it is water-based,<sup>56</sup> but it remains a two-step process as the polymer needs to be dissolved in an organic solvent for spinning.

Solution polymerization of acrylonitrile (AN) is a free radical process. A free radical initiator is required to create an active centre from which the polymer chain starts to emerge, with the initiator then attacking the monomer leading to propagation of the polymer chain. Combining two active chains results in the termination of the polymerization reaction.<sup>55</sup> This method involves long reaction times ~20 h and provides limited control over the MW and PDI of the resulting polymer.

Low PDI refers to consistency of the polymer chain lengths and assists the easy dissolution of the polymer due to elimination of larger, less soluble, high MW fractions. Narrow MWD or low PDI of the polymer has also been considered as a likely feature to produce carbon fibers with high tensile strength.<sup>57</sup> Conventionally as the MW of the polymer increases, its PDI increases likewise. Therefore obtaining a HMW with a low PDI is a challenge. In more recent times, considerable attention has focused on using so called living or controlled radical polymerization techniques such as reversible addition fragmentation chain transfer (RAFT)<sup>58,59</sup> and atom transfer radical polymerization (ATRP)<sup>60</sup> to prepare PAN-based polymers.

Using a RAFT agent in the polymerization process is one technique that is used to achieve better control over the MW and the PDI. Moad *et al.*<sup>59</sup> introduced RAFT polymerization as a technique to produce polymers with a well-defined architecture. This work opened up space for using RAFT polymerization for the manufacture of the PAN-based polymers for carbon fiber production, as recently shown by Cai.<sup>40</sup>

There are very few reports on the RAFT polymerization of AN due to its high reactivity. In one report, although low PDI has

been achieved, the MW obtained was low (70,000 g/mol).<sup>58,61,62</sup> Another important aspect is the monomer conversion yield, which should be as high as possible and certainly >70%. Control over MW, PDI, and conversion yield (>70%) are important requirements for producing superior PAN polymers. In a recent study, although a HMW (>100,000) and lower PDI (<1.4) was achieved, for reasonable conversion yield, higher reaction times of >26 h were needed.<sup>63</sup> Lack of high MW fractions due to low PDI can have certain challenges, such as low structural viscosity. Therefore one topical research question is to see if such polymers can be spun into fibers and whether they can be thermally converted to produce carbon fibers with high average tensile strength. In a recent study by Sporn *et al.*,<sup>64</sup> a high yield RAFT-mediated synthesis of PAN homopolymer and copolymer was achieved. Although low PDI of 1.34 was achieved but MW of 133 kDa will be too low to produce high-quality precursor fibers.

In a recent patent by Cytec,<sup>65</sup> it has been documented that carbon fibers, produced from RAFT polymers with PDI of 2 or less *via* a special RAFT agent, exhibited uniform cross section and low microdefects during the carbon fiber manufacturing process. The average tensile strength of the carbon fibers produced was up to 5.5 GPa and the average tensile modulus was up to 289 GPa.<sup>65</sup> In a patent by Asahi Chem. Ind. Co Ltd., an AN polymer with a particular stereochemistry (isotactic with a triad fraction of 0.52) was used. The average tensile strength of the carbon fibers claimed in this attempt was 603 kg/mm<sup>2</sup> or 5.9 GPa.<sup>66</sup>

Another controlled polymerization technique called ATRP has been used to prepare PAN with a MW of 120,000 g/mol and a PDI of ~2, which is not low enough PDI.<sup>60</sup> Despite offering improvements in the preparation of PAN-based polymers, most of the ATRP techniques developed to date inherently introduce transition metal residues into the resulting polymer, which is detrimental for the manufacture of carbon fiber.

In order to produce precursor fibers with high average tensile strength, the precursor polymer should possess characteristics such as HMW (~10<sup>5</sup>), an appropriate MW distribution (i.e. PDI of <2) and minimum molecular defects.<sup>7</sup>

### Polymer Composition

Homopolymer, copolymer, and terpolymer systems are used to synthesize PAN-based polymers.<sup>67–69</sup> The PAN homopolymer has limited drawability due to extensive hydrogen bonding in its structure. The copolymer and terpolymer play an important role in enhancing drawability, increasing the hydrophilicity and solubility of the polymer. The enhanced drawability leads to the formation of the finer and high strength fibers.

Using AN as a homopolymer results in large molecular chains due to its polar nitrile groups that lead to high reactivity. This results in poor control over its MW and PDI, making it difficult to spin. Mitsubishi uses at least 95 wt % AN, while Toray uses at least 92 wt %<sup>70,71</sup> with the balance made up of comonomer. Addition of comonomers results in better control over MW and PDI by production of smaller molecular chains that make their dissolution, filtration, and spinning ability easier.<sup>40,64</sup>

Different comonomers are used depending on the properties required in the polymer. Generally acrylic esters (e.g. methylacrylate) improve drawability of PAN-based copolymers and free acids (e.g. itaconic acid, methylacrylic acid) are added to lower the onset temperature of copolymer oxidation.<sup>64</sup> Typically monomers like itaconic acid and acrylic acid are used as densification accelerators, which inhibit the formation of microvoids. Another class known as drawing promoters (e.g., vinyl carboxylates, butyl esters, and propyl esters) is used to increase the fiber orientation by lowering the  $T_g$  (glass transition temperature).<sup>72–74</sup> These act as plasticizers which increase the chain mobility and help in drawability.<sup>75</sup> Other comonomers categorized as stabilization accelerators (e.g., itaconic acid, methylmethacrylic acid) and oxygen permeation promoters (e.g., vinyl carboxylates) have roles during the thermal treatment process and improve the average tensile strength of the carbon fibers. Comonomers have a significant influence on both PAN precursor fiber and carbon fiber properties. The MW, polydispersity, and comonomer distribution in the polymer chain are the variables that can be controlled during the polymerization process. A higher comonomer content than 8 wt % can reduce the carbon yield during the carbonization stages.<sup>8</sup>

When carbon nanotubes (CNTs) were used as additives in the PAN polymer dope solution, the stretching of the coagulated polymer was enhanced during the drawing stage. This led to an increase in average tensile strength of the resulting PAN precursor fibers.<sup>76</sup> Although CNTs can provide nucleation sites for the development of graphitic structures leading to improvement in thermal and electrical conductivities, carbon fibers obtained from PAN/CNTs showed reduced strength.<sup>76</sup> The reduction in the average strength of carbon fibers has been associated with the voids created due to nonuniform length of CNTs and due to metallic impurities associated with CNT synthesis.<sup>76</sup>

### MW of the Polymer

The polymer MW has significant influence on the performance of the final fiber produced. It determines the strength and application of the produced fibers. For instance, molecular weights of AN-based polymers in the range 70,000 to 200,000 are used for textile grade applications.<sup>37</sup> Polymers with higher MW are used for high-performance applications such as carbon fibers.<sup>77</sup> Producing PAN polymers with high MW is more difficult, since this affects properties such as solubility, filtration, and spinnability.<sup>77</sup> Low MW causes an increased number of broken filaments and low drawability.<sup>78</sup> Very HMW (VHMW) (~500 kDa) and ultra HMW (UHMW) (1700 kDa) polymer has been produced recently to obtain a high-quality precursor fiber. Mitsubishi uses MW of 500 to 1000 kDa to produce special PAN-based fibers for aerospace applications.<sup>79</sup> The MW of the polymer affects the viscosity of the dope prepared. Viscosity further affects the wet spinning parameters and therefore the ease of spinning of the polymer solution.

### PREPARATION OF POLYMER SOLUTION

After polymer synthesis, the polymer solution is prepared for spinning. A known amount of polymer is added to an organic solvent (usually an aprotic polar solvent with large dipole

moment and low molecular weight) to form a polymer solution. The polymer solution needs to be prepared in certain ways for obtaining high-quality PAN precursor fibers from it. These are discussed in the following sections.

### Polymer Content

Conventionally a high polymer content in the solution will result in high crystallinity and high average tensile strength in the fibers. Increasing the amount of polymer present in the solution improves the homogeneity of the fiber structure by reduction of the number of voids,<sup>80</sup> and maintaining a circular fiber cross section.<sup>67</sup> When the polymer content in the solution is high (~28%), the diffusion gradient between the polymer solution and the coagulant will be low, leading to slow dual diffusion and therefore less voids.<sup>69</sup>

But if the MW of the polymer is very high or ultra-high, then the solution may be difficult to dissolve, filter, and spin due to its high viscosity. Therefore either HMW polymers (300,000 g/mol) which can make 15 to 20% w/w of spinnable polymer solution are used, or ultra HMW polymers of low concentration of about 6% w/w are spun using a slight modification of wet spinning known as gel spinning.<sup>77</sup>

### Solvent

Various solvents are used for dissolving PAN-based polymers, including organic solvents such as *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAc), and aqueous solvents such as sodium thiocyanate (NaSCN, 51%), nitric acid (HNO<sub>3</sub>), and aqueous zinc chloride (ZnCl<sub>2</sub>).<sup>81–84</sup> All these solvents are difficult to recover and are unfriendly to the environment. But the most common solvents used in industry are DMF, DMSO, and DMAc, as these solvents are also used in polymerization, allowing the polymer to be directly fed into the spinning line.

The type of solvent used affects the viscosity of the polymer solution.<sup>85</sup> The solution viscosity determines its flow behaviour, sol-gel transition, and spinnability. The viscosity of the solution depends on the type of interaction between the polymer and the solvent. Depending on this, spinnable polymer solutions with different solid contents can be prepared. For instance, a 28% w/w spinnable PAN solution in DMF is possible due to the low viscosity of DMF. However, such high concentration of 28% w/w is not possible with DMSO.<sup>86</sup> Nonsolvents such as water have also been used in a definite ratio with an organic solvent (DMSO, DMF) to prepare PAN solutions in order to reduce their viscosity and make spinnable solutions.<sup>85</sup>

Ionic liquids have been used as solvents for polymer dissolution.<sup>87–90</sup> This is due to their nonvolatile nature which makes them ecofriendly. But there are concerns about their toxicity, as they easily dissolve in water and pose a threat to aquatic organisms.<sup>91</sup> These also cause degradation of the polymer during its dissolution.<sup>88</sup> The use of ionic liquids as a substitute for common organic industrial solvents remains questionable.

### Homogeneous Mixing and Deaeration

Polymer solution should be mixed well to obtain a homogeneous solution. Different types of high-speed custom built mixers are used.<sup>77</sup> Homogeneous mixing of the polymer solution is

required to prevent any blockages in the filter that might occur due to the presence of undissolved large particles.

Deaeration of the polymer solution is important to remove any bubbles or dissolved gases, which can result in voids or defects in the precursor fiber and carbon fiber produced from them.<sup>77</sup> The polymer solution is typically deaerated in vacuum for 24 h.

### Heating and Filtering of Polymer Solution

Increased dope temperatures are normally used, ranging from 70 to 100 °C.<sup>92</sup> Heating affects the dope viscosity and therefore its ease of spinning.<sup>93</sup> A higher concentration polymer solution that may not be spinnable at room temperature may be spinnable at higher temperature, as the polymer chains are able to move more freely due to higher kinetic energy.

Filtration of polymer solution is important to get rid of any insoluble material, including dust or dirt, which might be present in the solution as these can cause blockage in the spinneret. The solution is filtered before pumping through the spinneret.<sup>69</sup> Different size inline filters are used to filter the dope. A 140 μm Swagelok inline screen filter was used to filter the dope by Morris *et al.*<sup>77</sup>

The above-mentioned parameters enable the production of a polymer solution that can spin a homogeneous PAN-based precursor fiber with minimal defects.

## SPINNING OF PAN POLYMER SOLUTION INTO PRECURSOR FIBER

Precursor fibers that will have a high average tensile strength should possess special characteristics, including being circular, having a homogeneous sheath and core, smoothness, fineness (10–12 μm), having a broad exothermic peak, having at least 90% crystallinity, and a high carbon yield (>50%). A smooth surface morphology for precursor fiber is indicated by a high level of lustre, which is an important feature for a high quality PAN-based precursor fiber. A high-quality PAN fiber should have minimal voids. A homogeneous sheath and core structure of PAN precursor fiber will provide high tensile strength to the carbon fibers.

### Formation of a Circular PAN Precursor Fiber from Polymer Solution

Circular PAN fiber cross sections are necessary to obtain good physical and mechanical properties of carbon fibers. The cross sectional shape of the fiber depends on the coagulation process.<sup>68</sup> Any deviation from a circular cross sectional shape affects the mechanical properties of the fiber.<sup>94</sup> Other types of cross sections can be made depending on the requirement of the fiber properties. For instance, a triangular cross section produces high lustre PAN.<sup>94</sup>

Circular fibers are considered to be better precursors, as the stress is distributed in all directions in a symmetric fashion, thus preventing fiber breakage during the carbon fiber formation process. Moreover, circular fibers are more evenly heated when passed through the oxidation and carbonization ovens. Fibers with noncircular cross sections cannot bear a high draw ratio during spinning, oxidation, and carbonization.<sup>78</sup> Although precursor fibers with circular cross sections are required to be

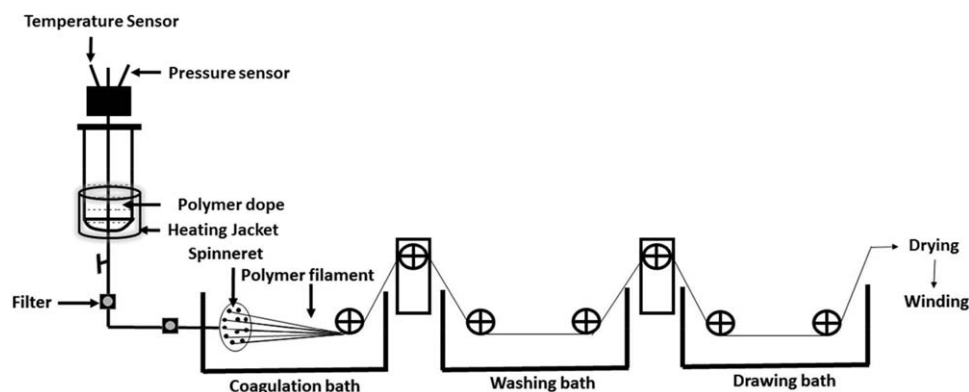


Figure 2. Wet jet spinning set-up.

obtained, for some applications, noncircular fibers are preferred in carbon fiber reinforced plastics. The noncircular fibers have a higher ratio of surface area to volume, which enhances the fiber-matrix bonding that increases the compressive strength of the carbon fiber reinforced plastics.<sup>95</sup> The coagulation bath temperature and concentration are the most important factors that decide the shape of the fiber cross section. This is discussed later in the review.

#### Minimizing the Voids and Defects in PAN Precursor Fiber

Voids and defects in the PAN precursor fiber and the carbon fiber are the main cause of reduction in tensile strength.<sup>96</sup> There is a chance of development of voids at various stages of wet spinning. The voids formed are of different shapes, such as cylindrical, elongated, or circular, depending on their cause.<sup>77,97,98</sup>

Voids are formed during the preparation of the polymer solution in which dissolved gases and bubbles if not deaerated result in the formation of circular voids.<sup>77,99</sup> These voids also result from impurities in the dope, such as dirt or dust. Tear-shaped voids are formed in the fiber due to imperfections in the spinneret holes.<sup>97</sup> This causes the penetration of solvent into the fiber through these voids. Voids are also formed due to very fast removal of residual solvent from the fibers, leaving behind open pores.<sup>100</sup> The size of the void is another important factor that is affected by the coagulation conditions.<sup>101</sup>

The number of pores reduces with increasing polymer content.<sup>80</sup> Increased stretching also leads to pore collapse and hence less voids.<sup>102</sup> It is important that any activity involving carbon fiber production, starting from polymer synthesis to producing a carbon fiber, be done in clean room conditions with laminar air flow filters.<sup>103,104</sup>

#### Preferred Method of Spinning PAN Polymers into High-Quality Precursor Fibers

Solution spinning is the traditional method used commercially for producing PAN precursor fiber since this provides a reliable and robust route to carbon fibers with the best strength properties.

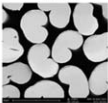
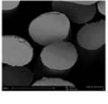
There are many parameters that need to be optimized in solution spinning. Researchers have attempted to optimize one or two parameters in their reported literature works. Studies were

reported using different spinning lines that differ in their configurations and therefore results obtained from these studies are not comparable. Moreover, the starting polymer materials in the various studies are diverse, which makes the results obtained in different studies also not comparable. The solution spinning can further be done in different ways referred as wet jet spinning, air gap spinning, and gel spinning.

The quality of the precursor fiber has a large impact on carbon fiber performance, production yield, and cost.<sup>105</sup> Understanding and controlling the structure of the precursor fiber during spinning can significantly improve the tensile strength of the carbon fibers without using harsh surface treatments or high temperatures later during conversion of precursor fiber into carbon fiber.<sup>2</sup> This initiative can reduce costs and minimize use of harsh chemicals on the precursor fiber.

Other spinning techniques that have been used but did not result in high strength PAN-based fibers are melt, dry, and electrospinning. Melt spinning is used for spinning polymers that melt without being degraded and is a much cheaper method of producing fibers. The molten polymer is extruded through a spinneret and then the fibers are solidified by cooling in air.<sup>106</sup> PAN fibers are difficult to melt spin as they degrade below their melting point, but by using certain additives that lower its melting point it can be made spinnable. Additives such as water and water-soluble polyethylene glycol have been used.<sup>107</sup> Additionally, different comonomers have been added to PAN to reduce its melting point, hence making it easily melt spinnable.<sup>106,108</sup> The fibers produced using melt spinning contain many internal voids and surface defects.<sup>7</sup> The melt spinning process can be optimized to produce better quality fibers.

In dry spinning, the polymer is dissolved in a suitable solvent and then pumped through the spinneret and forced into a chamber containing inert gas or air.<sup>86,109</sup> The solvents used in dry spinning are required to have high vapour pressure (e.g. DMF) to facilitate evaporation. PAN fibers have been produced by dry spinning, but only to obtain textile grade PAN and not to produce carbon fiber precursor, since it introduces significant numbers of defects into the fiber. Electrospinning has been used to spin polymer solutions and obtain fiber mats.<sup>110</sup> This is a quick method to check the spinnability of PAN dopes. In electrospinning the fibers produced are much thinner ( $\sim 0.3 \mu\text{m}$ )

DMSO concentration	Cross section shape	Average tensile strength (cN/dtex)
< 45%	<p>Bean</p> 	0.49
> 65%	<p>Circular</p> 	0.72

**Figure 3.** Cross section and tensile strength of the nascent fiber for different solvent (DMSO) concentrations.<sup>67,95</sup>

than those produced from conventional spinning ( $\sim 10\text{--}12\ \mu\text{m}$ ) methods. In electrospinning the fibers are short and are collected in the form of fiber mats rather than a continuous fiber.<sup>10</sup>

### Role of Spinneret Parameters

Spinneret shape and the hole size determines the cross sectional shape and diameter of the fiber, respectively. Spinnerets are available that can produce fibers with different shapes, including circular, triangular, or rectangular.<sup>94</sup> The variation in hole diameters is from 0.05 to 0.5 mm depending on the diameter of the precursor fiber that is aimed for.<sup>64,68,76–78,82,88,95,102,111–115</sup> The number of spinneret holes decide the number of fiber filaments. After the fibers are spun, these are combined together in a bundle to form a fiber tow. Tows containing 1 to 3000 fiber filaments have been used for lab scale spinning.<sup>64,67,76–78,94,111–114,116</sup> While for industrial scale spinning much bigger tows are used consisting of 1000 to 350,000 filaments. In industry, smaller tows with (1–24,000) filaments are used for aerospace applications.<sup>11</sup> This is because variation on carbon fiber yield is only 3% which ensures better quality carbon fibers. For tows made from filaments higher than 24,000 filaments, the variation on yield can be up to 15%.<sup>11</sup> Nevertheless, producing bigger tows can save the cost of producing carbon fibers.

### Wet-Jet Spinning

Wet-jet spinning of PAN precursor polymer was patented by DuPont in 1946.<sup>117</sup> Figure 2 shows the basic set up of wet jet spinning. In this process, a viscous polymer solution is extruded through small holes of a spinneret immersed in a solvent bath. When the polymer dope comes in contact with the coagulant in the bath, a dual diffusion process occurs between the freshly

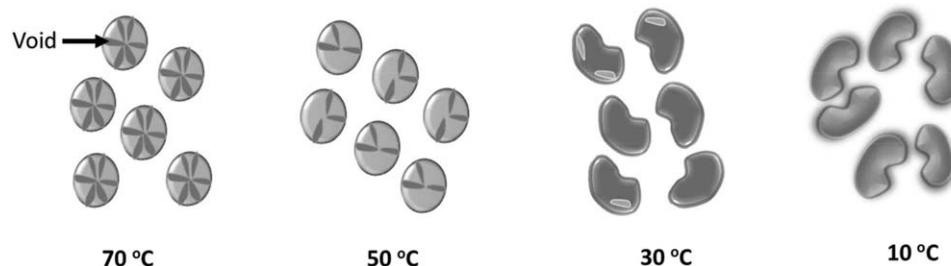
formed polymer fluid filament and the bath containing a mixture of solvent plus a nonsolvent (usually water). The two diffusion processes that occur are: outflux of the solvent and influx of the nonsolvent. When the concentrations of polymer, solvent, and nonsolvent are in equilibrium, the polymer coagulates in the form of a fiber.<sup>78</sup> This process is called coagulation and this occurs within 10 to 50 s.<sup>80,116</sup> During coagulation the fiber solidification starts from the boundary and moves towards the centre as a result of diffusion.<sup>78</sup> The rate of diffusion controls the coagulation and shape of the fiber.<sup>69</sup>

There are certain variables that affect the rate of diffusion during coagulation and therefore determine the fiber shape and size. These are coagulant concentration, coagulant temperature, and the amount of stretching in the coagulation bath, also called jet stretch. These are explained in the following sections.

### Effect of Coagulant Concentration on Cross Sectional Shape and Strength of the Precursor Fiber

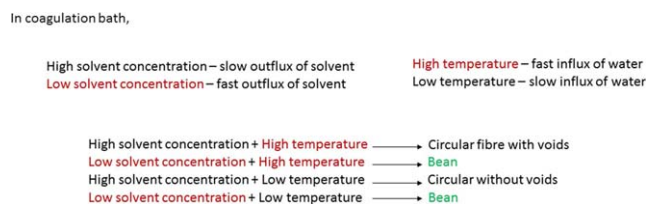
The shape of the PAN precursor fiber cross section depends on the rate of diffusion during the coagulation process. The rate of diffusion directly affects the rigidity of the solidified fiber layer formed due to phase separation. A soft skin results in a circular cross section while a rigid skin results in noncircular (bean-shape) cross sections. Figure 3 shows the cross section of PAN nascent fiber for different solvent concentration<sup>95</sup> at 50 °C coagulant temperature. At high solvent concentrations >65%, e.g., (DMSO/Water 70:30) in coagulation bath, due to a lower diffusion gradient the diffusion process is slow. This leads to less outflux of solvent and consequently less water can influx *via* counter-diffusion. The diffusion occurs from the fiber surface as well as from within the fiber. This forms a structure which is dense and compact throughout, with fewer voids, leading to a circular cross section.<sup>95</sup> PAN precursor fibers with circular cross sections have higher average tensile strength (0.72 cN/dtex).<sup>67</sup>

When the solvent concentration is low (<45%), the diffusion gradient is higher, leading to faster diffusion, causing more rapid outflux and producing a bean-shaped PAN precursor fiber and these have lower average tensile strength (0.49 cN/dtex). Diffusion occurs rapidly from the fiber surface and solidifies the surface. This solid fiber surface restricts further diffusion from inside the fiber. This forms a fiber structure which is solid at the boundary while fluid on the inside which causes the fiber to shrink, leading to a kidney shaped structure with voids.<sup>95</sup>



**Figure 4.** Effect of coagulation temperature on cross sectional shape and homogeneity of fibers (redrawn from Ref. 80)—Reprinted by Permission of SAGE Publications, Ltd. – Copyright 1963.





**Figure 5.** Schematic representation of the effect of combination of coagulation variables on the shape of the PAN precursor fiber. Red colour represents variables leading to fast coagulation while black colour represents variables leading to slow coagulation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Effect of Coagulant Bath Temperature on Cross Sectional Shape and Strength of the Precursor Fiber.** Figure 4 shows the effect of coagulation temperature on cross sectional shape and homogeneity of PAN precursor fibers. The effect of bath temperature on the fiber structure was seen in different spinning systems. In this the coagulant bath concentration was 55% DMSO solvent which is considerably high. High bath temperature ( $\geq 40^\circ\text{C}$ ) causes more influx rate of nonsolvent (compared to outflux rate). This results in high rates of diffusion resulting in faster coagulation. Higher bath temperatures lead to the formation of circular cross sections (Figure 4).<sup>80</sup> These circular fibers formed *via* fast diffusion have low density due to the presence of voids.<sup>80</sup> At low temperature, the influx rate of nonsolvent is low (compared to outflux rate), leading to slow diffusion and resulting in bean-shaped fibers (Figure 4). Bean-shaped fibers have high density and less voids, as these are formed *via* slow diffusion.<sup>80</sup>

The coagulation variables influence the strength of the freshly coagulated fiber. PAN precursor fibers with circular cross sections have higher average tensile strength when formed by slow diffusion process and poor average tensile strength (0.59 cN/dtex) when formed by fast diffusion. The bean-shaped fibers show higher density and higher average tensile strength (0.677 cN/dtex) when formed by a slow diffusion process and poor strength when formed by a fast diffusion process.<sup>67</sup> The coagulation variables should be optimized to produce a circular and homogeneous fiber. These fibers should be produced by a slow diffusion process so that they have high average strength.

In summary, Figure 5 shows schematic representation of the effect of combination of coagulant concentration and coagulant temperature on the precursor fiber shape.

**Effect of Jet Stretch on Diameter and Strength of Precursor Fiber.** Jet swell refers to swelling of the fiber in the coagulant bath due to diffusion during wet spinning.<sup>111</sup> To cope with fiber

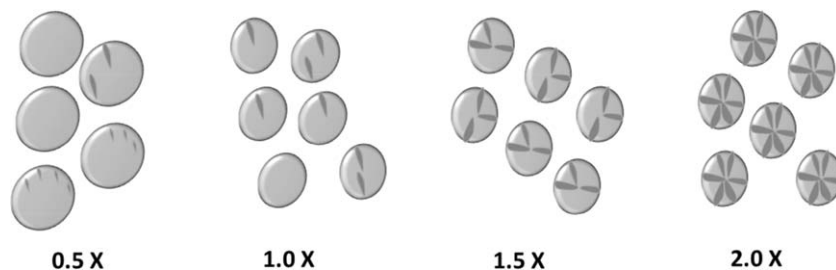
swelling, the fiber has to be stretched. This is referred to as jet stretch. Jet stretch prevents relaxation of the PAN chains and maintains a stretched state. The amount of stretching applied on the fiber without breakage depends on the velocity of swelled fiber and not the extrusion velocity ( $V_0$ ) of the spinning solution from the spinneret as this does not consider fiber swelling.

A freely extruded fiber without any jet stretch can lead to voids due to disorientation and relaxation of PAN molecules and random coil chains due to jet swell and radial expansion of the fiber. Figure 6 shows that when jet stretch is low ( $0.5\times$ ), the fiber diameter is larger and has more voids due to more influx of the nonsolvent, as the fiber remains in the coagulation bath for a longer period. When medium jet stretch is applied, high density is obtained in the fibers. When jet stretch is too high, more voids are seen that result from defibrillation due to stretching.<sup>111,118</sup> Therefore the required jet stretch for production of a high-quality PAN precursor fiber is a medium jet stretch ratio of 1. This means that the fiber should be stretched to obtain a diameter equal to that of the spinneret hole.<sup>111</sup>

The jet stretch affects the tensile strength of the freshly coagulated PAN precursor fibers. High jet stretch produces higher strength fibers. High jet stretch helps the outward diffusion of the solvent and aligns the polymer chains and prevents the entry of nonsolvent into the core.<sup>82</sup> These aligned polymer chains tend to push the solvent out during the alignment process. More alignment gives high density to the fibers.

After coagulation, the solid fiber is washed to remove residual solvents using water. Washing leads to high diffusion of water into fiber, which can cause large voids. This causes reduction in fiber strength, as the void size increases due to high water influx.<sup>86</sup> Therefore a combination of water and organic solvents in a defined ratio is used, to prevent rapid influx of water. To do so, more than one washing bath is used. The high solvent concentration bath is placed nearest to the coagulation bath, which leads to formation of denser filaments with less voids.<sup>119</sup>

**Drawing/Stretching.** After washing the precursor fibers are drawn. Drawing enhances the axial orientation of the PAN fibrils. High crystallinity increases the average strength and modulus of the fibers.<sup>80,102,118</sup> In the stretching process, the fiber is heated above its  $T_g$  (glass transition temperature) where it becomes soft and flexible and can be stretched to about 10 times the original fiber length, usually in hot water or steam.<sup>86</sup>



**Figure 6.** Effect on fiber homogeneity of increasing jet stretch (redrawn from Ref. 80)—Reprinted by Permission of SAGE Publications, Ltd. – Copyright 1963.

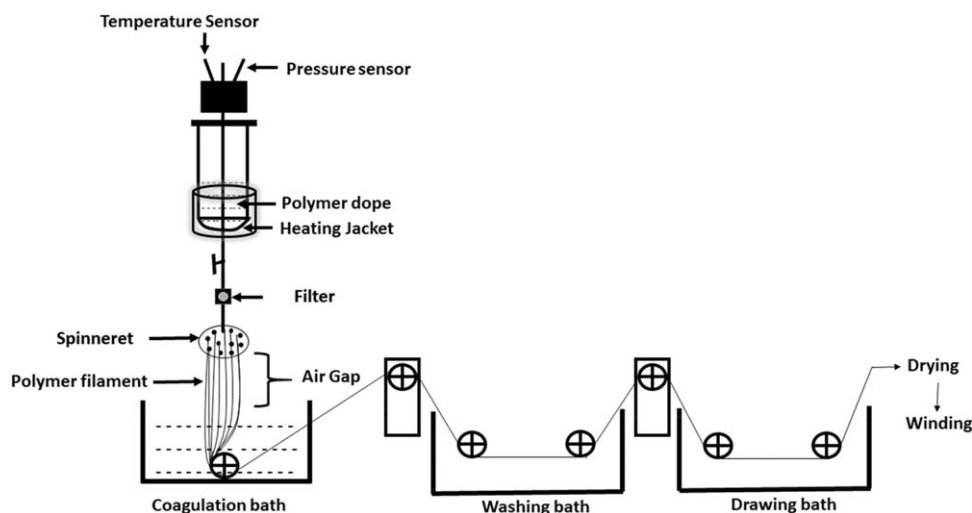


Figure 7. Air gap spinning.

The drawn fibers have reduced diameter due to stretching of polymer chains and collapsing of pores. The pores that are formed in the washing step get stretched during the drawing process. If the fibers are overstretched, this leads to defibrillation and causes fiber breakage.<sup>82</sup> Therefore the maximum jet stretch ratio should be decided carefully. The drawing step involves various variables such as draw ratio, feed velocity, delivery speed, draw medium, temperature of drawing, and number of drawing stages.<sup>86</sup>

Drawing is the main area where commercial manufacturers have attempted to improve the average tensile strength of the precursor fibers. Mitsubishi achieved a drawing ratio of 4.5 times which was higher than the conventional 2.9 to 4.3 times.<sup>120</sup> Further increase in drawing ratio of up to 15 times was achieved by Mitsubishi by performing drawing in multisteps in warm water with temperature inclination. The resulting fiber was initially dried with heated rollers at 50 to 100 °C and subsequently dried at 150 to 230 °C to make the draw ratio 15 times.<sup>121</sup> Toray performed drawing using a ratio of 2.5 to 6 in a heated bath and further drawing was done in a pressurised steam of 160 to 180 °C, giving a total draw ratio of 20.<sup>122</sup> High drawing ratios of 15 to 20 times have obtained average tensile strength of 20 g/denier.<sup>123,124</sup> Further to this, attempts were made by Mitsubishi to further draw the PAN-based fiber to 25 times their original length in an atmosphere of pressurised steam.<sup>125</sup> All these attempts to achieve a higher drawing ratio were made to produce a precursor fiber with higher tensile strength.

Fiber finishing is carried out after the drawing process. During this, a chemical treatment is applied to the fiber to assist it through the subsequent steps of drying and collapsing. Oil treatment in a bath, particularly silicone oil, has been used by Toray for treating PAN-based fiber. This treatment prevents the fibers from sticking together to obtain carbon fibers of high average tensile strength.<sup>126</sup>

**Postspinning.** Postspinning refers to enhanced stretching of the precursor fiber under different chemical and heat conditions. Such treatment have a direct benefit of improving the

orientation and strength of the fiber.<sup>9,127</sup> Precursor fiber needs to be thinner to produce carbon fibers with 4.5 to 5 μm in diameter than the existing 7 to 8 μm.<sup>9</sup> Thin fibers help in uniform stabilization avoiding the skin-core structure. These treatments also indirectly help induce cyclization reaction and reduce the exotherm during thermal conversion.<sup>128</sup> Postspinning modifications have been made by coating or impregnation of chemicals and by stretching fibers in plasticizer.<sup>21</sup> Various plasticizers such as DMF (10–80%), DMSO (20–80%), hot solution of copper chloride (5–20%), zinc chloride (10–30%), supersaturated steam, acetic acid, boric acid,<sup>129</sup> and succinic anhydride reduce the dipole interactions between the nitrile groups of PAN-based polymers, thus help stretching.<sup>9,130,131</sup> Chemicals such as potassium permanganate (KMnO<sub>4</sub>),<sup>128</sup> cobalt sulfate (CoSO<sub>4</sub>),<sup>132</sup> cobalt chloride (CoCl<sub>2</sub>),<sup>133</sup> have been used to impregnate the spun fibers. These transition metal compounds have vacant *d* shells which can accept electron from N (nitrogen atom) of C≡N, thus help in cyclization. Carbon fiber strength increased from 2.1 to 4.2 GPa in KMnO<sub>4</sub><sup>128</sup> and from 2.5 to 3.2 GPa in CoSO<sub>4</sub>.<sup>132</sup> Coating of spun PAN-based fibers with lubricants can increase the carbon fiber strength as these prevent inter fiber cohesion which is the cause of breaks. Examples of various lubricants that have been used are silicone oil, fatty acid derivatives, guar gum, etc. It has been seen that most of the postspinning experiments have been done on commercial fibers. These commercial fibers already have some finishes on them which may prevent the chemicals from penetrating into the fibers. Therefore postspinning treatments on freshly coagulated fibers may be more beneficial.

Postspinning treatments have only been proven to improve strength at lab scale and are not being used commercially. This is because the industrial method of carbon fiber production have been well established and are producing fibers with promising strength for current applications. In order to obtain fibers with extremely high strength such as next generation carbon fibers, the gap between the achieved average tensile strength and the theoretical strength needs to be bridged. This can be done by using postspinning treatments at commercial scale.

### Air Gap Spinning

In air gap spinning the dope is extruded into an air gap<sup>134</sup> followed by a similar coagulation process as conventional wet spinning, with all the same variables. Figure 7 shows fiber production using air gap spinning. The cross sectional shape of the fiber is controlled by varying the air gap.<sup>135</sup> A range of air gap distances is used, normally in the range 0.05 to 25 mm.<sup>77,82,88,135,136</sup>

Air gap spinning is generally faster than wet spinning.<sup>137</sup> In air gap spinning, the jet stretch can be increased for faster spinning without actually increasing the stress on the fiber. This is because lower forces act on the polymer solution in the air gap compared to the coagulation bath.<sup>119,137</sup> Much finer and smoother fibers are obtained. In air gap spinning the dope is spun at higher temperature, therefore solutions with higher concentrations can easily flow due to heating. High concentration polymer solutions will therefore produce fibers with high average tensile strength.

Although air gap spinning is a faster and better method of producing high-quality PAN precursor fiber, it is not a preferred method in industry because of challenges involved in handling of the fibers in the air gap which can introduce defects. Industry mainly uses the traditional method of wet jet spinning, as this method has been thoroughly understood and optimized over the years. Nevertheless, a few attempts have been made by Toray in order to enhance average tensile strength of carbon fibers.<sup>138</sup> Using this method average carbon fiber strength of 580 kg/mm<sup>2</sup> or 5.6 GPa was achieved as the fibers could be drawn up to seven times.<sup>138</sup>

### Gel Spinning

Wet spinning and air gap spinning are used for commercial production of PAN polymer of MW upto 200,000 g/mol. For HMW or UHMW polymers, gel spinning is used which is a slight modification of wet spinning. In this a three-dimensional gel network of polymer solution is formed by keeping the polymer solution at a specific temperature (called thermal induced gelation) or definite time before spinning.<sup>139</sup>

Since HMW polymer solutions have a lower polymer solids content to keep their viscosity in the spinnable range, it is more challenging to coagulate these solutions using wet spinning. Such solutions lead to the formation of a large amount of pores which cause strength reduction, but using gel spinning for HMW polymers can lead to increased drawability which can increase strength.<sup>115</sup> In this process, two modifications are made to the conventional wet spinning process. Either a low temperature coagulation bath is used that helps the spinning solution to gel, or pregelling the polymer solution takes place at 25 °C over a period (2–3 h) before spinning.<sup>115,140</sup> In recent publication, very high average tensile strength (5.5–5.8 GPa) and average tensile modulus (354–375 GPa) carbon fibers have been achieved by gel spinning of PAN precursor polymer with CNTs.<sup>141</sup>

Gel spinning is possible for PAN due to the dipole-dipole interactions between the nitrile groups in the polymer dope, leading to the formation of cross-links.<sup>93</sup> Gel-spun fibers have reduced

core-shell differences, circular cross sections, fewer internal pores, and higher crystallinity.<sup>140</sup>

### CONCLUSIONS

This review identifies opportunities for producing high-quality PAN fibers by improving polymer characteristics, control of spinning, and postspinning conditions. Use of HMW polymers for wet spinning is uncommon due to difficulties in producing dopes containing high polymer content, as the solutions formed are too viscous to wet spin. But HMW polymers synthesized using advanced polymerization techniques such as RAFT can form solutions that have high polymer content but have dope viscosities which are straightforward to spin. Optimizing the comonomer content and distribution to make polymers which are easy to dissolve in solvents, can act as plasticizers for stretching fibers, can contribute to cyclization during thermal oxidation without reducing the carbon fiber yield during carbonization can help to achieve high-quality precursor fibers. Further, spinning process parameters need to be optimized to obtain a high-quality precursor. Enhanced stretching of the fibers by postspinning treatments can directly benefit the orientation and strength of the precursor fibers. Other advanced spinning techniques such as air gap and gel spinning can lead to production of high-quality precursor fibers. Production of high-quality PAN-based precursors is complex, but this review outlines that there is plenty of scope for research to produce premium quality precursor fiber for production of new generation carbon fiber.

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