Carbon Fibers Derived from Commodity Polymers: A Review

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Abstract

Carbon fiber composites are prohibitively expensive for a wide array of applications that would greatly benefit from their superior specific strength and specific stiffness. Replacing the market-dominant carbon fiber precursor material, polyacrylonitrile, with a low-cost alternative would significantly reduce the cost of carbon fiber production. Commodity polymers may provide such an alternative thanks to their abundance and ease of production into fibers. This review presents state-of-the-art carbon fiber production from polyacrylonitrile, an overview of melt-spinnable alternative precursors broadly, and an in-depth review of the latest advances in the synthesis of carbon fibers from low-cost, commodity thermoplastics such as polyethylene, polyamide, polystyrene, polyester, and poly(vinyl chloride).

Keywords: low-cost carbon fiber, alternative precursor, commodity plastics, synthetic polymers, melt spinnable, conversion methods

Abbreviations

CFRP	Carbon fiber reinforced polymers
CPVC	Chlorinated poly(vinyl chloride)
EtOH	Ethanol
HDPE	High-density polyethylene
HRTEM	High resolution transmission electron microscopy
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
PA 6	Polyamide 6
PA 6,6	Polyamide 6,6

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PAN	Polyacrylonitrile
PBO	Poly(p-phenylene-2,6-benzobisoxazole), Zylon
PE	Polyethylene
PE-g-VTMS	Polyethylene graft vinyl trimethoxysilane
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Poly(vinyl chloride)
ReaxFF	Reactive force field
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UHMWPE	Ultra-high molecular weight polyethylene

1 Introduction

Carbon fibers are thin filaments containing at least 92 wt% carbon atoms arranged in planar hexagonal networks [1]. Consequently, they possess high elastic modulus (up to 940 GPa for pitch-derived carbon fibers) and strength (up to 5.7 GPa for polyacrylonitrile-derived carbon fibers) as well as low density due to their atomic composition [2]. Combining these fibers with a polymer resin matrix forms a composite material, called carbon fiber reinforced polymer (CFRP) composites, that can be formed into rigid components with tailored directional properties for great weight savings compared to conventional engineering metals [3]. These properties have been leveraged in cost insensitive applications, such as motorsports, aerospace, and high-end sporting equipment, for decades, but broader adoption has been limited by the high cost of carbon fiber production [4]. CFRP composites have the potential to greatly improve the energy efficiency of human mobility, the productivity of renewable power generation, and resilience of domestic infrastructure if they were less costly [5–7]. Accordingly, research and development has been focused on reducing the cost of CFRP composites by reducing the cost of producing carbon fibers. This would allow for broader application to address the most pressing socio-economic and environmental challenges worldwide [8].

Generally, high-performance carbon fibers suitable for structural applications are produced by exposing organic fibers, called precursor fibers, to high temperatures to expel the fibers' noncarbon atoms [9,10]. The chemical and microstructural properties of the precursor fibers greatly affect the properties of the resulting carbon fibers [11] and contribute more than half of the cost of a completed carbon fiber [12]. Therefore, material selection and precursor fiber spinning parameters must be carefully considered. Not all organic materials are suitable for this conversion procedure and of the materials that have been successfully converted into carbon fibers only two are of commercial significance today: polyacrylonitrile (PAN), and mesophase pitch. PAN precursors account for 90% of the carbon fiber market with the remainder derived from pitch [12]. Thus, reducing the cost of carbon fiber production begins with replacing PAN with a low-cost alternative precursor material. Two main factors affect the cost of the precursor: the feedstock materials and the fiber spinning method required. Many materials have been considered over the past several decades including textile-grade PAN, biopolymers such as lignin and cellulose, and pitch with limited success. Recently, commodity plastics have received growing attention as an alternative precursor because they are globally abundant and can be spun into fibers at much lower cost due to the simplicity of the fiber melt spinning process compared to the solution spinning process required for PAN precursors.

In this review we will present the contemporary PAN-derived carbon fiber production process as a baseline, introduce the fiber melt spinning process as a framework for selecting a low-cost precursor, briefly discuss the broader families of melt spinnable precursors, and present recent progress towards converting common melt-processible commodity plastics into carbon fibers.

1.1 Contemporary PAN-based Carbon Fibers

Contemporary carbon fiber production from PAN requires solution spinning PAN into fibers, thermo-oxidatively stabilizing the fibers in air in the temperature range of 200-400°C, then carbonizing the fibers at high temperature in the range of 1000°C to 1700°C [2,9,13,14]. Ultra-high performance carbon fibers can be created by graphitizing the fibers at temperatures ranging from 2500°C to 3000°C after carbonization [14,15], but this is an expensive procedure often reserved for special applications. PAN achieved dominance as a precursor due to its relatively high carbon yield, highly tunable processing parameters, and the superior properties of the carbon fibers it yields [16,17]. Although this precursor is referred to simply as PAN, it is most commonly a copolymer of PAN and another acrylic comonomer, such as acrylic acid, methacrylic acid, or methacrylate amongst others, to improve drawability [18]. The critical advantage of PAN is that the material can be stabilized at temperatures below its melting point, thereby retaining the fibers' morphology during subsequent thermo-oxidative stabilization. Strong interactions of highly polar nitrile groups allow for the cyclization of PAN molecules in the temperature range of 180-250°C whereas it melts at 317°C [11,19,20]. However, producing PAN fibers is expensive; the precursor fibers account for 53% of the total cost of a carbon fiber [12]. Because PAN cyclizes and degrades before it melts, it must be dissolved in a highly polar solvent, such as dimethylformamide or dimethyl sulfoxide, to be spun into fibers [21]. This process is called solution spinning, which is subdivided into three types: wet spinning, dry-jet wet spinning, and dry spinning. Wet spinning is the most common method of solution spinning employed to form PAN fibers and involves the injection of a PAN/solvent solution from small orifices into a solvent/non-solvent coagulation bath to induce the precipitation of fibers, **Fig. 1** [22]. Dry-jet wet spinning is a modification of wet spinning wherein an air gap of 10-200mm is established between the point of extrusion and the coagulation bath [11]. It can enable non-circular fiber cross sections and result in greater mechanical properties, faster spinning, and higher solid content [18]. However, it is limited to filament counts less than 12,000 whereas wet spinning can achieve filament counts greater than 50,000 [11]. Both wet spinning processes involve a series of coagulation baths of different compositions and temperatures to achieve the desired fiber shape, dimensions, and properties by controlling the flux of solvent out of and water into the fiber [23,24]. The fibers are typically stretched after they are formed to improve molecular alignment, dried to remove water content, and relaxed to reduce internal stresses induced by the stretching process following their formation [11,25]. The wet spinning process is relatively slow because it is limited by the rate at which the fibers can form while achieving desired properties, and it is expensive because it requires constant maintenance, turnover, and disposal of the hazardous coagulation bath solution [12].

Dry spun fibers are formed by extruding a polymer solution into a heated gas atmosphere where the solvent evaporates leaving a solidified fiber. A suitable solvent for this process must not only readily solvate PAN but must also have a low vapor pressure and high stability with PAN at its boiling point. Accordingly, dimethylformamide or dimethylacetamide are commonly used [26]. The dry spinning process enables the production of fibers with non-circular cross sections but requires careful control of the drying process so that enough solvent is retained as a plasticizer whilst capturing as much solvent as possible to be reused and prevent pollution. The complicated equipment required to achieve the desired fiber morphology and safely contain the vaporized volatile organic solvents makes this a costly process. The dry spinning of acrylic fibers was well-reviewed by Imura et al. in 2014 including a schematic of a typical acrylic fiber dry spinning system, shown in **Fig. 2** [27].

Replacing the solution spinning process with a more economical fiber spinning method may greatly reduce the cost of producing precursor fibers and thus carbon fibers. An attractive alternative to wet spinning is melt spinning, which is one of the most popular fiber spinning methods due to its simplicity, high throughput, and low cost.

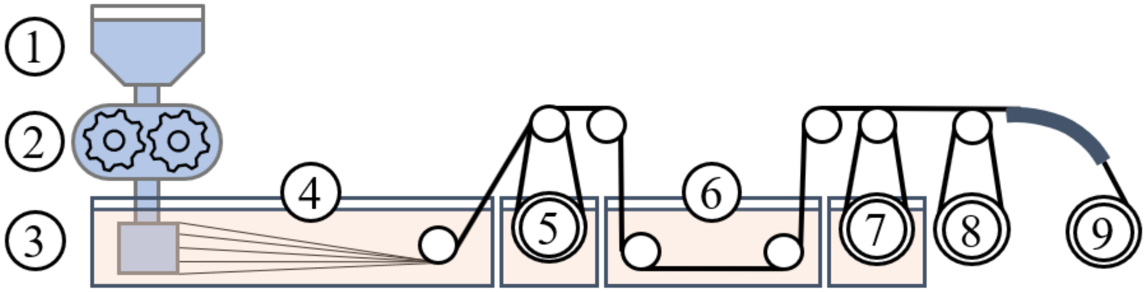

Fig. 1. Abbreviated schematic of a wet spinning line composed of 1) polymer solution reservoir, 2) metering pump, 3) spinneret, 4) coagulation bath, 5) washing bath, 6) drawing bath, 7) secondary washing bath, 8) drying godet, and 9) dry-heated stretching and takeup [22]. Wet spinning lines can feature several washing baths in series to achieve proper solvent exchange [24]

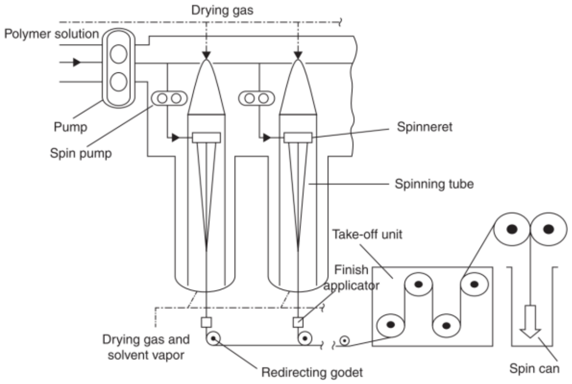

Fig. 2. Schematic of a typical dry-spinning system for acrylic fibers [27].

1.2 About Melt Spinning

Fiber melt spinning is used extensively to produce textile fibers for numerous applications. Melt spinning involves the extrusion of melted polymers through small orifices. The extruded material cools in air and solidifies in the form of fibers. The fibers are drawn down in diameter during the cooling process to improve molecular alignment. Additional drawing may be applied to further reduce fiber diameter and increase mechanical properties [28], as shown in **Fig. 3**. The fiber formation process is highly controllable through many parameters and is very well understood because it has been practiced for hundreds of years. Consequently, many resources have been compiled that provide great depth on the topic of melt spinning. The authors refer the reader to the recent review by Hufenus et al. [29] for a broader and deeper technical discussion of the fiber melt-spinning process. Crucial to the reduction of carbon fiber production cost, the throughput of melt spinning far exceeds that of solution spinning and does not require the maintenance and disposal of large quantities of solvents. Many natural and synthetic materials can be melt spun, and many of these materials have been demonstrated as suitable carbon fiber precursors. Four main categories of melt-spinnable carbon fiber precursors have arisen: melt-processible PAN [30–32], mesophase pitch [33–35], biomaterials such as lignin and cellulose [10,12], and synthetic polymers (Sections 3-7). In this review, we will acknowledge the first three with a brief review of their current state and challenges, which will motivate an in-depth discussion of the nascent field of commodity synthetic polymer conversion to carbon fiber.

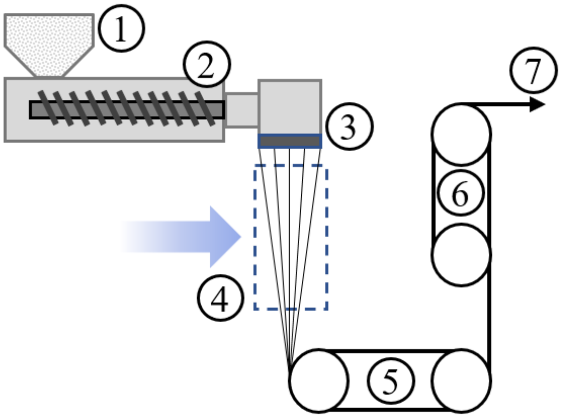

Fig. 3. Schematic of a generalized melt spinning line composed of 1) pelletized resin input hopper, 2) single screw extruder, 3) spin pack with orifices for fiber extrusion, 4) convective air-cooling region for fiber solidification, 5) initial collection rollers for internal stress relaxation, 6) heated drawing rollers for additional fiber diameter reduction and molecular alignment, and 7) exit to final takeup onto spools [29].

2 Melt-spinnable Alternatives to Wet-Spun PAN

2.1 Melt-Processible PAN

The benefits of melt spinning over wet spinning have prompted many attempts to develop a melt-spinnable formulation of PAN; it has been shown that melt processible PAN would be cost-competitive with commodity fibers and could reduce the cost of PAN precursor fibers by more than 30% [30,31]. In general, melt-processible PAN is enabled by interrupting PAN’s strong nitrile-nitrile bonds with the addition of a non-solvent plasticizer or other monomers to reduce its melting temperature below its decomposition temperature [32]. Water was discovered to be an effective plasticizer for PAN in 1948 [36] and has received great attention due to its benignity. In 1988, Grove et al. [37] first demonstrated the synthesis of carbon fibers from water-plasticized PAN with a notable average tensile strength of 2.5 GPa and a tensile modulus of 174-214 GPa, but they also showed significant porosity and surface defects, which led to inconsistent and broken fibers. Despite these results, work on water-based plasticizers has continued; In 2019, Yu et al. [38] demonstrated the effect of water on the melting temperature and viscosity for PAN melt spinning, and Yu and Baird [39] showed that a mixture of water and ethanol (PAN/H_2O/EtOH at 70/15/15 wt%) could significantly reduce the size of voids in melt processed PAN fibers (**Fig. 4ab**). However, the authors did not publish properties for carbon fibers derived from these precursors.

Organic plasticizers, such as ethylene carbonate [40], propylene carbonate [40,41], gamma-butyrolactone [42–45], N-acetyl morpholine [42,46], ethylene cyclic sulfite [43], dimethyl sulfoxide, succinonitrile, dimethyl sulfoxide dimethyl sulfoxone [47], various ethylene glycols [48,49], formamide, acetamide, ethyl cyanoacetate [48], acetonitrile [45,50], C_1 to C_2 nitroalkanes and C_1 to C_4 monohydroxy alkanol with methanol [51], and glycerol [49,52,53], alone or in some combination often including water, have also been used to make melt processible PAN. Although data on the mechanical properties of carbon fibers derived from melt-spun PAN fibers formulated with organic plasticizers is scant, recent studies have shown that stabilization of these fibers yields the same functional groups found in conventional PAN precursor fibers after stabilization, more stable release of volatiles [52], a higher degree of stabilization, reduced skin-core structure, and higher density [54] than conventional PAN precursor fibers. However, the evolution of these compounds must be carefully controlled to minimize the formation of deleterious voids in the precursor fibers during formation. This can require a complex spinning apparatus involving pressurized chambers, inert atmospheres, and series of fiber conditioning rolls (**Fig. 4c**) [50]. The formation of voids and the complex apparatus to minimize their formation have limited the commercial adoption of this method.

Ionic liquids have received growing interest as a non-solvent PAN plasticizer because they are easy to handle, produce few volatile compounds unlike organic plasticizers, and can improve carbon yield by co-carbonizing with the precursor material [55–57]. 1-Butyl-3-methylimidazolium chloride ionic salt is one such ionic liquid that has been extensively studied for melt spinning PAN precursor fibers. It has been shown to induce cyclization during twin-screw compounding [58] and fiber spinning [59,60] thereby reducing stabilization time. The effects of compounding extruder residence time, fiber spinning speed [61], melt temperature [62], and air circulation rate during stabilization [63] have all been explored. In 2020, Martin et al. [64] compared 1-butyl-3-methylimidazolium chloride as a PAN plasticizer with other ionic salts: 1-Propyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium bromide, 1-(3-cyanopropyl)-3-methylimidazolium bromide, and 1-(3-cyanopropyl)-3-methylimidazolium chloride. Each ionic salt was shown to reduce the melting temperature of the PAN by 150°C and imbued appropriate melt rheology for melt spinning of homogeneous fibers with smooth surfaces and dense cross sections. Washing the fibers after spinning significantly increased carbon yield in all cases. Fibers treated with an ionic liquid containing bromine exhibited a greater carbon yield than those containing chloride and greater precursor mechanical properties from single-filament tensile tests. Furthermore, reducing the spinneret die diameter from 3175 μm to 100 μm and increasing the mass throughput scale improved the precursor tensile strength from 100 MPa to 240 MPa. The authors did not publish any results of subsequent conversions of these precursor fibers into carbon fibers.

As explained in section 1.1, solution spun PAN is rarely homopolymer PAN; instead, it is a copolymer consisting of small amounts of acrylic acid, methacrylic acid, methacrylate, or other comonomers that act as plasticizers to improve the drawability of the fibers after formation [18]. Similarly, comonomers can be used to reduce the melting temperature of PAN. The comonomers displace portions of the PAN chain so that fewer nitrile groups can correspond spatially. This can be achieved by introducing comonomers without side groups or with small side groups. It can also be accomplished via comonomers with large side groups that induce steric hindrance sufficient to reduce the amount of nitrile groups that can interface [32]. Melt processible copolymers of acrylonitrile and many comonomers, such as methyl acrylate [65–70], methacrylic acid [71], itaconic acid [68,71–73], vinyl acetate [68,73], vinylimidizole [53], acrylic acid [53], styrene [74], and acryloyl benzophenone [75] alone or in partial combination, have been demonstrated and characterized extensively. However, properties of carbon fibers derived from these precursors are less reported. Carbon fibers derived from melt spun PAN copolymers underperform conventionally produced carbon fibers because the same nitrile-nitrile bond interruption that enables melt spinning also limits the cyclization of these same nitrile groups, which is critical to proper stabilization and the development of mechanical properties in carbon fibers [9]. For example, in 2019, Lee et al. [76] demonstrated carbon fibers with densified cross sections from electron-beam irradiation stabilized, melt spun poly(acrylonitrile-co-methyl acrylate) precursors with a tensile strength of 1.37 GPa and a tensile modulus of 110 GPa.

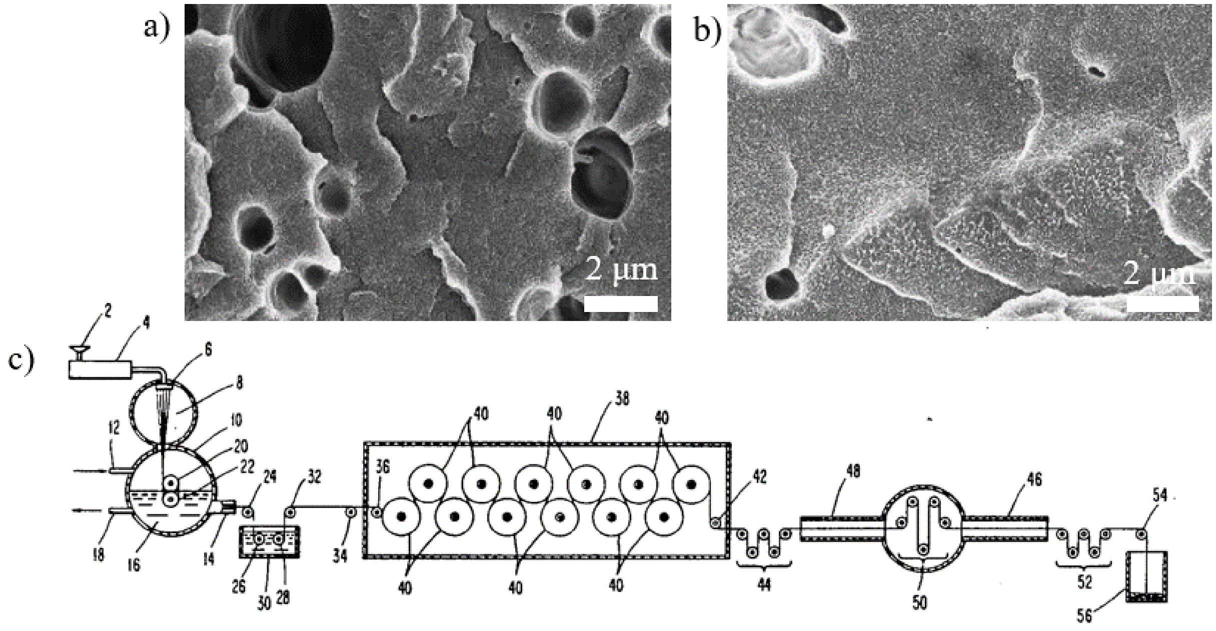

Fig. 4. a) Scanning electron microscopy (SEM) image of large pores present in water-plasticized PAN fibers [39], b) SEM image showing significantly reduced porosity, in both size and count, in water/ethanol-plasticized PAN fibers [39], c) a schematic of a water- and acetonitrile-plasticized PAN fiber melt spinning system showing the great complexity required [50].

2.2 Mesophase Pitch

Pitch is a tar-like material derived from the pyrolysis of natural carbonaceous materials, such as fuel oil, biomass-derived tar [12], coal tar [77], or catalytic slurry oil [78]. Synthetic pitch can also be produced via polymerization of highly aromatic compounds such as naphthalene to produce a more idealized material [79]. In raw form it is highly heterogeneous, composed mostly of aromatic groups with some methyl side groups, and with proper distillment the material can be used as a precursor for melt-spinnable fibers. Post distillment, pitch is said to be an isotropic material which can be converted to anisotropic, called mesophase, following further refinement. Both can yield carbon fibers with functional properties, but carbon fibers derived from mesophase pitch possess greater mechanical properties [11]. Pitch-based carbon fibers are often characterized by a much higher tensile modulus, but lower tensile strength than PAN-based carbon fibers. The low strength prevents them from being used in high strength applications, but the high modulus makes them superior for vibration-damping applications. Therefore, they are used in applications such as in robot arms and machining tools to reduce takt time and increase positional accuracy; and in the sports/leisure industry to enhance response of equipment [80]. More than the high modulus, pitch fibers have excellent thermal and electrical conductivities, and negative thermal expansion coefficient which can be manipulated to produce materials with zero thermal expansion coefficients. Due to these properties, mesophase pitch carbon fibers serve many different applications including: (i) high temperature components – aircraft/formula racing brakes [81]; (ii) electromagnetic and strain-sensing – electromagnetic shielding for aircraft and infrastructure [82,83]; and (iii) negative thermal expansion coefficient applications – satellites' antenna reflectors and solar arrays [84].

Broader adoption of pitch-based carbon fibers is hampered by their mechanical characteristics and the challenges of purifying and spinning the precursor. Melt spinning pitch fibers is notoriously challenging because the material properties are highly sensitive to its processing conditions. The melt must be maintained in an inert atmosphere to prevent oxidation and crosslinking, and small variations in the spinning temperature, capillary design, and die geometry can induce vastly different and heterogeneous microstructures with significant effect on the fibers' properties [22,85–88], **Fig. 5**. The production of pitch-based carbon fibers is well reviewed in literature as recently as 2021 [33–35,77], and the readers are referred to such publications for more in-depth discussion of this precursor.

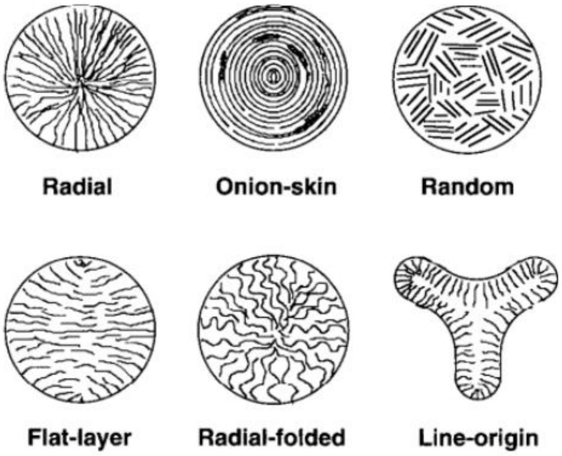

Fig. 5. Various cross-sectional microstructures that can occur in mesophase pitch fibers depending on the fiber spinning conditions [22].

2.3 Lignin and Cellulose

Biologically derived precursors have received great attention due to their potential to replace precursors derived from fossil fuels with a renewable material. The two most common bio-based precursors are lignin and cellulose. Lignin is a naturally occurring biopolymer composed of randomly distributed aromatic subunits called phenylpropanoids [89]. Industrially, lignin has long been a waste byproduct of the paper production process that had only found re-use as a low-level fuel source via incineration. However, its abundance, low-cost, high carbon content, aromatic structure, and thermoplastic-like rheology make it an attractive opportunity for an alternative carbon fiber precursor material. Not all lignins can be melt spun; some require plasticizers or thermal treatments to imbue the characteristics required for successful melt spinning [11]. Alternatively, the organosolv process can produce high purity lignin with a low glass transition temperature and stable melt viscosity suitable for melt spinning without additives [90]. Despite strenuous efforts, the mechanical properties of carbon fibers derived from melt spun lignin precursors have fallen short of the level required for structural applications [91]. Lignin as a carbon fiber precursor was well reviewed by Ogale et al. [10] in 2016, wherein the authors noted two main technical challenges hindering the progress of lignin as a precursor: 1) the glass transition temperature must be sufficiently low to enable stable melt spinning, but sufficiently high to enable rapid stabilization, and 2) the fibers must be sufficiently chemically stable to prevent crosslinking at melt spinning temperatures but not so stable that crosslinking is not possible at stabilization temperatures. Despite the enticing abundance, low-cost, and high carbon content, the inferior tensile strength makes commercial production of lignin-derived carbon fiber impractical currently.

Cellulose is another common biopolymer that finds widespread industrial use in the packaging industry [92]. Like lignin, its natural origin, low cost, and abundance make it an attractive candidate as a carbon fiber precursor. Unlike lignin, carbon fibers derived from cellulose have shown mechanical properties tantamount to mesophase pitch- and PAN- derived carbon fibers with tensile strength and Young’s modulus as high as 2.52 and 517.0 GPa, respectively [93]. However, solution spinning is required to form conventional cellulose fibers because its melting temperature is greater than its decomposition temperature [94]. Furthermore, the low carbon content present in cellulose, approximately 44 wt%, yields a carbon conversion percentage in the range of 10-30% after carbonization [95]. Several methods of modifying cellulose to achieve melt-processability have been demonstrated [96–99], but this low carbon conversion percentage makes producing cellulose derived carbon fibers on an industrial scale unrealistic and economically unsustainable.

2.4 Commodity Synthetic Plastics

Synthetic plastics have replaced natural and metallic materials in many applications since their invention in the 1930’s due to their highly tunable and desirable mechanical and chemical properties. This flexibility led to the domination of PAN-based carbon fibers and offers opportunities to supplant PAN with a low-cost alternative. For instance, high-performance poly(p-phenylene-2,6-benzobisoxazole) (PBO, tradename Zylon) fibers can be converted into carbon fibers without the thermo-oxidative stabilization required for PAN-based carbon fibers [100–102]. However, the fibers are expensive to produce; The polymerization of PBO is complex and the material cannot be melted, so it must be dry-jet wet spun [103–105]. Additionally, the resulting carbon fibers have only attained modest mechanical properties to date [100]. Thus, research attention has turned to the conversion of melt-spinnable, commodity thermoplastics to replace PAN.

Commodity thermoplastics are those that are made in the greatest volume worldwide and are thus common and inexpensive. This classification typically includes polyolefins, poly(vinyl chloride), polystyrene, polyesters, and polyamides [106,107]. Unlike pitch and bio-precursors, synthetic plastic fibers can be produced with high molecular and microstructural homogeneity, and unlike melt-spinnable PAN, the process can achieve fibers without voids at ambient environmental conditions with simple equipment. The major challenge to the use of commodity melt spinnable synthetic polymers as carbon fiber precursors is that their chemical structure is typically insufficiently stable for the thermal processes required for conversion to carbon fibers. Researchers have made great progress developing methods of overcoming this challenge, and in the following sections we will present an in-depth discussion of the current state of development of polyolefin-, polyamide-, polystyrene-, polyester-, and poly(vinyl chloride)-derived carbon fibers.

3 Polyolefins

Polyolefins encompass all synthetic plastics that share a common class of monomers, called alkenes. Polyethylenes (PEs) and polypropylene (PP) are the most economically significant polyolefins. The family of PEs combined are the most produced plastics in the world, and PP is the most commonly produced individual plastic [107,108]. This economy of scale poses a significant opportunity to shift carbon fiber production from PAN to polyolefins. Furthermore, the empirical composition of polyolefins is $[-CH_2]_n$, so a carbon yield of approximately 85.7% is theoretically possible. This would enable greater carbon fiber production than is currently possible with PAN, which achieves a carbon yield of approximately 67.9% [109]. Accordingly, great research and development effort has been expended over the past fifty years towards this goal. Significant success in converting various PEs and some limited progress in converting polypropylenes into carbon fibers has been demonstrated [110,111].

3.1 Polyethylenes

PE describes a class of polymers that are composed of ethylene monomers and are classified by their density and degree of branching into the several categories including the four most common types: linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and ultra-high molecular weight polyethylene (UHMWPE) [112]. **Fig. 6** schematically illustrates the differences in molecular structure of these PEs [113]. LDPE exhibits extensive long-chain branching and thus the lowest density of all PEs. The highly branched structure also yields the lowest melting temperature of all PEs of 80-110°C [113]. LLDPE, is a copolymer of ethylene with a few percent of an α-olefin comonomer that exhibits short-chain branching, which results in slightly higher tensile strength, impact resistance, melting temperature (115-125°C) and density compared to LDPE [113]. HDPE has a melting temperature of approximately 120-140°C and exhibits limited short-chain branching [112]. UHMWPE exhibits branching similar to HDPE, but the major difference between HDPE and UHMWPE is that the molecular chain length of UHMWPE is about 10 times higher than the molecular chain length in HDPE, yielding a polymer with the highest tensile strength and impact resistance of all PEs [112,114].

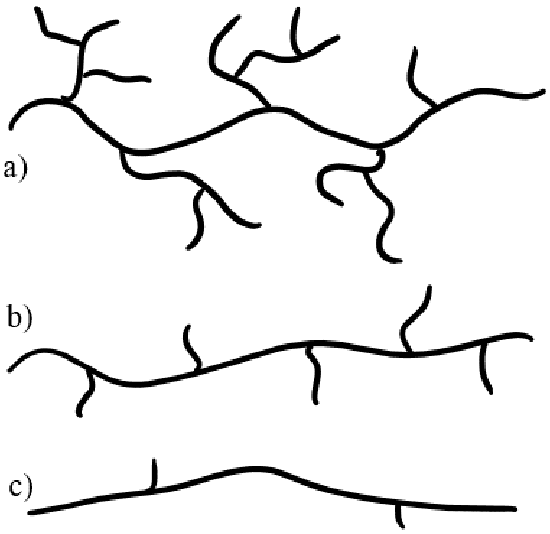

Fig. 6. Schematic representation of polymer chain crosslinking in a) LDPE, b) LLDPE, and c) HDPE [113].

The combined production of all classifications of PE accounts for approximately 30% of global plastic production making it one of the most widely available commodity plastics on the market. Accordingly, PE has received great attention from the academic and commercial realms as a potential alternative carbon fiber precursor. In 1978, Shozo Horikiri [110] published the first patent to manufacture PE-derived carbon fibers using the sulfonation method most commonly used today. Since then, many grades of PE have been successfully converted into carbon fibers including LLDPE [115–117], LDPE [118], HDPE [119,120], and UHMWPE [121,122]. This attention is well warranted; in 2019, Choi et al. [12] estimated that PE-derived carbon fibers could cost 38% less than PAN-derived carbon fibers due to the low cost of PE and the melt spinning process. LLDPE, LDPE, and HDPE are readily and commonly melt spun into fibers appropriate for carbon fiber production, whereas UHMWPE is most commonly gel spun because the long molecular chains make the rheological properties of the material unsuitable for melt spinning. The toxic and costly solvents required to gel spin UHMWPE preclude it from consideration in the scope of the commodity thermoplastic precursors in this review, but recent progress toward melt-spinnable UHMWPE by blending with lower molecular weight PEs [123,124] may provide new opportunities for low-cost UHMWPE-derived carbon fibers in the future. The methods of converting PE to carbon fibers have been reviewed as recently as 2020 by Aldosari et al. [125], and we will build on their work in this section.

PEs do not inherently possess the thermal stability required for successful carbon fiber conversion, so a method of crosslinking the polymer chains of the precursor fibers is required. Many methods of crosslinking PEs have been developed for many purposes and a subset of those have been applied to carbon fiber synthesis. Sulfonation has emerged as the leading stabilization method for PE-derived carbon fiber synthesis, which will be reviewed in the following section, and several promising alternatives that have arisen recently will be discussed afterwards.

3.1.1 Carbon Fibers Derived from Sulfonation Stabilized Polyethylenes

Sulfonation is the process of exposing PE fibers to high-concentration sulfuric acid at elevated temperatures. Sufficiently sulfonated PE fibers can proceed directly to carbonization without further thermos-oxidative stabilization. The 1978 patent by Horikiri et al. [110] is credited as the first demonstration of this process, and the mechanical properties they reported, up to 147 GPa elastic modulus and 2.53 GPa tensile strength, initiated decades of subsequent investigation. Pioneering academic studies conducted in the 1990s shed some light on the chemical, mechanical, and microstructural evolution of sulfonated PE into carbon fibers. Postema et al. [117] melt spun LLDPE fibers and stabilized the fibers via exposure to chlorosulfonic acid at room temperature. Infrared spectroscopy revealed the formation of sulfonic-group bridges, which indicated that treatment with sulfuric acid could achieve the same crosslinking effect. The fibers were then carbonized at 900℃ for 5 min under constant tension, and the final fibers exhibited a tensile strength of 1.15 GPa and Young’s modulus of 60 GPa. The chlorosulfonation process induced axial and radial cracks on the surface of the stabilized fibers, and the carbonized fibers exhibited an amorphous microstructure with significant surface defects. In a series of publications from 1993 to 1996, Zhang [122] with Bhat [121] and later with Sun [126] demonstrated the production of carbon fibers from sulfonation stabilized PE and explored the effects of fiber molecular weight and order and sulfonation conditions and duration on resulting carbon fiber properties. In 1993, Zhang [122] showed that UHMWPE could be converted to carbon fibers via sulfonation at 130-160℃ for at least 75 min. The resulting carbon fibers exhibited a tensile strength of 2.1 GPa and Young’s modulus of 210 GPa with densified cross sections. Zhang and Sun [126] showed that high temperature sulfonation is required for full stabilization, and that improper sulfonation would yield a hollow core where the polymer had been insufficiently stabilized. In this study it was also shown that the molecular order of the precursor affects the required time for complete sulfonation; the less-ordered, highly drawn PE precursor fiber could be sulfonated in as little as 45 minutes compared with the 75 min minimum found for UHMWPE precursor fibers in Zhang's earlier study. The mechanical properties of carbon fibers were also shown to be directly related to sulfonation temperature; increasing the sulfonation temperature from 130℃ to 180℃ yielded greater mechanical properties [126]. The mechanism underlying sulfonation-induced crosslinking was proposed in 2013 by Younker et al. [127] and demonstrated in 2015 by Barton et al. [128]. Younker et al. [127] proposed a radical chain reaction wherein sulfonic groups on the polymer chain, introduced by the sulfuric acid, decompose into a hydroxyl radical and hydroxysulfonyl radical. The former abstracts hydrogen from the polymer while the latter further decomposes into another hydroxyl radical, which removes more hydrogen and sulfur dioxide to complete the cycle. The resulting aromatic structure is then sufficiently stable to conduct carbonization, which drives off the remaining noncarbon elements. This process is shown in **Fig. 7**. Barton et al. [128] confirmed this mechanism by identifying sulfonic groups on PE fibers sulfonated with sulfuric acid via Fourier transform infrared spectroscopy, the evolution of sulfur dioxide and water vapor during carbonization via evolved gas analysis-gas chromatography, and a decrease in S=O bonds via attenuated total reflectance infrared spectroscopy.

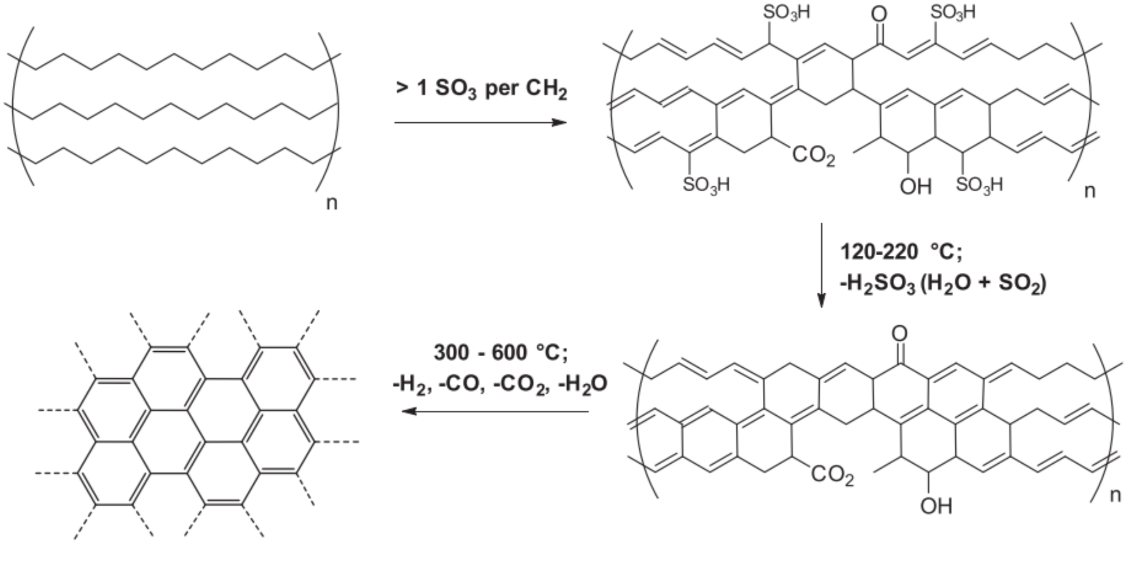

Fig. 7. Schematic of the transformation of PE into carbon as demonstrated by Barton et al. [128]

After settling the mechanism of sulfonation, Barton joined Behr et al. [129] in establishing a structure-property model for PE-derived carbon fibers in 2016. The authors conducted a series of experiments synthesizing carbon fibers from HDPE at carbonization temperatures ranging from 900℃ to 2400℃. Single-fiber tensile tests were used to determine the mechanical properties of the carbon fibers. Wide-angle X-ray diffraction was used to assess the orientation of graphitic layers. These results were used to apply Northolt et al.'s [130] uniform stress structure-property model for PAN-derived carbon fibers. The authors were able to show that the relationship between microstructure orientation and tensile modulus is different from each PAN- and pitch-derived carbon fibers and the shear modulus between graphitic layers of PE-derived carbon fibers was lower than both. This insight implies that the crosslink density in PE-derived carbon fibers is lower, which could indicate a greater propensity for orientation during graphitization and thus greater mechanical properties. This relationship can be used to estimate the level of orientation required to achieve high properties or predict properties based on an observed level of orientation. Critically, their experimental results can be extrapolated to show that highly oriented PE-derived carbon fibers could achieve tensile properties that meet or exceed PAN-derived carbon fibers, **Fig. 8** [129]. Expanding on their previous work, Barton and Behr [131] recently utilized a graphitization process with the addition of boron to yield LLDPE-derived carbon fibers with a tensile modulus greater than 400 GPa when graphitized at 2400 °C. The boron additive was shown to reduce the necessary temperature for graphitization and produces fibers with superior modulus at lower temperatures.

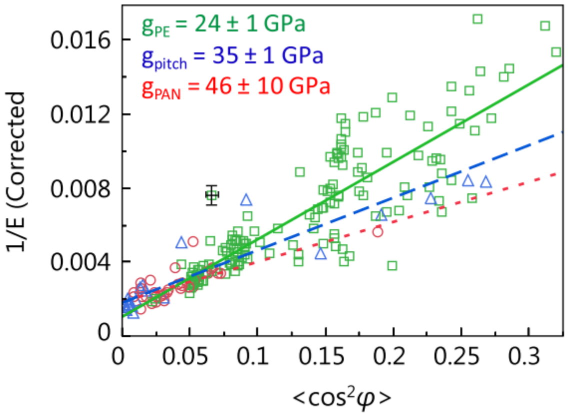

Fig. 8. Compliance (1/E) vs. orientation parameter for PE- (green squares), PAN- (red circles), and pitch- (blue triangles) derived carbon fiber. Shear moduli calculated from the data for each type are included. Note that the tensile moduli for the PE-derived carbon fiber are corrected for porosity, and the error bars were estimated from replicated measurements of the same fiber [129].

Many aspects of the precursor fibers and the processing conditions affect the properties of the PE-derived carbon fibers. Sufficient sulfonation is the most important factor in synthesizing carbon fibers from precursors, and it has been shown that the diameter of the precursor fiber, fiber crystallinity, and the sulfonation temperature are inversely proportional to the required sulfonation time [116,119]. Recent advances in the sulfonation process, such as applying hydrostatic pressure, up to 5 bar, have been used to increase the rate of sulfuric acid penetration into the precursor fibers, accelerate the sulfonation process, and overcome limitations induced by the crystallinity of the precursor fibers [132]. Reducing precursor fiber diameter also results in increased carbon fiber mechanical properties [115], as does careful control of tension applied to the fibers during sulfonation and carbonization [116]. Applying tension during conversion processing increases the degree of alignment in the carbon chains that make-up the backbone of carbon fiber, which has a direct correlation to increased mechanical properties and the anisotropic microstructure of the carbonized fiber.

Although sulfonation stabilized-PE derived carbon fibers show great promise, it must be acknowledged that the sulfonation process is costly and ecologically unfriendly because the best results require the use of high- or fuming-concentration sulfuric acid at high temperature. Accordingly, recent research has focused on the application of electron beam irradiation to lower the requirements for successful stabilization via sulfonation. In 2019, Choi et al. [133] were the first to demonstrate the production of carbon fibers from PE precursors that were pretreated with electron beam irradiation prior to sulfonation. In their work, the LLDPE precursor fibers were exposed to 500-1500 kGy prior to sulfonation in 98% sulfuric acid at 95℃ followed by carbonization. The resultant carbon fibers exhibited functional mechanical properties of 1.3 GPa tensile strength, 89.9 GPa tensile modulus, and 1.5% elongation at break as well as a carbon yield of 44.6% for fibers pretreated with 1500 kGy irradiation. In addition to greatly reducing the sulfuric acid concentration and temperature (from 120% to 98% and 140℃ to 95℃ respectively), the authors were also able to achieve these results in one less hour of sulfonation duration [133]. In 2021, Kang et al. [134] performed a similar procedure with HDPE precursor fibers and achieved a carbonization yield of 40% with consistent, densified cross-section fibers, but did not publish mechanical properties for the carbon fibers.

3.1.2 Alternative PE Stabilization Methods

Despite the promising results of sulfonated-PE-derived carbon fibers, the challenges of the sulfonation process, well exemplified by the complex multiphase reactor developed by Hukkanen et al. in 2018 [135], **Fig. 9**, have led researchers to explore alternative PE stabilization pathways. Some well documented methods, such as peroxide crosslinking, silane crosslinking, and irradiative methods without sulfonation, yield crosslinking densities too low for carbonization [136], whereas others, such as halogenation, ammoxidation, and sulfurization have shown potential.

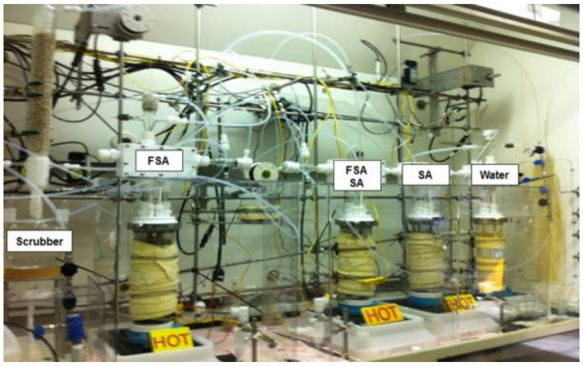

Fig. 9. Example of a continuous fiber sulfonation reactor system for sulfonating tows of polyethylene fibers for carbon fiber production [135].

The highly reactive nature of halogen elements creates an attractive opportunity to strip the hydrogen from polymer chains to form carbon fibers. Generally, the halogen attaches to the hydrogen atoms of the polymer to form hydrohalogens, and a succeeding dehydrohalogenation process removes these molecules to reveal a carbon-only structure. A pathway to converting chlorine-saturated PE into carbon fiber was introduced as early as 1972. Saglio et al. [137] demonstrated that LDPE saturated to 73.7 wt% chlorine could be wet spun and converted into carbon fibers through a thermal dehydrochlorination process followed by carbonization. The resulting carbon fibers displayed turbostratic carbon regions after a carbonization stage conducted at 800°C and graphitization was possible at much higher temperatures. This conversion method leaves much to be desired due to the wet spinning fiber formation method, the substantial consumption of chlorine, and significant generation of HCl gas, and was thus abandoned in favor of sulfonation.

Halogenation was revisited recently by Laycock et al. in 2020, [138] who demonstrated the pyrolysis of brominated PE fibers and proposed a possible conversion mechanism, shown in **Fig. 10**. The authors brominated melt spun PE fibers, and blends of PE with other materials such as kraft lignin, under ultraviolet irradiation and converted the brominated precursors into carbon fibers through a two-stage process involving a dehydrobromination at 180°C followed by carbonization at ≥ 800°C. Dow ASPUN LLDPE, metallocene LLDPE, HDPE, and LDPE were all used in this study. Carbon yields greater than 90% were achieved, but the fiber morphology could not be retained due to its solubility with liquid bromine. Such a high carbon yield is attractive and the ability to recover and reuse bromine from the process makes this method promising, so the authors acknowledge that future work will involve the exploration of gas-phase bromination to maintain fiber morphology for carbon fiber production.

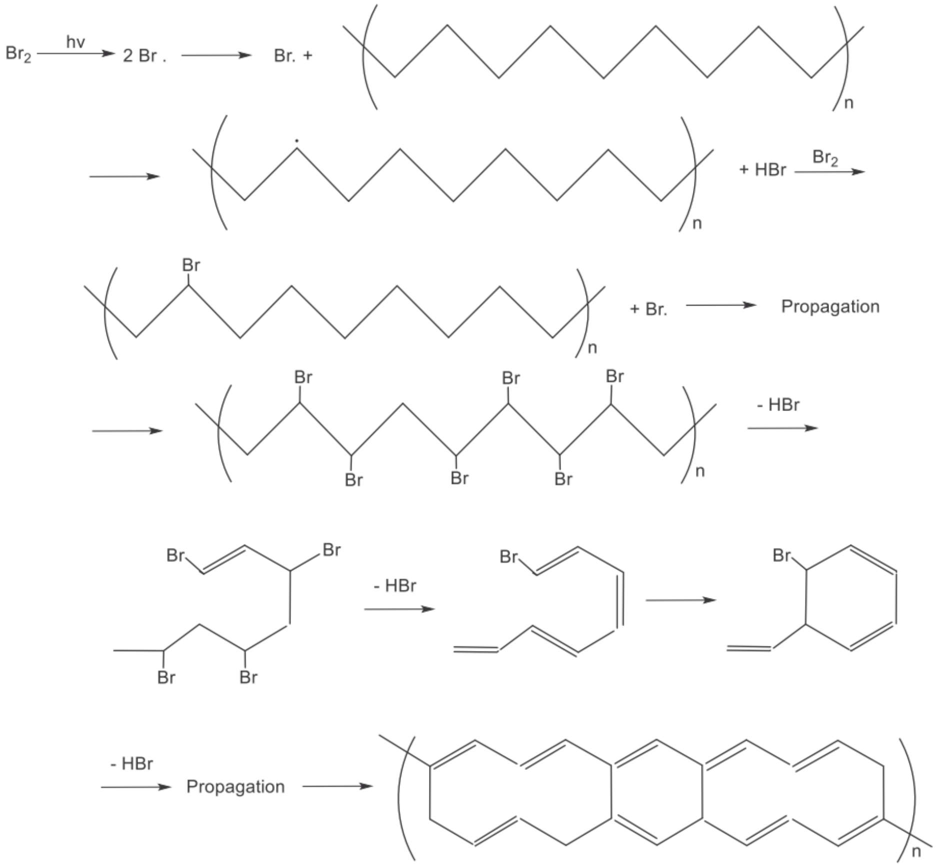

Fig. 10. Proposed mechanism for the conversion of PE into carbon fibers via bromination [138].

In pursuit of an air-oxidation method, Barton et al. [139] discovered in 2018 that ammoxidized silane grafted-PE could be converted to carbon fibers with a carbon yield up to 70%. The authors formed crosslinked PE film and fibers by immersing LLDPE graft vinyl trimethoxysilane (PE-g-VTMS) in a sulfonic acid catalyst and then heating in air at 100% humidity. The initial intent was to demonstrate an air oxidation method of the crosslinked PE-g-VTMS, but lackluster results prompted the exploration of ammoxidation as an alternative. Samples that were immersed in air-sparged 5M anhydrous ammonia prior to oxidation demonstrated aromatic structures and high mass retention after oxidation and carbon yields up to 70% after carbonization. The resulting carbonaceous material was largely amorphous but graphitic regions were evident via high resolution transmission electron microscopy (HRTEM), **Fig. 11a**. Although the precursor morphology was identifiable after pyrolysis, the fibers were fused together after oxidation, **Fig.**

11b. Therefore, this method requires more development to realize its potential as an alternative to high temperature sulfonation.

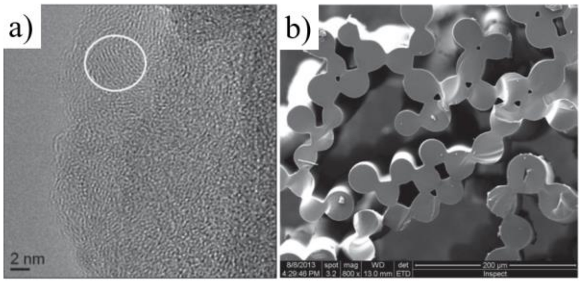

Fig. 11. a) HRTEM image of an ammoxidation-stabilized carbon fiber exhibiting graphitic regions including extended stacking of lattice fringes in the encircled region, and b) SEM image of the cross section of fused, carbonized PE fibers [139].

The latest development in alternative stabilization methods for PE involves elemental sulfur rather than sulfuric or sulfonic acid. In 2021, Frank et al. [140] irradiated various grades of PE (low, middle, and high molecular weight HDPE, and low-density PE all derived from sugar cane plants) fiber with an electron beam and then sulfurized the fibers in molten elemental sulfur. The irradiation step provides sufficient initial crosslinking for immersion in the molten sulfur at temperatures greater than 240°C. Sulfurization was first shown to convert PE into a semi-aromatized material containing poly(thienothiophene) and poly(naphthothienothiophene) blocks by Trofimov et al. in 2000 [141]. Frank et al. [140] applied this chemistry to their precursor PE fibers and then successfully carbonized the resulting fibers. The authors achieved carbon yields up to 76% and the synthesized carbon fibers showed dense cross sections with few voids, **Fig. 12**. The carbon content of the resulting fibers was measured to be 98.7%, thus the input sulfur could be considered entirely removed. The authors noted that sulfur-capture technology has long been matured due to extensive use of the vulcanization process at industrial scale, so input sulfur can readily be captured and re-used. The authors did not publish mechanical results and cited a need for production scale-up of the process to truly demonstrate the mechanical characteristics of carbon fibers produced in this method.

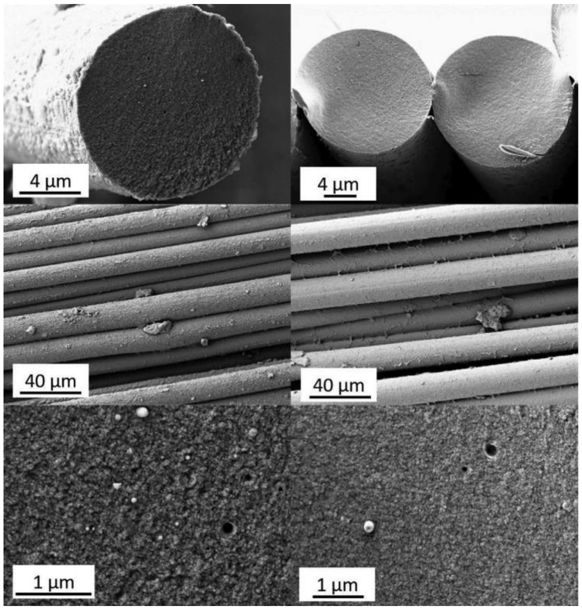

Fig. 12. SEM images of carbon fibers derived from sulfurized HDPE (left column) and sulfurized LDPE (right column) showing the resultant morphology including smooth exterior surfaces and minor voids and inclusions [140].

3.2 Polypropylene

The second most abundant polyolefin, polypropylene (PP), is used for industrial applications in carpets, geotextiles, ropes and reinforcing fibers and is the fourth most produced artificial fiber after polyesters, polyamides, and acrylics [142]. Furthermore, the cost of PP resin is lower than that of LDPE, LLDPE, HDPE and UHMWPE [143]. PP is a thermoplastic polymer composed of a repeating methylene-unit backbone, like PE, with methyl side groups. These side groups stiffen the polymer chain resulting in a higher melt temperature, 160-176℃, compared to PE [109,144]. The stereoregularity (tacticity) of these side groups can be controlled by applying different polymerization techniques, which affects the crystallinity and thus properties of the resulting polymer [144].

In 2001, Leon y Leon et al. [109] demonstrated that carbon fibers can be derived from PP by following a similar process to that of PE. PP fiber tows are immersed in a sulfonation agent to induce the crosslinking required for the precursor to undergo carbonization. Immersion in chlorosulfonic acid and sulfuric acid can both be used to induce crosslinking in PP fibers, but sulfuric acid is approximately 10 times cheaper than chlorosulfonic acid and yields more control of dissipated heat during sulfonation, so it was deemed superior for the sulfonation process. Leon y Leon et al. proceeded to immerse the PP precursors in a sulfuric acid bath at 140°C for two separate durations of time, 1.9 and 3.3 hours. After carbonization in a nitrogen rich environment at 1,000°C, thermogravimetric analysis (TGA) was used to measure the resulting carbon yield from the two batches and it was observed that the carbon fibers sulfonated for 3.3 hours, and 1.9 hours yielded carbon contents of 54% and 9% respectively. These results suggest that carbon content post-carbonization is strongly correlated with the time of sulfonation and the degree of crosslinking in the precursor. Finally, the mechanical properties of the PP-derived carbon fibers were measured and the tensile strength and Young’s modulus was determined to be 0.20 GPa and 26 GPa respectively. Ten years later, Karacan et al. [111] further studied the effect of sulfonation treatment on isotactic PP fibers prior to carbonization and discovered the harsh conditions during sulfonation resulted in surface irregularities at low sulfonation times and fiber fractures and reduced crystallinity at high sulfonation times which significantly reduced mechanical properties of the precursor fiber. **Fig. 13**, from Karacan et al. [111], illustrates fiber damage from the harsh conditions during sulfonation.

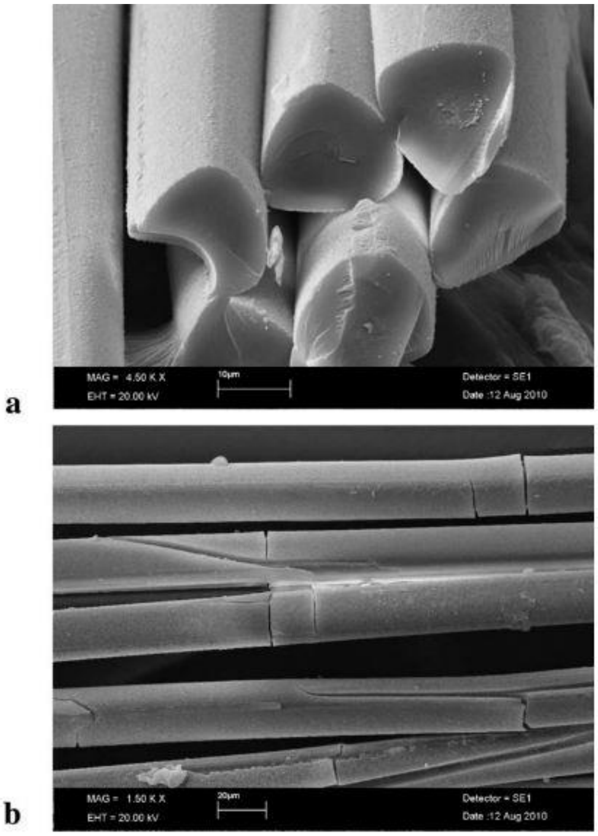

Fig. 13. SEM images of isotactic polypropylene fiber sulfonated at (a) 120°C for 30 minutes; (b) 120°C for 4h [111].

4 Polyamides

Polyamides are commonly categorized by their molecular structure into two groups, aliphatic polyamides, or aromatic polyamides (aramids). Aromatic polyamides (such as Kevlar) cannot be melt spun because its melt temperature exceeds its degradation temperature and therefore is typically solution spun. The resulting fibers are characterized by excellent mechanical, thermal, and chemical properties due to their conjugated ring structure. The properties of these fibers enable direct carbonization into carbon fibers. The resulting carbon fibers have a carbon yield that ranges from 39-65% and fiber diameters that range from 5-30 μm [101,145–147]. No mechanical properties have been presented in available literature. The largest drawback to the Kevlar fibers is the cost of producing the fibers, which has stymied the advancement of these fibers as precursors to commercial scale. Aliphatic polyamides, commonly referred to as nylons, are much easier and cheaper to mass produce and possess mechanical and chemical properties well suited for use in a broad range of consumer products. It is estimated that 5.5 million tons of polyamide fiber were produced in 2016 [148], indicating a wide availability for use as feedstock for carbon fiber production. Researchers have taken notice of this opportunity and recent efforts have delivered promising results.

A method of converting aliphatic polyamide to graphite fibers was first patented in the United States in 1970 by Joseph G. Santangelo, wherein high thermal stability polyamides, such as nylon 6T, were thermally treated in air between 200°C and 350°C and then graphitized at 3000°C [149]. However, aliphatic polyamides generally do not possess the thermal stability to undergo this oxidation and carbonization routine, so much research focus has been devoted to imbuing commodity polyamides, such as polyamide 6 (PA 6), with the thermal stability required for conversion. A promising method is the inclusion of metal salts, which have been used for decades to reduce the oxidative degradation of polyamides [150–154]. Specifically, they have been shown to form complexes with the amide groups of the polymer resulting in greater thermo-oxidative stability [155,156]. Cerruti et al. [157] showed that copper salts were most efficient stabilizing species, and Karacan and Baysal [158] demonstrated the potential of cupric chloride-treated PA 6 fibers as carbon fiber precursors shortly after. It is hypothesized that cupric ion-amide bonds replace hydrogen bonds and encourage coordination of chains into a ladder structure capable of withstanding carbonization. In their work, they demonstrated that increased duration of stabilization in air at 180°C increased char yield via thermogravimetric analysis. In 2018, Karacan and Meşeli [159] demonstrated the synthesis of amorphous carbon fibers from PA 6 treated with cupric chloride via immersion in a heated solution for one hour. In this work, the researchers found that a two-stage stabilization procedure, 12 h stabilization in air at 180°C followed by 0-4 h in nitrogen at 250°C, **Fig. 14a**, was required to adequately stabilize the precursor for carbonization. Infrared spectroscopy showed the evolution of chemical bonds and molecular phases throughout the process and confirmed the elimination of oxygen and hydrogen containing groups by the conclusion of the carbonization. Elemental analysis showed a notable carbon yield of 43.1% for samples carbonized at 1000°C, and X-ray diffractometry showed that the fibers achieved a turbostratic carbon structure.

In 2021, Erzurumluoglu et al. [160] continued Karacan and Meşeli's 2018 work by studying the conversion of polyamide 6,6 (PA 6,6) into carbon fibers and publishing the first mechanical properties of PA 6,6-derived carbon fibers. The authors pretreated PA 6,6 fibers in a yarn using a 1% (w/v) cupric chloride-ethanol solution, applied a single, continuous thermo-oxidative stabilization with two temperature stages with individual ramp rates and varied dwell times, then carbonized the fibers ramping to between 500°C and 1100°C in 100°C increments without any dwell time. In so doing, the authors showed that the inert-atmosphere pre-carbonization described by Karacan and Meşeli [159] was not necessary to achieve carbonized fibers and that the stabilization step could be reduced from 880 to 370 minutes for a total process time reduction of 48.6% after pretreatment, **Fig. 14b**. A range of stabilization and carbonization temperatures as well as temperature ramp rates were investigated. The greatest mechanical properties were achieved from fibers that underwent stabilization with a 1°C/min ramp up to 190°C then 0.3°C/min ramp up to 250°C with no dwell time at either temperature followed by carbonization with a ramp up to 1100°C. The resulting fibers exhibited amorphous structure with cross sectional and surface voids amounting to 12.81% porosity. The tensile properties of the fibers, 80.55 ± 5.75 GPa tensile modulus and 194 ± 17 MPa tensile strength, fall well below those of commercial wet spun-PAN derived fibers [2], but the significant reduction in processing time shows that there is potential for significant development with continued research.

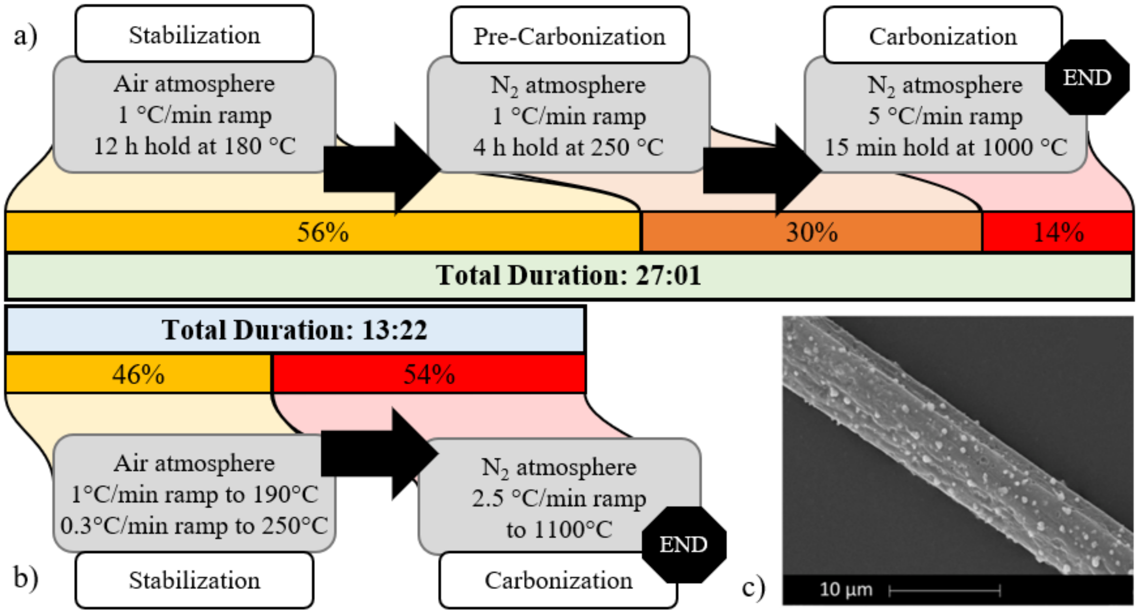

Fig. 14. a) Timeline for the conversion of PA 6 fibers as described by Karacan and Meşeli [159] in 2018, b) a much shorter timeline for converting PA 6,6 into carbon fibers as described by Erzurumluoglu et al. [160] in 2021, and c) an SEM image of the carbon fibers derived from cupric chloride-treated PA 6,6 showing agglomerations, roughness, and voids on the surface of the fiber [160].

5 Polystyrene

Polystyrene (PS) is a polymer of styrene monomers, which are most commonly produced via catalytic dehydrogenation of ethylbenzene [161]. Several types of PS with a wide range of properties due to differences in tacticity can be produced depending on what polymerization method, radical, anionic, cationic, or coordination polymerization, is employed [162]. PS finds widespread use in food and consumer good packaging but is notoriously difficult to recycle [163], so upcycling PS into carbon fibers presents a unique opportunity to tackle two challenges at once. Carbonization of PS yields very little carbon material because the monomers easily split into gaseous hydrocarbons and small molecules [164,165], but studies have demonstrated several methods of modifying PS to generate carbonaceous materials [166–169]. In 2010, Jung et al. [170] demonstrated a two-step chemical treatment for PS that enabled the synthesis of carbon fibers. The authors synthesized polystyrene with a molecular weight of 160,000 and polydispersity index of 2.7 via solution polymerization. The synthesized PS was modified by a mixture of nitric acid and sulfuric acid, which nitrate the PS. The resulting material was then washed with distilled water to halt the reaction. The modified PS was then combined with a solution of tin (II) chloride and hydrochloric acid and allowed to stabilize for 24 hours. Afterwards, the modified PS was dissolved in a solution of tetrahydrofuran and N,N-dimethylformamide and electrospun into fibers with an average diameter of 1.8 μm, **Fig. 15a**. TGA showed that the modified PS achieved a carbon yield of 36.3% at 800°C, **Fig. 15b**. The authors did not comment on the stereochemistry of the PS that was used. Syndiotactic PS can be melt spun into fine fibers [171], but the crystallinity and melt rheology of the modified PS was not explored in the study so the ability to reduce the cost of this precursor via melt spinning has yet to be evaluated. Alternatively, PS has been successfully combined with other precursor materials to create carbon fibers, such as pitch [172,173] and PAN [174].

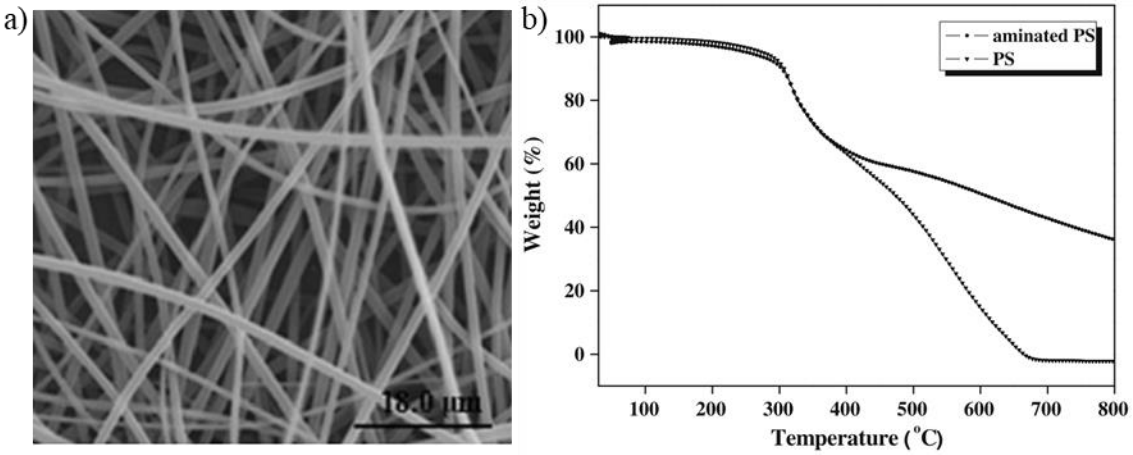

Fig. 15. a) SEM image of electrospun modified PS fibers, and b) TGA curves of raw PS and modified, “aminated”, PS showing a significant increase in carbon yield at carbonization temperatures, [170].

6 Polyesters

Polyethylene terephthalate (PET) is a polyester typically produced from esterification of monoethylene glycol and purified terephthalic acid, or transesterification of dimethyl terephthalate with purified terephthalic acid, followed by polycondensation of the esterification or transesterification product [175]. PET features high specific strength, low CO_2 permeability, high light transmittance, biological non-reactivity, and high formability, and thus has found use in many applications, including textile fibers, food and beverage containers, and medical instruments [106,175,176]. The melt spinning of PET is well studied and easily accomplished at very high throughput [177]. Furthermore, it presents an opportunity to upcycle a common waste plastic into a value-added material; the majority of the recycled PET is turned into fibers [178–181], so a feedstock is readily available. This abundance has encouraged the conversion of PET or recycled PET into several carbonaceous forms [182], such as graphite and graphene [183], carbon spherules [184], carbon nanotubes [185,186], two- and three-dimensional nanoporous carbon [187–191], and mesoporous activated carbon [192,193]. However, no method of converting PET fibers into carbon fibers has yet been published, which may be due to its relatively low carbon content (58 wt%), compared to 92 wt% for pitch, 85 wt% for polyethylene, and 68 wt% for PAN [194].

Nevertheless, PET is not absent from alternative precursor research; PET has received attention as a constituent in blended precursor materials like lignin [195]. In 2005, Kubo and Kadla [196] showed that PET with viscosity-average molecular weight of 18,000 is miscible in lignin and that blended lignin/PET precursor fibers can be successfully converted into carbon fibers. Several different PET/lignin ratios were melt spun together, thermally stabilized, and carbonized. Thermo-oxidative stabilization was carried out at a range of ramp rates up to 250℃ with a 1-hour dwell time at that temperature. The stabilized fibers were carbonized with a 180 ℃/hour ramp up 1000℃. The mechanical testing results were comparable to the tensile properties of commercial isotropic pitch-derived carbon fibers, and blends containing 25% or less PET exhibited carbon yields greater than that of tar-based pitch, **Fig. 16**. More recent work from Svinterikos and Zuburtikudis [197] focused on forming carbon nanofibers from precursor fibers composed of kraft lignin and PET from waste water bottles. The two materials were solution blended in trifluoroacetic acid and it was determined that the two constituents were miscible via differential scanning calorimetry. The lignin mass ratio in the polymer blend was varied from 20% to 50%. The dope was electrospun into fibers, which were subsequently thermos-oxidatively stabilized at a heating rate of 120℃/h up to 260℃ with a 1 h dwell at the target temperature. The stabilized fibers were then carbonized with a heating rate of 180℃/h up to 1000℃ with no dwell time. The resulting carbon nanofiber mats showed wrinkled and fused morphology. A subsequent study published in 2019 by Svinterikos et al. [198] explored the size effect of fiber diameter on fiber decomposition and morphology and showed that fibers with diameters greater than 387 nm exhibited less deleterious effect on the fiber morphology than smaller fibers, which may indicate opportunities for creating micron-scale carbon fibers from this combination. In 2020, Qu and Bai [199], blended PET with a molecular weight of 25,000 Da into pyrolytic lignin at 5 wt% and 20 wt% PET via melt-phase mixing. Fibers were melt spun onto a take-up winder operating at 100 m/min. Compared to their control sample of pure pyrolytic lignin, the blended precursors exhibited better processability and improved molecular orientation. The precursor fibers were then converted to carbon fibers by applying a thermo-oxidative stabilization at 260℃ and carbonization at 1000℃, and the resulting fibers exhibited densified cross sections and smooth outer surfaces with minor pitting, **Fig. 17**. Samples of the 5 wt% PET blend held in tension during the conversion process showed the best mechanical properties: 925 ± 141 MPa elastic modulus and 98.0 ± 11.8 MPa tensile strength.

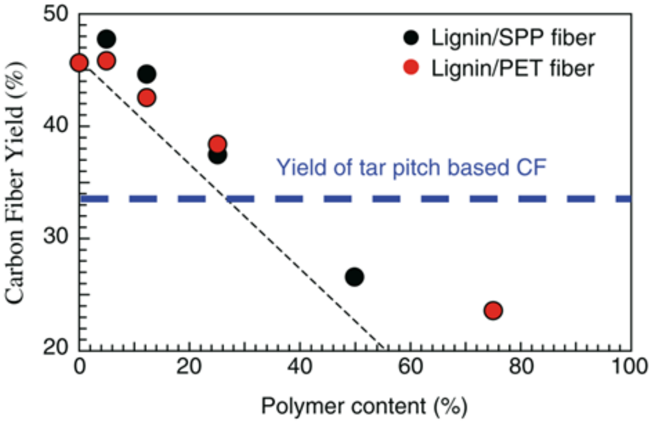

Fig. 16. Carbon yield as a function of polymer content for blends of lignin and PP and lignin and PET [196].

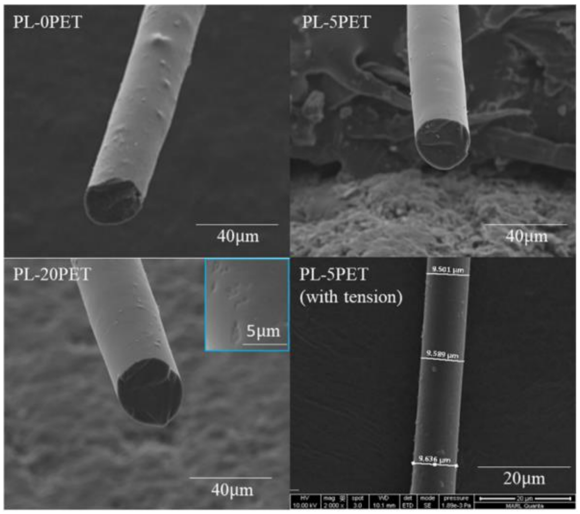

Fig. 17. SEM images of carbon fibers derived from pyrolytic lignin (PL-0PET) and blends of pyrolytic lignin and PET at 5 wt% PET (PL-5PET) and 20 wt% PET (PL-20PET). Included is an image of the PL-5PET carbon fibers as produced with tension applied during the conversion steps [199].

7 Poly(vinyl chloride)

Perhaps most commonly known for its application as fluid transfer piping, poly(vinyl chloride) (PVC), often referred to simply as vinyl, finds many applications due to its processibility and properties. PVC can be formulated to be flexible or rigid with or without the addition of plasticizers, and the chlorine atom included in the backbone makes PVC flame retardant. It can be extruded, injection molded, calendared, and blow molded just to name a few suitable processing methods [200]. It was the fifth most produced plastic in the world in 2015 when as much as 38 million tons were produced [107].

In a way, PVC was used as a carbon fiber precursor as early as 1965. Sugio Ōtani [201] demonstrated that the pyrolysis product of PVC could be melt-spun into pitch fibers and converted into carbon fibers with appreciable mechanical properties (tensile strength up to 1.57 GPa and tensile modulus up to approximately 53.9 GPa). This method has returned to relevance due to increasing interest in valorizing waste plastic; in 2007, Qiao et al. [202] demonstrated the production of carbon fibers from pitch derived from waste PVC. Recently, PVC fibers have been successfully used as a carbon fiber precursor. Kim et al. [203] demonstrated the conversion of chlorinated PVC (CPVC) into carbon fibers. CPVC is a derivative of PVC wherein the chlorine content of PVC is increased from 56% to 65%. The authors wet spun CPVC into fibers and then elongated the fibers at a series of rates at elevated temperature to explore the effect. The CPVC fibers could be carbonized directly, which provides a cost advantage over precursors that require an oxidation stage, and full carbonization was complete at 900°C. The stretched precursors exhibited increases in crystallinity and tensile strength with increasing elongation. The resulting carbon fibers were densified, pore-free, and achieved a final diameter as small as 6.7 μm from the precursors elongated by 125%. These fibers also achieved a tensile strength up to 1.83 GPa and tensile modulus up to 172 GPa at an elongation at break of 1%, and the authors claim that it could be produced for as little as $6/kg [204]. The inclusion of chlorine in the backbone of the polymer chain makes this precursor attractive compared to polyethylene or polyamide, which require treatment with heteroatoms such as sulfur or halogens to affect successful abstraction of the noncarbon atoms during conversion. Although CPVC does not have favorable rheology for melt spinning, blends of CPVC with poly(methyl methacrylate) have been shown to be melt processible [205].

8 Challenges and Opportunities

Commodity synthetic plastics offer a potential pathway to produce low-cost carbon fiber, but challenges remain. Common to the commodity plastic precursors presented in this review is the insufficient thermal stability of the virgin polymers for successful carbonization. The process of modifying the fibers to achieve thermal stabilization, such as the immersion of polyethylene fibers in high concentration sulfuric acid at high temperature, adds cost and complexity that limits or erases the advantages gained from feedstock abundance and melt spinning throughput.

Additionally, regardless of cost, the mechanical properties of carbon fibers derived from commodity plastic precursors have yet to reach those of PAN-based fibers (see **Fig. 18** and **Table 1**). Although mechanisms have been proposed for the stabilization and conversion of these materials into carbon fibers, much remains to be learned about the conversion process at a molecular level. Furthermore, the evolution of graphitic structures from the precursor polymer molecular structure is largely unknown or unreported. Gaining a fundamental understanding of these processes will enable optimization for increased mechanical properties and reduced cost. To that end, modern computational methods are enabling new explorations into the molecular interactions of these plastics as they undergo conversion to carbon fibers. For example, atomistic ReaxFF simulations have been used to probe the formation of graphitic carbon during the conversion of PAN/PBO blends to observe the activity of nitrogen and oxygen containing groups and their effect on the formation of carbon rings during carbonization [206]. This has a great effect on the mechanical properties of the resulting carbon fibers. Such results demonstrate the promise of discovering cost-saving and performance-enhancing process optimizations driven by first principles.

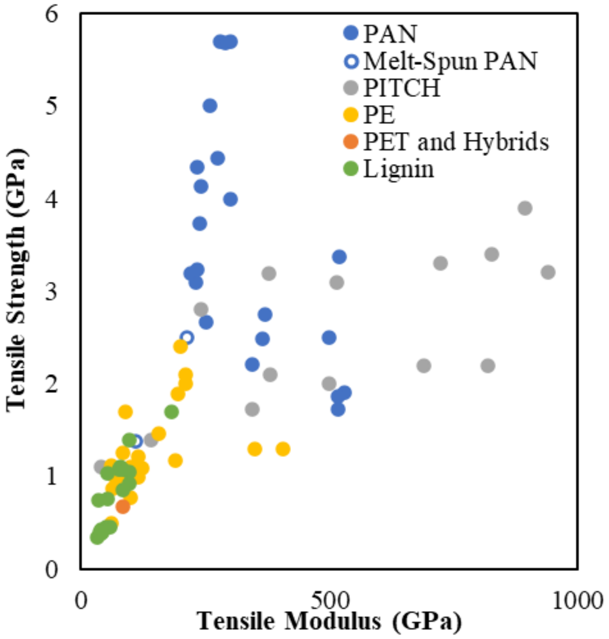

Fig. 18. Mechanical properties of carbon fibers derived from different precursors (data derived from [2,37,211–218,76,95,126,129,207–210]).

Recent advances in nanoparticle and polymer nanocomposite synthesis present an additional opportunity to raise the performance threshold for carbon fiber derived from commodity synthetic plastics [219–223]. It has been demonstrated that the inclusion of graphene, a two-dimensional allotrope of carbon, in PAN spinning solution reduced the porosity of wet spun PAN fibers, increased molecular alignment, and improved the mechanical properties of the resulting fibers. Molecular dynamics simulations showed that the graphene particles encouraged molecular alignment at and beyond the nanoparticle [219]. The graphene content required to achieve this improvement was a miniscule 0.075 wt%, so the added cost would be small. Similarly, graphene oxide nanoparticles were used to greatly reinforce and increase the crystallinity of PAN precursor fibers [220]. This effect may thus be extended to commodity plastic precursors to improve mechanical properties and increase the value of the resulting carbon fibers. Nanoparticles may also play a role in the chemical evolution of the materials. It has been shown that functionalized carbon nanotubes can greatly reduce the activation energy of PAN by initiating cyclization and generating free radicals. The lower activation energy enabled stabilization at a lower temperature resulting in greater mechanical properties attributed to reduced thermal damage to the surface of the fibers [221]. Using nanoparticles as a vector for radical generation may accelerate or improve the stabilization of commodity plastic precursors.

Commodity synthetic plastics also offer opportunities to reduce the cost of carbon fiber production through combination with other alternative precursors. Precursor blending with commodity plastics has been recognized as a potential pathway to overcoming the processing and performance issues associated with pitch and lignin precursors. It is surmised that combining pitch and PE may improve the spinnability of pitch precursor fibers and the ductility of pitch-based carbon fibers [125]. Indeed, researchers demonstrated in 2019 that PE-co-pitch precursors can be melt spun and can yield carbon fibers with over 70% carbon yield from a single-step carbonization process [224]. Lignin has long been attractive as a filler to displace more expensive primary constituents because it is an inexpensive byproduct. Today, it can be found in plastics and elastomers for cost reduction and property modification purposes [225,226]. This same principle is applied to alternative carbon fiber precursors; Lignin has been blended with PAN [211,227–232] and commodity plastics such as PP and PET [196]. The former of these pairings outperforms the latter and has received commensurate attention, but the combination of commodity synthetic plastics with a bio-based and inexpensive material poses a great opportunity for very low-cost precursors. The benefits may be extended even further in the case of recycled synthetic commodity plastics blended with lignin, but this presents even greater challenges due to contemporary constraints in recycled plastic quality.

Table 1. Conversion parameters and resultant carbon fiber properties for the major conventional carbon fiber precursors, wet-spun PAN and mesophase pitch, compared with low-cost commodity plastic alternative precursors and lignin.

Precursor	Stabilization	Carbonization	Graphitization	Carbon Yield (%) / Fiber Diameter (μm)	Tensile Strength (MPa) / Modulus (GPa)	Ref.
PAN *(wet spun)*	180-300°C 3-20 hr in Air	1100-1500°C in N_2	≥2500°C	~50/ 6-10	1720-5700/ 220-530	[2]
PAN *(melt spun)*	220-280°C 2-4 hr in Air	1200°C in N_2	-	-/-	2000-2300/ 156-202	[37]
Pitch *(mesophase)*	250-400°C 4-24hr in Air	1100-1500°C in N_2	1800-2800°C	60-88/ 10-12	1400-3900/ 140-940	[2]
Lignin	250-280°C 1-5hr in Air	1000°C in N_2	-	25-65/ 5-90	290-1070/ 30-180	[90,93]
UHMWPE	Sulfonation 130-140°C 45-120 min 0-1 bar pressure	1100-1200°C in N_2	-	50-80/ -	700-2100/ 100-210	[121,122]
HDPE	Sulfonation 180-200°C 60-150 min 0-5 bar pressure	1000-1200°C in N_2	-	70-76/ 10-15	2000-2300/ 140-150	[110,120,132]
LLDPE	Various Sulfonation treatments: (i) Sulfonation 95-160°C 1-4 hours, 0-5 bar pressure (ii) Fuming Sulfuric Acid 23-120°C 0.5-24 hours (iii) Boric Acid 50-140°C 120min, 1bar pressure	900-1000°C in N_2	1800-2400°C	12-75/ 6-40	630-2400/ 28-200	[12,116,131–133]
PP	Sulfonation 90-120°C 1-3 hrs	1000°C in N_2	-	50-65/ 10-15	200/ 26	[109,158]
Kevlar (Aramid)	-	800-1000°C in N_2	-	38-65/ 5-30	-/-	[101,145–147]
PA 6 (Aliphatic)	Metal salt impregnation, two-staged ramped oxidation in air	500-1100°C in N_2	-	44-60/ 6-12	194/ 81	[160]
PET/Lignin	Auto-oxidation during carbonization	1000°C in N_2	-	23-45/ 31-45	669-703/ 84-94	[196]
PS	Chemical treatment with various acids and metal salts	800°C in N_2	-	36/-	-/-	[170]
CPVC	-	900°C in N_2	-	29/ 6.7	1830/ 172	[204]

9 Summary

The high cost of carbon fiber production is limiting the proliferation of CFRP composites that could greatly improve vehicle energy efficiency, expand renewable energy production, and reinforce domestic infrastructure. Commodity plastics have the potential to greatly reduce the cost of carbon fibers by replacing costly PAN, and its slow and expensive solution spinning process, as a precursor to carbon fibers. They are mass-produced globally at low cost due to their melt processibility, and oftentimes broadly available as a recycled feedstock for further cost savings. The state of the art of carbon fiber synthesis from commodity plastic precursors has been presented in this review, and their conversion methods and the resulting carbon fiber properties are summarized in **Table 1**. Polyethylene has received the greatest attention and achieved the highest mechanical properties of the precursors presented in this review, but much remains to be learned and explored about the more nascent options like polyamides, polystyrene, polyesters, and poly(vinyl chloride). Despite the challenges facing the commercialization of these precursors and their production methods, advances in computational methods and polymer nanocomposites are creating new opportunities to push the boundaries of commodity plastic-derived, low-cost carbon fibers.

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References

[1] E. Fitzer, Carbon Fibres — Present State and Future Expectations, in: J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Eds.), Carbon Fibers Filaments Compos., Springer Netherlands, Dordrecht, 1990: pp. 3–41. https://doi.org/10.1007/978-94-015-6847-0_1.

[2] D.D.L. Chung, Carbon Fiber Composites, 1994. https://doi.org/10.1016/B978-0-08-050073-7.50010-5.

[3] R.J. Diefendorf, High performance carbon fibers, 1975. https://doi.org/https://doi.org/10.1002/pen.760150306.

[4] E. Fitzer, M. Heine, Carbon fibre manufacture and surface treatment, in: A.R. Bunsell (Ed.), Fiber Reinf. Compos. Mater., Elsevier, New York, 1988: pp. 73–146. https://doi.org/10.13140/RG.2.1.4782.5128.

[5] B.L. Ennis, C.L. Kelley, B.T. Naughton, R.E. Norris, S. Das, D. Lee, D.A. Miller, Optimized Carbon Fiber Composites in Wind Turbine Blade Design, Albuquerque, New Mexico, 2019. https://classic.ntis.gov/help/order-methods/ (accessed August 13, 2021).

[6] Lightweight Materials R&D Annual Progress Report 2013, 2014.

[7] W. Zhang, Q. Zheng, A. Ashour, B. Han, Self-healing cement concrete composites for resilient infrastructures: A review, Compos. Part B Eng. 189 (2020) 107892. https://doi.org/10.1016/j.compositesb.2020.107892.

[8] R.A. Sullivan, Automotive carbon fiber: Opportunities and challenges, JOM. 58 (2006) 77–79. https://doi.org/10.1007/s11837-006-0233-3.

[9] X. Huang, Fabrication and properties of carbon fibers, Materials (Basel). 2 (2009) 2369–2403. https://doi.org/10.3390/ma2042369.

[10] A.A. Ogale, M. Zhang, J. Jin, J.J. Amod A. Ogale, Meng Zhang, Recent advances in carbon fibers derived from biobased precursors, J. Appl. Polym. Sci. 133 (2016). https://doi.org/https://doi.org/10.1002/app.43794.

[11] E. Frank, L.M. Steudle, D. Ingildeev, J.M. Spörl, M.R. Buchmeiser, D.E.F.D. -Chem. L.M.S.D.D.I.D. -Chem. J.M.S.P.M.R. Buchmeiser, Carbon fibers: Precursor systems, processing, structure, and properties, Angew. Chemie - Int. Ed. 53 (2014) 5262–5298. https://doi.org/10.1002/anie.201306129.

[12] D. Choi, H.S. Kil, S. Lee, Fabrication of low-cost carbon fibers using economical precursors and advanced processing technologies, Carbon N. Y. 142 (2019) 610–649. https://doi.org/10.1016/j.carbon.2018.10.028.

[13] L.H. Peebles, Carbon Fibers from Acrylic Precursors, in: Carbon Fibers Form. Struct. Prop., CRC Press Inc., Boca Raton, FL, 1995: pp. 7–27.

[14] M.L. Minus, S. Kumar, The processing, properties, and structure of carbon fibers, JOM. 57 (2005) 52–58. https://doi.org/https://doi.org/10.1007/s11837-005-0217-8.

[15] L. Fischer, W. Ruland, The influence of graphitization on the mechanical properties of carbon fibers, Colloid Polym. Sci. 258 (1980) 917–922.

[16] E. Fitzer, PAN-based carbon fibers-present state and trend of the technology from the viewpoint of possibilities and limits to influence and to control the fiber properties by the process parameters, Carbon N. Y. 27 (1989) 621–645. https://doi.org/10.1016/0008-6223(89)90197-8.

[17] S.K. Nataraj, K.S. Yang, T.M. Aminabhavi, Polyacrylonitrile-based nanofibers - A state-of-the-art review, Prog. Polym. Sci. 37 (2012) 487–513. https://doi.org/10.1016/j.progpolymsci.2011.07.001.

[18] D.D.L. Chung, Processing of Carbon Fibers, in: Carbon Fiber Compos., 1st ed., Butterworth-Heinemann, Boston, 1994: pp. 13–53. https://doi.org/10.1016/b978-0-08-050073-7.50006-3.

[19] K. Sada, K. Kokado, Y. Furukawa, Polyacrylonitrile (PAN), in: Encycl. Polym. Nanomater., Springer Berlin Heidelberg, 2015: pp. 1745–1750. https://doi.org/10.1007/978-3-642-29648-2_249.

[20] G. Konstantopoulos, S. Soulis, D. Dragatogiannis, C. Charitidis, Introduction of a Methodology to Enhance the Stabilization Process of PAN Fibers by Modeling and Advanced Characterization, Materials (Basel). 13 (2020) 2749. https://doi.org/10.3390/ma13122749.

[21] H. Khayyam, R.N. Jazar, S. Nunna, G. Golkarnarenji, K. Badii, S.M. Fakhrhoseini, S. Kumar, M. Naebe, PAN precursor fabrication, applications and thermal stabilization process in carbon fiber production: Experimental and mathematical modelling, Prog. Mater. Sci. 107 (2020). https://doi.org/10.1016/j.pmatsci.2019.100575.

[22] D.D. Edie, The effect of processing on the structure and properties of carbon fibers, Carbon N. Y. 36 (1998) 345–362. https://doi.org/10.1016/S0008-6223(97)00185-1.

[23] J. Chen, C.G. Wang, X.G. Dong, H.Z. Liu, Study on the coagulation mechanism of wet-spinning PAN fibers, J. Polym. Res. 13 (2006) 515–519. https://doi.org/10.1007/s10965-006-9075-5.

[24] E. Morris, M. Weisenberger, G. Rice, Properties of PAN Fibers Solution Spun into a Chilled Coagulation Bath at High Solvent Compositions, Fibers. 3 (2015) 560–574. https://doi.org/10.3390/fib3040560.

[25] S. Edrington, The Limits & Effects of Draw on Properties and Morphology of PAN-Based Precursor and the Resultant Carbon Fibers, University of Kentucky, 2017. https://doi.org/10.13023/ETD.2017.165.

[26] B.A. Newcomb, Processing, structure, and properties of carbon fibers, Compos. Part A Appl. Sci. Manuf. 91 (2016) 262–282. https://doi.org/10.1016/j.compositesa.2016.10.018.

[27] Y. Imura, R.M.C. Hogan, M. Jaffe, Dry spinning of synthetic polymer fibers, in: D. Zhang (Ed.), Adv. Filam. Yarn Spinn. Text. Polym., Woodhead Publishing, 2014: pp. 187–202. https://doi.org/10.1533/9780857099174.2.187.

[28] A. Rawal, S. Mukhopadhyay, Melt spinning of synthetic polymeric filaments, in: Adv. Filam. Yarn Spinn. Text. Polym., Elsevier Ltd., 2014: pp. 75–99. https://doi.org/10.1533/9780857099174.2.75.

[29] R. Hufenus, Y. Yan, M. Dauner, T. Kikutani, Melt-spun fibers for textile applications, Materials (Basel). 13 (2020) 1–32. https://doi.org/10.3390/ma13194298.

[30] S.R. Hutchinson, Thermoplastic Polyacrylonitrile, North Carolina State University, n.d. https://repository.lib.ncsu.edu/bitstream/handle/1840.16/2678/etd.pdf?sequence=1&isAllowed=y (accessed December 5, 2020).

[31] F. Paulauskas, Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers, 2016.

[32] J. Udakhe, V. Goud, Melt processing of Polyacrylonitrile (PAN) polymers, J. Text. Assoc. 71 (2011) 233–241.

[33] Y. Arai, Pitch-Based Carbon Fibers, in: Soc. Fiber Sci. Techno J. High-Performance Spec. Fibers, Springer, Tokyo, 2016: pp. 343–354. https://doi.org/https://doi.org/10.1007/978-4-431-55203-1_21.

[34] J. Liu, X. Chen, D. Liang, Q. Xie, Development of pitch-based carbon fibers: a review, Energy Sources, Part A Recover. Util. Environ. Eff. 00 (2020) 1–21. https://doi.org/10.1080/15567036.2020.1806952.

[35] C. Daulbayev, B. Kaidar, F. Sultanov, B. Bakbolat, G. Smagulova, Z. Mansurov, The recent progress in pitch derived carbon fibers applications. A Review, South African J. Chem. Eng. 38 (2021) 9–20. https://doi.org/10.1016/J.SAJCE.2021.07.001.

[36] C.D. Coxe, Preparation of Shaped Articles from Acrylonitrile Polymers, 2585444, 1952. https://patentimages.storage.googleapis.com/2c/a0/8a/41415a990ed03b/US2585444.pdf (accessed December 7, 2020).

[37] D. Grove, P. Desai, A.S. Abhiraman, Exploratory experiments in the conversion of plasticized melt spun PAN-based precursors to carbon fibers, Carbon N. Y. 26 (1988) 403–411. https://doi.org/10.1016/0008-6223(88)90233-3.

[38] J. Yu, G.C. Miller, J.S. Riffle, D.G. Baird, Identifying Melt Processing Conditions for a Polyacrylonitrile Copolymer Plasticized with Water, Acetonitrile and their Mixtures, Int. Polym. Process. 34 (2019) 307–313. https://doi.org/10.3139/217.3750.

[39] J. Yu, D.G. Baird, Study of Melt Spinning Processing Conditions for a Polyacrylonitrile Copolymer with a Water/Ethanol Mixture as a Plasticizer, Int. Polym. Process. 34 (2019) 557–563. https://doi.org/10.3139/217.3847.

[40] B.L. Batchelor, S.F. Mahmood, M. Jung, H. Shin, O. V. Kulikov, W. Voit, B.M. Novak, D.J. Yang, Plasticization for melt viscosity reduction of melt processable carbon fiber precursor, Carbon N. Y. 98 (2016) 681–688. https://doi.org/10.1016/j.carbon.2015.10.096.

[41] S. Kanishke Atureliya, Z. Bashir, Continuous plasticized melt-extrusion of polyacrylonitrile homopolymer, (1993).

[42] D.L. Green, W.A. Hare, Preparation of spinning mixtures, 2699433, 1955. https://patents.google.com/patent/US2699433A/en?oq=US2699433 (accessed July 14, 2021).

[43] G.M. Rothrock, Melt spinning polyacrylonitriles, 2706674, 1955.

[44] Z. Bashir, S.P. Church, D.M. Price, The formation of polymer-solvent complexes of polyacrylonitrile from organic solvents containing carbonyl groups, Acta Polym. 44 (1993) 211–218. https://doi.org/10.1002/ACTP.1993.010440501.

[45] G.A. Serad, Polyacrylonitrile composition admixed with low boiling acetonitrile fraction and high boiling compatible plasticizer, 3940405, 1976.

[46] W.A. Hare, Method of preparing resilient acrylonitrile polymer fibers, 2764468, 1956.

[47] J. Farago, Process for preparing filaments from acrylonitrile polymer-containing compositions, 3094502, 1963.

[48] R.E. Opferkuch, J.C. Ross, Method of melting acrylonitrile polymers and copolymers, 3388202, 1968.

[49] N. Pereira Alves, Thermoplastic polyacrylonitrile production process, 2011/0024939, 2011.

[50] G.P. Daumit, Y.S. Ko, C.R. Slater, J.G. Venner, C.C. Young, Melt-spun acrylic fibers possessing a highly uniform internal structure which are particularly suited for thermal conversion to quality carbon fibers, 5168004, 1992. https://patentimages.storage.googleapis.com/b6/e6/9d/3d7b85fb18c2bc/US5168004.pdf (accessed March 30, 2022).

[51] G.P. Daumit, C.R. Slater, J.G. Venner, C.C. Young, M.M. Zwick, Formation of melt-spun acrylic fibers which are well suited for thermal conversion to high strength carbon fibers, 4981752, 1991.

[52] R. Fleming Ribeiro, L. Claudio Pardini, N. Pereira Alves, C. Alberto Rios Brito Júnior, Thermal Stabilization study of polyacrylonitrile fiber obtained by extrusion, 25 (2015) 523–530. https://doi.org/10.1590/0104-1428.1938.

[53] Y.M. Im, H.M. Choi, A.J. Nathanael, M.H. Jeong, S.O. Lee, S.N. Yun, T.H. Oh, Effects of Glycerol on Melt Spinning of Polyacrylonitrile Copolymer and Tetrapolymer, Fibers Polym. 2020 212. 21 (2020) 376–383. https://doi.org/10.1007/S12221-020-9412-Z.

[54] Xiang Li, Xiaofei Ji, Chunju He, Evolution of the morphological and structural properties of plasticized spinning polyacrylonitrile fibers during the stabilization process, RSC Adv. 5 (2015) 81399–81406. https://doi.org/10.1039/C5RA14391H.

[55] M. Maghe, C. Creighton, L.C. Henderson, M.G. Huson, S. Nunna, S. Atkiss, N. Byrne, B.L. Fox, Using ionic liquids to reduce energy consumption for carbon fibre production, J. Mater. Chem. A. (2016) 16619–16626. https://doi.org/10.1039/c6ta06842a.

[56] M. Zhen, J. Yu, S. Dai, Preparation of Inorganic Materials Using Ionic Liquids, Adv. Mater. 22 (2010) 261–285. https://doi.org/10.1002/ADMA.200900603.

[57] N. Byrne, J. Chen, B. Fox, Enhancing the carbon yield of cellulose based carbon fibres with ionic liquid impregnates, J. Mater. Chem. A. (2014) 15758–15762. https://doi.org/10.1039/c4ta04059g.

[58] Y. Tian, K. Han, W. Zhang, J. Zhang, H. Rong, D. Wang, B. Yan, S. Liu, M. Yu, Influence of residence time on the structure of polyacrylonitrile in ionic liquids during melt spinning process, Mater. Lett. 92 (2013) 119–121. https://doi.org/v.

[59] X. Li, A. Qin, X. Zhao, B. Ma, C. He, The plasticization mechanism of polyacrylonitrile/1-butyl-3-methylimidazolium chloride system, Polymer (Guildf). 55 (2014) 5773–5780. https://doi.org/10.1016/J.POLYMER.2014.08.057.

[60] S. Liu, K. Han, L. Chen, Y. Zheng, M. Yu, Structure and properties of partially cyclized polyacrylonitrile-based carbon fiber—precursor fiber prepared by melt-spun with ionic liquid as the medium of processing, Polym. Eng. Sci. 55 (2015) 2722–2728. https://doi.org/10.1002/PEN.24121.

[61] X. Li, Z. Li, X. Dang, D. Luan, F. Wang, H. Chen, C. Wang, Structural and thermal property changes of plasticized spinning polyacrylonitrile fibers under different spinning speeds, J. Appl. Polym. Sci. 134 (2017) 45267. https://doi.org/10.1002/APP.45267.

[62] Y. Tian, K. Han, W. Zhang, J. Zhang, R. Zhang, S. Lui, M. Yu, Influence of melt temperature on structure of polyacrylonitrile in Ionic Liquids during Plasticized melt spinning process, Appl. Mecha. 268–270 (2013) 483–486. https://doi.org/10.4028/www.scientific.net/AMM.268-270.483.

[63] S. Liu, K. Han, L. Chen, Y. Zheng, M. Yu, Influence of air circulation on the structure and properties of melt-spun PAN precursor fibers during thermal oxidation, RSC Adv. 5 (2015)

37669–37674. https://doi.org/10.1039/C5RA00476D.

[64] H.J. Martin, H. Luo, H. Chen, C.L. Do-Thanh, L.T. Kearney, R. Mayes, A.K. Naskar, S. Dai, Effect of the Ionic Liquid Structure on the Melt Processability of Polyacrylonitrile Fibers, ACS Appl. Mater. Interfaces. 12 (2020) 8663–8673. https://doi.org/10.1021/ACSAMI.9B19704/SUPPL_FILE/AM9B19704_SI_001.PDF.

[65] P. Rangarajan, J. Yang, V. Bhanu, D. Godshall, J. McGrath, G. Wilkes, D. Baird, Effect of comonomers on melt processability of polyacrylonitrile, J. Appl. Polym. Sci. 85 (2002) 69–83. https://doi.org/10.1002/APP.10655.

[66] V.A. Bhanu, P. Rangarajan, K. Wiles, M. Bortner, M. Sankarpandian, D. Godshall, T.E. Glass, A.K. Banthia, J. Yang, G. Wilkes, D. Baird, J.E. McGrath, Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors, Polymer (Guildf). 43 (2002) 4841–4850. https://doi.org/10.1016/S0032-3861(02)00330-0.

[67] G.C. Miller, J. Yu, R.M. Joseph, S.R. Choudhury, S.J. Mecham, D.G. Baird, M. Bortner, R.E. Norris, F.L. Paulauskas, J.S. Riffle, Melt-spinnable polyacrylonitrile copolymer precursors for carbon fibers, Polymer (Guildf). 126 (2017) 87–95. https://doi.org/10.1016/J.POLYMER.2017.08.023.

[68] D. Alcalá-Sánchez, J.C. Tapia-Picazo, A. Bonilla-Petriciolet, G. Luna-Bárcenas, J.M. López-Romero, A. Álvarez-Castillo, Analysis of Terpolymerization Systems for the Development of Carbon Fiber Precursors of PAN, Int. J. Polym. Sci. 2020 (2020). https://doi.org/10.1155/2020/8029516.

[69] M.C. Paiva, P. Kotasthane, D.D. Edie, A.A. Ogale, UV stabilization route for melt-processible PAN-based carbon fibers, Carbon N. Y. 41 (2003) 1399–1409. https://doi.org/10.1016/S0008-6223(03)00041-1.

[70] N. Han, X.X. Zhang, W.Y. Yu, X.Y. Gao, Effects of copolymerization temperatures on structure and properties of melt-spinnable acrylonitrile-methyl acrylate copolymers and fibers, Macromol. Res. 2010 1811. 18 (2010) 1060–1069. https://doi.org/10.1007/S13233-010-1115-7.

[71] P. Bajaj, T. V. Sreekumar, K. Sen, Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers, Polymer (Guildf). 42 (2001) 1707–1718. https://doi.org/10.1016/S0032-3861(00)00583-8.

[72] G.S. Krishnan, P. Thomas, N. Murali, Synthesis, characterization, and thermo-mechanical properties of poly(acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-itaconic acid) as carbon fibre polymer precursors, RSC Adv. 6 (2016) 6182–6190. https://doi.org/10.1039/C5RA24185E.

[73] S. Faraji, M.F. Yardim, D.S. Can, A.S. Sarac, Characterization of polyacrylonitrile, poly(acrylonitrile-co-vinyl acetate), and poly(acrylonitrile-co-itaconic acid) based activated carbon nanofibers, J. Appl. Polym. Sci. 134 (2017). https://doi.org/10.1002/APP.44381/FORMAT/PDF.

[74] R. Fleming, T.O. Candido, N.P. Granado, L.C. Pardini, Melt spinning of poly(acrylonitrile)-co-styrene copolymer, Polym. Degrad. Stab. 192 (2021) 109702. https://doi.org/10.1016/j.polymdegradstab.2021.109702.

[75] T. Mukundan, V.A. Bhanu, K.B. Wiles, H. Johnson, M. Bortner, D.G. Baird, A.K. Naskar, A.A. Ogale, D.D. Edie, J.E. McGrath, A photocrosslinkable melt processible acrylonitrile

terpolymer as carbon fiber precursor, Polymer (Guildf). 47 (2006) 4163–4171. https://doi.org/10.1016/j.polymer.2006.02.066.

[76] J.H. Lee, J.U. Jin, S. Park, D. Choi, N.H. You, Y. Chung, B.C. Ku, H. Yeo, Melt processable polyacrylonitrile copolymer precursors for carbon fibers: Rheological, thermal, and mechanical properties, J. Ind. Eng. Chem. 71 (2019) 112–118. https://doi.org/10.1016/J.JIEC.2018.11.012.

[77] C. Banerjee, V.K. Chandaliya, P.S. Dash, Recent advancement in coal tar pitch-based carbon fiber precursor development and fiber manufacturing process, J. Anal. Appl. Pyrolysis. 158 (2021) 105272. https://doi.org/10.1016/J.JAAP.2021.105272.

[78] J. Kim, U.S. Im, B. Lee, D.H. Peck, S.H. Yoon, D.H. Jung, Pitch-based carbon fibers from coal tar or petroleum residue under the same processing condition, Carbon Lett. 19 (2016) 72–78. https://doi.org/10.5714/CL.2016.19.072.

[79] G. Yuan, Z. Xue, Z. Cui, A. Westwood, Z. Dong, Y. Cong, J. Zhang, H. Zhu, X. Li, Constructing the Bridge from Isotropic to Anisotropic Pitches for Preparing Pitch-Based Carbon Fibers with Tunable Structures and Properties, (2020). https://doi.org/10.1021/acsomega.0c03226.

[80] H. Hoshiro, R. Endo, F.E. Sloan, High-Performance and Specialty Fibers, Springer Japan, Tokyo, 2016. https://doi.org/10.1007/978-4-431-55203-1.

[81] G. Yuan, X. Li, Z. Dong, X. Xiong, B. Rand, Z. Cui, Y. Cong, J. Zhang, Y. Li, Z. Zhang, J. Wang, Pitch-based ribbon-shaped carbon-fiber-reinforced one-dimensional carbon/carbon composites with ultrahigh thermal conductivity, Carbon N. Y. 68 (2014) 413–425. https://doi.org/10.1016/j.carbon.2013.11.018.

[82] S. Wen, D.D.L. Chung, Pitch-matrix composites for electrical, electromagnetic and strain-sensing applications, J. Mater. Sci. 40 (2005) 3897–3903. https://doi.org/10.1007/s10853-005-0717-5.

[83] S. Muthusamy, D.D.L. Chung, Carbon-Fiber Cement-Based Materials for Electromagnetic Shielding, ACI Mater. J. 107 (2010) 602–610. https://doi.org/10.14359/51664047.

[84] H. Hoshiro, R. Endo, F.E. Sloan, High-Performance and Specialty Fibers, Springer Japan, Tokyo, 2016. https://doi.org/10.1007/978-4-431-55203-1.

[85] S. Otani, A. Oya, Progress of Pitch-Based Carbon Fiber in Japan, in: ACS Symp. Ser., ACS, 1986: pp. 323–334. https://doi.org/10.1021/bk-1986-0303.ch022.

[86] S. Kundu, Investigation of flow and microstructure in rheometric and processing flow conditions for liquid crystalline pitch, Clemson University, 2006. https://tigerprints.clemson.edu/all_dissertations/38 (accessed November 8, 2020).

[87] B. Rahman, Flow Modeling of Synthetic Pitch Extrusion through Spinnerets for Continuous Fibers, Clemson University, 2018. https://tigerprints.clemson.edu/all_theses (accessed November 2, 2020).

[88] Z. Jiang, T. Ouyang, X. Yao, Y. Fei, The effect of the spinning conditions on the structure of mesophase pitch-based carbon fibers by Taguchi method, Carbon Lett. 19 (2016) 89–98. https://doi.org/10.5714/CL.2016.19.089.

[89] Lignin – a natural resource with huge potential - Bioeconomy, (n.d.). https://www.biooekonomie-bw.de/en/articles/dossiers/lignin-a-natural-resource-with-huge-potential (accessed April 20, 2021).

[90] O. Hosseinaei, D. P. Harper, J. J. Bozell, T. G. Rials, Role of Physicochemical Structure of Organosolv Hardwood and Herbaceous Lignins on Carbon Fiber Performance, ACS Sustain. Chem. & Eng. 4 (2016) 5785–5798. https://doi.org/10.1021/acssuschemeng.6b01828.

[91] Y.Y. Wang, X. Meng, Y. Pu, A.J. Ragauskas, Recent advances in the application of functionalized lignin in value-added polymeric materials, Polymers (Basel). 12 (2020) 1–24. https://doi.org/10.3390/polym12102277.

[92] Y. Liu, S. Ahmed, D.E. Sameen, Y. Wang, R. Lu, J. Dai, S. Li, W. Qin, W.Q. Yaowen Liu, Saeed Ahmeda, Dur E. Sameena, Yue Wanga, Rui Lua, Jianwu Dai, Suqing Lia, A review of cellulose and its derivatives in biopolymer-based for food packaging application, Trends Food Sci. Technol. 112 (2021) 532–546. https://doi.org/https://doi.org/10.1016/j.tifs.2021.04.016.

[93] O.P. Bahl, Z. Shen, J.G. Lavin, R.A. Ross, Manufacture of Carbon Fibers, in: J.B. Donnet, T.K. Wang, J.C.M. Peng, S. Rebouillat (Eds.), Carbon Fibers, Third, Marcel Dekker, Inc., New York, 1998: pp. 1–84.

[94] A.G. Dumanlı, A.H. Windle, Carbon fibres from cellulosic precursors: A review, J. Mater. Sci. 47 (2012) 4236–4250. https://doi.org/10.1007/S10853-011-6081-8/FIGURES/11.

[95] A. Bengtsson, P. Hecht, J. Sommertune, M. Ek, M. Sedin, E. Sjöholm, Carbon Fibers from Lignin-Cellulose Precursors: Effect of Carbonization Conditions, ACS Sustain. Chem. Eng. 8 (2020) 6826–6833. https://doi.org/10.1021/acssuschemeng.0c01734.

[96] H.P. Fink, P. Weigel, H.J. Purz, J. Ganster, Structure formation of regenerated cellulose materials from NMMO-solutions, Prog. Polym. Sci. 26 (2001) 1473–1524. https://doi.org/10.1016/S0079-6700(01)00025-9.

[97] Y. Zhang, H. Li, X. Li, M.E. Gibril, K. Han, M. Yu, Green chemical preparation of cellulose/high performance elastomer blend fibers by melt-spinning method, J. Polym. Res. 20 (2013) 1–9. https://doi.org/10.1007/S10965-013-0171-Z/FIGURES/10.

[98] Y. Aranishi, Y. Nishio, Cellulosic Fiber Produced by Melt Spinning, in: Blends Graft Copolym. Cellul., Springer, Cham, 2017: pp. 109–125. https://doi.org/10.1007/978-3-319-55321-4_5.

[99] P. Willberg-Keyriläinen, T. Rokkonen, T. Malm, A. Harlin, J. Ropponen, Melt spinnability of long chain cellulose esters, J. Appl. Polym. Sci. 137 (2020). https://doi.org/10.1002/APP.49588.

[100] L. Zhang, M. Kowalik, Z. Gao, C.M. Ashraf, S. Rajabpour, C. Bumgardner, Y. Schwab, B. Damirchi, J. Zhu, D. Akbarian, J.W. Klett, A.C.T. van Duin, X. Li, Converting PBO fibers into carbon fibers by ultrafast carbonization, Carbon N. Y. 159 (2020) 432–442. https://doi.org/10.1016/j.carbon.2019.12.067.

[101] Y. Kawahara, S. Otoyama, K. Yamamoto, H. Wakizaka, Y. Shinahara, H. Hoshiro, N. Ishibashi, N. Iwashita, Direct Carbonization of High-performance Aromatic Polymers and the Production of Activated Carbon Fibers, J Text. Sci Eng. 5 (2015) 6. https://doi.org/10.4172/2165-8064.1000219.

[102] J.A. Newell, D.K. Rogers, D.D. Edie, C.C. Fain, Direct carbonization of PBO fiber, Carbon N. Y. 32 (1994) 651–658. https://doi.org/10.1016/0008-6223(94)90086-8.

[103] Zylon Fibers, (n.d.). https://polymerdatabase.com/Fibers/PBO.html (accessed August 13, 2021).

[104] E.W. Choe, S.N. Kim, Synthesis, spinning, and fiber mechanical properties of poly(p-phenylenebenzobisoxazole), Macromolecules. 14 (1981) 920–924. https://doi.org/10.1021/MA50005A006.

[105] S. Kumar, S. Warner, D.T. Grubb, W.W. Adams, On the small-angle X-ray scattering of rigid-rod polymer fibres, Polymer (Guildf). 35 (1994) 5408–5412. https://doi.org/10.1016/S0032-3861(05)80003-5.

[106] A.L. Andrady, M.A. Neal, Applications and societal benefits of plastics, Philos. Trans. R. Soc. B Biol. Sci. 364 (2009) 1977–1984. https://doi.org/10.1098/rstb.2008.0304.

[107] R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, Sci. Adv. 3 (2017) e1700782. https://doi.org/10.1126/sciadv.1700782.

[108] E. Beckman, The world of plastics, in numbers, Conversat. (2018). https://theconversation.com/the-world-of-plastics-in-numbers-100291 (accessed May 3, 2021).

[109] C.A. Leon y Leon, R.A. O'Brien, J.J. McHugh, H. Dasarathy, W.C. Schimpf, Polyethylene and polypropylene as low cost carbon fiber (LCCF) precursors, Int. SAMPE Tech. Conf. 33 (2001) 1289–1296.

[110] A. Shozo Horikiri, T. Jiro Iseki, I. Masao Minobe, Process for production of carbon fiber, 4070446, 1978.

[111] I. Karacan, H. Benli, The effect of sulfonation treatment on the structure and properties of isotactic polypropylene fibers prior to the carbonization stage, J. Appl. Polym. Sci. 123 (2012) 3375–3389. https://doi.org/10.1002/app.34187.

[112] Polyethylene (PE) Plastic: Properties, Uses & Application, (n.d.). https://omnexus.specialchem.com/selection-guide/polyethylene-plastic (accessed May 18, 2021).

[113] T. Okamura, Polyethylene (PE; Low Density and High Density), in: S. Kobayashi, K. Müllen (Eds.), Encycl. Polym. Nanomater., Springer Berlin Heidelberg, Berlin, Heidelberg, 2015: pp. 1826–1829. https://doi.org/10.1007/978-3-642-29648-2_252.

[114] United States Plastic Corp., What's the difference between LDPE, LLDPE, MDPE, HDPE, XLPE and UHMW sheeting?, (n.d.).

[115] J.P. Penning, R. Lagcher, A.J. Pennings, The effect of diameter on the mechanical properties of amorphous carbon fibres from linear low density polyethylene, Polym. Bull. 25 (1991) 405–412. https://doi.org/10.1007/BF00316913.

[116] J.W. Kim, J.S. Lee, Preparation of carbon fibers from linear low density polyethylene, Carbon N. Y. 94 (2015) 524–530. https://doi.org/10.1016/j.carbon.2015.06.074.

[117] A.R. Postema, H. De Groot, A.. Pennings, Amorphous carbon fibres from linear low density polyethylene, J. Mater. Sci. 25 (1990) 4216–4222. https://doi.org/https://doi.org/10.1007/BF00581075.

[118] K.-W. Kim, H.-M. Lee, B.S. Kim, S.-H. Hwang, L.-K. Kwac, K.-H. An, B.-J. Kim, Preparation and thermal properties of polyethylene-based carbonized fibers, Carbon Lett. 16 (2015) 62–66. https://doi.org/10.5714/CL.2015.16.1.062.

[119] G.S. Wortberg, A. De Palmenaer, M. Beckers, G. Seide, T. Gries, Polyethylene-based carbon fibers by the use of sulphonation for stabilization, Fibers. 3 (2015) 373–379. https://doi.org/10.3390/fib3030373.

[120] A. De Palmenaer, G. Wortberg, F. Drissen, G. Seide, T. Gries, Production of Polyethylene Based Carbon Fibres, Chem. Eng. Trans. 43 (2015) 1699–1704. https://doi.org/10.3303/CET1543284.

[121] D. Zhang, G.S. Bhat, Carbon Fibers from Polyethylene-Based Precursors, Mater. Manuf. Process. 9 (1994) 221–235. https://doi.org/10.1080/10426919408934900.

[122] D. Zhang, Carbon Fibers from Oriented Polyethylene Precursors, J. Thermoplast. Compos. Mater. 6 (1993) 38–48. https://doi.org/10.1177/089270579300600104.

[123] F. Wang, L. Liu, P. Xue, M. Jia, Crystal Structure Evolution of UHMWPE/HDPE Blend Fibers Prepared by Melt Spinning, Polymers (Basel). 9 (2017). https://doi.org/10.3390/POLYM9030096.

[124] S.J.A. Houben, R.C.P. Verpaalen, T.A.P. Engels, Processing and Properties of Melt Processable UHMW-PE Based Fibers Using Low Molecular Weight Linear Polyethylene's, Macromol. Mater. Eng. 305 (2020) 2000360. https://doi.org/10.1002/MAME.202000360.

[125] S.M. Aldosari, M.A. Khan, S. Rahatekar, Manufacturing carbon fibres from pitch and polyethylene blend precursors: a review, J. Mater. Res. Technol. 9 (2020) 7786–7806. https://doi.org/10.1016/j.jmrt.2020.05.037.

[126] D. Zhang, Q. Sun, Structure and properties development during the conversion of polyethylene precursors to carbon fibers, J. Appl. Polym. Sci. 62 (1996) 367–373. https://doi.org/10.1002/(SICI)1097-4628(19961010)62:2<367::AID-APP11>3.0.CO;2-Z.

[127] J.M. Younker, T. Saito, M.A. Hunt, A.K. Naskar, A. Beste, Pyrolysis Pathways of Sulfonated Polyethylene, an Alternative Carbon Fiber Precursor, (2013). https://doi.org/10.1021/ja3121845.

[128] B.E. Barton, J. Patton, E. Hukkanen, M. Behr, J.C. Lin, S. Beyer, Y. Zhang, L. Brehm, B. Haskins, B. Bell, B. Gerhart, A. Leugers, M. Bernius, The chemical transformation of hydrocarbons to carbon using SO3 sources, Carbon N. Y. 94 (2015) 465–471. https://doi.org/10.1016/J.CARBON.2015.07.029.

[129] M.J. Behr, B.G. Landes, B.E. Barton, M.T. Bernius, G.F. Billovits, E.J. Hukkanen, J.T. Patton, W. Wang, C. Wood, D.T. Keane, J.E. Rix, S.J. Weigand, Structure-property model for polyethylene-derived carbon fiber, Carbon N. Y. 107 (2016) 525–535. https://doi.org/10.1016/j.carbon.2016.06.032.

[130] M.G. Northolt, L.H. Veldhuizen, H. Jansen, Tensile deformation of carbon fibers and the relationship with the modulus for shear between the basal planes, Carbon N. Y. 29 (1991) 1267–1279. https://doi.org/10.1016/0008-6223(91)90046-L.

[131] B.E. Barton, M.J. Behr, J.T. Patton, E.J. Hukkanen, B.G. Landes, W. Wang, N. Horstman, J.E. Rix, D. Keane, S. Weigand, M. Spalding, C. Derstine, High-Modulus Low-Cost Carbon Fibers from Polyethylene Enabled by Boron Catalyzed Graphitization, Small. 13 (2017) 1701926. https://doi.org/10.1002/smll.201701926.

[132] J.H. Eun, J.S. Lee, Study on polyethylene-based carbon fibers obtained by sulfonation under hydrostatic pressure, Sci. Rep. 11 (2021) 18028. https://doi.org/10.1038/s41598-021-97529-4.

[133] D. Choi, S.H. Yoo, S. Lee, Safer and more effective route for polyethylene-derived carbon fiber fabrication using electron beam irradiation, Carbon N. Y. 146 (2019) 9–16. https://doi.org/10.1016/j.carbon.2019.01.061.

[134] S.-H. Kang, K.-W. Kim, B.-J. Kim, Carbon Fibers from High-Density Polyethylene Using a Hybrid Cross-Linking Technique, Polymers (Basel). 13 (2021) 2157. https://doi.org/10.3390/POLYM13132157.

[135] E.J. Hukkanen, B.E. Barton, J.T. Patton, D.R. Schlader, Y. Zhang, X. Qiu, L. Brehm, B. Haskins, W. Wang, N. Horstman, M.A. Spalding, D.A. Hickman, C.W. Derstine, A Novel Continuous Multiphase Reactor for Chemically Processing Polymer Fibers, Ind. Eng. Chem. Res. 57 (2018) 6123–6130. https://doi.org/10.1021/ACS.IECR.8B00482.

[136] K.-W. Kim, H.-M. Lee, J.-H. An, B.-S. Kim, B.-G. Min, S.-J. Kang, K.-H. An, B.-J. Kim, A. Info, Effects of cross-linking methods for polyethylene-based carbon fibers: review, Carbon Lett. 16 (2015) 147–170. https://doi.org/10.5714/CL.2015.16.3.147.

[137] N. Saglio, P. Berticat, G. Vallet, Study of the Pyrolysis of Saturated Chlorinated Polyethylene Fibers, 16 (1972) 2991–3002.

[138] B. Laycock, X. Wang, R.F. Liu, P.K. Annamalai, J. Cork, C. Derstine, M. Mills, E.W. McFarland, Pyrolysis of brominated polyethylene as an alternative carbon fibre precursor, Polym. Degrad. Stab. 172 (2020) 109057. https://doi.org/10.1016/j.polymdegradstab.2019.109057.

[139] B.E. Barton, E.J. Hukkanen, G.F. Billovits, D. Schlader, M.J. Behr, D. Yancey, M. Rickard, X.H. Qiu, D.M. Mowery, L. Brehm, B. Haskins, W. Wang, M.S. Spalding, C. Derstine, Ammoxidation of polyethylene: A new route to carbon, Carbon N. Y. 130 (2018) 288–294. https://doi.org/10.1016/j.carbon.2018.01.031.

[140] E. Frank, E. Muks, A. Ota, T. Herrmann, M. Hunger, M.R. Buchmeiser, Structure Evolution in Polyethylene-Derived Carbon Fiber Using a Combined Electron Beam-Stabilization-Sulphurization Approach, Macromol. Mater. Eng. (2021) 2100280. https://doi.org/10.1002/MAME.202100280.

[141] B.A. Trofimov, T.A. Skotheim, A.G. Mal'kina, L. V. Sokolyanskaya, G.F. Myachina, S.A. Korzhova, E.S. Stoyanov, I.P. Kovalev, Sulfurization of polymers, Russ. Chem. Bull. 2000 495. 49 (2000) 863–869. https://doi.org/10.1007/BF02494710.

[142] A. Menyhárd, J.D. Menczel, T. Abraham, T.A. lfréd Menyhárd, Joseph D. Menczel, Polypropylene fibers, in: Therm. Anal. Text. Fibers, Elsevier, 2020: pp. 205–222. https://doi.org/10.1016/B978-0-08-100572-9.00012-4.

[143] Feedstock, Petrochemical and Polymer Prices and Margins: Forecast Through 2004, Millwood, New York, New York, 1999.

[144] Y. Takashima, Polypropylene, in: S. Kobayashi, K. Müllen (Eds.), Encycl. Polym. Nanomater., Springer Berlin Heidelberg, Berlin, Heidelberg, 2015: pp. 2043–2047. https://doi.org/10.1007/978-3-642-29648-2_254.

[145] K.S. Ko, C.W. Park, S.H. Yoon, S.M. Oh, Preparation of Kevlar-derived carbon fibers and their anodic performances in Li secondary batteries, Carbon N. Y. 39 (2001) 1619–1625. https://doi.org/10.1016/S0008-6223(00)00298-0.

[146] L. Giraldo, Y. Ladino, J.C.M. Piraján, M.P. Rodríguez, J.. M. Pirajánc, M.P. Rodríguez, J.C.M. Piraján, M.P. Rodríguez, Synthesis and characterization of activated carbon fibers from Kevlar, Eclet. Quim. 32 (2007) 55–62. https://doi.org/10.1590/S0100-46702007000400008.

[147] D. Karthik, V. Baheti, V. Tunakova, J. Militky, Carbonization of Kevlar Fabrics for Effective EMI Shielding Applications, Vlakna a Text. 25 (2018) 41–44.

https://doi.org/10.1177/0040517514555802.

[148] Polyamide Production, Pricing and Market Demand, Plast. Insights. (n.d.). https://www.plasticsinsight.com/resin-intelligence/resin-prices/polyamide/ (accessed April 20, 2021).

[149] J.G. Santangelo, Graphitization of Fibrous Polyamide Resinous Materials, 3,547,584, 1970.

[150] Procédé pour empêcher des polymères linéaires contenant des groupes amides dans leur chaîne de devenir cassants, 906,893, 1944.

[151] G.S. Stamatoff, Heat stabilization of polyamides, 2,705,227, 1955. https://patentimages.storage.googleapis.com/5b/ab/ac/63a3ecd6761486/US2705227.pdf (accessed July 17, 2020).

[152] J.A. Zapp Jr., K. Square, Stabilized polyamides containing cupric acetate, cupric chloride and 2-mercaptobenzothiazole, 3,308,091, 1967.

[153] A. Anton, Nylon fabrics with cupric salt and oxanilide for improved dye-lightfastness, 4,902,299, 1990.

[154] A. El Sayed, E. Ostlinning, A. Hennen, G. Heger, W. Nielinger, K.-J. Idel, K. Sommer, R. Audenaert, Thermally stable copper-containing polyamide molding compounds, 5,965,652, 1999. https://patentimages.storage.googleapis.com/89/e2/2e/bb6f6b1e3a4995/US5965652.pdf (accessed July 17, 2020).

[155] Y.D. Andrichenko, T. V. Druzhinina, Fabrication of metal-containing carbon fibre based on modified polycaproamide fibre, Fibre Chem. 31 (1999) 1–7. https://doi.org/10.1007/BF02358692.

[156] P. Cerruti, J. Rychlý, L. Matisová-Rychlá, C. Carfagna, Chemiluminescence from oxidation of polyamide 6,6: II. The effect of metal salts, Polym. Degrad. Stab. 84 (2004) 199–206. https://doi.org/10.1016/j.polymdegradstab.2003.10.011.

[157] P. Cerruti, C. Carfagna, Thermal-oxidative degradation of polyamide 6,6 containing metal salts, Polym. Degrad. Stab. 95 (2010) 2405–2412. https://doi.org/10.1016/j.polymdegradstab.2010.08.014.

[158] I. Karacan, G. Baysal, Investigation of the effect of cupric chloride on thermal stabilization of polyamide 6 as carbon fiber precursor, Fibers Polym. 13 (2012) 864–873. https://doi.org/10.1007/s12221-012-0864-7.

[159] I. Karacan, H. Meşeli, Characterization of amorphous carbon fibers produced from thermally stabilized polyamide 6 fibers, J. Ind. Text. 47 (2018) 1185–1211. https://doi.org/10.1177/1528083716682922.

[160] L. Erzurumluoglu, M.M. Rahman, T. Demirel, I. Karacan, Fabrication of carbon fibers from the cupric ion impregnated and thermally stabilized poly(hexamethylene adipamide) precursor, J. Ind. Text. (2021) 152808372110569. https://doi.org/10.1177/15280837211056984.

[161] J.R. Wünsch, Polystyrene: Synthesis, Production, and Applications, Rapra Technology Ltd., Shawbury, Shrewsbury, Shropshire, UK, 2000.

[162] T. Terashima, Polystyrene (PSt), in: S. Kobayashi, K. Müllen (Eds.), Encycl. Polym. Nanomater., Springer Berlin Heidelberg, Berlin, Heidelberg, 2015: pp. 2077–2091. https://doi.org/10.1007/978-3-642-29648-2_255.

[163] N. Chaukura, W. Gwenzi, T. Bunhu, D.T. Ruziwa, I. Pumure, Potential uses and value-added products derived from waste polystyrene in developing countries: A review, Resour. Conserv. Recycl. 107 (2016) 157–165. https://doi.org/10.1016/j.resconrec.2015.10.031.

[164] F.G.F. de Paula, M.C.M. de Castro, P.F.R. Ortega, C. Blanco, R.L. Lavall, R. Santamaría, High value activated carbons from waste polystyrene foams, Microporous Mesoporous Mater. 267 (2018) 181–184. https://doi.org/10.1016/J.MICROMESO.2018.03.027.

[165] N. Kiran, E. Ekinci, C.E. Snape, Recyling of plastic wastes via pyrolysis, Resour. Conserv. Recycl. 29 (2000) 273–283. https://doi.org/10.1016/S0921-3449(00)00052-5.

[166] J. Gong, J. Liu, X. Chen, X. Wen, Z. Jiang, E. Mijowska, Y. Wang, T. Tang, Synthesis, characterization and growth mechanism of mesoporous hollow carbon nanospheres by catalytic carbonization of polystyrene, Microporous Mesoporous Mater. 176 (2013) 31–40. https://doi.org/10.1016/J.MICROMESO.2013.03.039.

[167] J. Du, L. Zhang, Y. Zhang, Y. Yu, Y. Gao, A. Chen, Fe modified mesoporous hollow carbon spheres for selective oxidation of ethylbenzene, Sci. China Mater. 2017 6012. 60 (2017) 1227–1233. https://doi.org/10.1007/S40843-017-9137-7.

[168] G. Gatti, M. Errahali, L. Tei, E. Mangano, S. Brandani, M. Cossi, L. Marchese, A Porous Carbon with Excellent Gas Storage Properties from Waste Polystyrene, (2019). https://doi.org/10.3390/nano9050726.

[169] C. Ma, J. Min, J. Gong, X. Liu, X. Mu, X. Chen, T. Tang, Transforming polystyrene waste into 3D hierarchically porous carbon for high-performance supercapacitors, Chemosphere. 253 (2020) 126755. https://doi.org/10.1016/J.CHEMOSPHERE.2020.126755.

[170] K.-H. Jung, J.-H. Byun, Y.-S. Lee, S.-J. Park, Synthesis and characterization of chemically modified polystyrene as processable carbon fiber precursors, Res. Chem. Intermed. 36 (2010) 621–627. https://doi.org/10.1007/s11164-010-0197-3.

[171] Y. Hada, H. Shikuma, H. Ito, T. Kikutani, Structure and Properties of Syndiotactic Polystyrene Fibers Prepared in High-speed Melt Spinning Process, Fibers Polym. 6 (2005) 19–27.

[172] J.W. Soehngen, A.G. Williams, Carbon fiber production, 4,020,145, 1977. https://patft.uspto.gov/netacgi/nph-Parser?Sect1=PTO2&Sect2=HITOFF&p=1&u=%2Fnetahtml%2FPTO%2Fsearch-bool.html&r=2&f=G&l=50&co1=AND&d=PTXT&s1=3547584&OS=3547584&RS=3547584.

[173] G.€ Ozsin, A. Ays¸, A.E. Pütün, K. Nakabayashi, J. Miyawaki, S.-H. Yoon, Environmental-friendly production of carbon fiber from isotropic hybrid pitches synthesized from waste biomass and polystyrene with ethylene bottom oil, (2019). https://doi.org/10.1016/j.jclepro.2019.118025.

[174] S. Bhoyate, P.K. Kahol, B. Sapkota, S.R. Mishra, F. Perez, R.K. Gupta, Polystyrene activated linear tube carbon nanofiber for durable and high-performance supercapacitors, Surf. Coatings Technol. 345 (2018) 113–122. https://doi.org/10.1016/J.SURFCOAT.2018.04.026.

[175] J. Li-Na, Study on Preparation Process and Properties of Polyethylene Terephthalate (PET), Appl. Mech. Mater. 312 (2013) 406–410. https://doi.org/10.4028/www.scientific.net/AMM.312.406.

[176] J. Pang, M. Zheng, R. Sun, A. Wang, X. Wang, T. Zhang, Synthesis of ethylene glycol and

terephthalic acid from biomass for producing PET, Green Chem. 18 (2016) 342–359. https://doi.org/10.1039/c5gc01771h.

[177] A. Dutta, V.M. Nadkarni, Identifying Critical Process Variables in Poly(ethylene Terephthalate) Melt Spinning 1, Text. Res. J. 54 (1984) 35–42. https://doi.org/10.1177/004051758405400108.

[178] J. Nakatani, M. Fujii, Y. Moriguchi, M. Hirao, Life-cycle assessment of domestic and transboundary recycling of post-consumer PET bottles, Int. J. Life Cycle Assess. 15 (2010) 590–597. https://doi.org/10.1007/s11367-010-0189-y.

[179] R. Zhang, X. Ma, X. Shen, Y. Zhai, T. Zhang, C. Ji, J. Hong, PET bottles recycling in China: An LCA coupled with LCC case study of blanket production made of waste PET bottles, J. Environ. Manage. 260 (2020) 110062. https://doi.org/10.1016/j.jenvman.2019.110062.

[180] E.M. Aizenshtein, Bottle Wastes − to Textile Yarns, Fibre Chem. 47 (2016) 343–347. https://doi.org/10.1007/s10692-016-9691-8.

[181] L. Shen, E. Worrell, M.K. Patel, Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling, Resour. Conserv. Recycl. 55 (2010) 34–52. https://doi.org/10.1016/j.resconrec.2010.06.014.

[182] J. Choi, I. Yang, S.S. Kim, S.Y. Cho, S. Lee, Upcycling Plastic Waste into High Value-Added Carbonaceous Materials, Macromol. Rapid Commun. 43 (2022) 2100467. https://doi.org/10.1002/MARC.202100467.

[183] S. Ko, Y.J. Kwon, J.U. Lee, Y.P. Jeon, Preparation of synthetic graphite from waste PET plastic, J. Ind. Eng. Chem. 83 (2020) 449–458. https://doi.org/10.1016/J.JIEC.2019.12.018.

[184] S. V. Pol, V.G. Pol, D. Sherman, A. Gedanken, A solvent free process for the generation of strong, conducting carbon spheres by the thermal degradation of waste polyethylene terephthalate, Green Chem. 11 (2009) 448–451. https://doi.org/10.1039/B819494G.

[185] A. Joseph Berkmans, M. Jagannatham, S. Priyanka, P. Haridoss, Synthesis of branched, nano channeled, ultrafine and nano carbon tubes from PET wastes using the arc discharge method, Waste Manag. 34 (2014) 2139–2145. https://doi.org/10.1016/J.WASMAN.2014.07.004.

[186] V. Sridhar, H. Park, Transforming Waste Poly(Ethylene Terephthalate) into Nitrogen Doped Carbon Nanotubes and Its Utility in Oxygen Reduction Reaction and Bisphenol-A Removal from Contaminated Water, Materials (Basel). 13 (2020). https://doi.org/10.3390/MA13184144.

[187] X. Mu, Y. Li, X. Liu, C. Ma, H. Jiang, J. Zhu, X. Chen, T. Tang, E. Mijowska, Controllable Carbonization of Plastic Waste into Three-Dimensional Porous Carbon Nanosheets by Combined Catalyst for High Performance Capacitor, Nanomater. 2020, Vol. 10, Page 1097. 10 (2020) 1097. https://doi.org/10.3390/NANO10061097.

[188] A.R. Kamali, J. Yang, Effect of molten salts on the structure, morphology and electrical conductivity of PET-derived carbon nanostructures, Polym. Degrad. Stab. 177 (2020) 109184. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2020.109184.

[189] B. Zhang, C. Song, C. Liu, J. Min, J. Azadmanjiri, Y. Ni, R. Niu, J. Gong, Q. Zhao, T. Tang, Molten salts promoting the “controlled carbonization” of waste polyesters into hierarchically porous carbon for high-performance solar steam evaporation, J. Mater. Chem. A. 7 (2019) 22912–22923. https://doi.org/10.1039/C9TA07663H.

[190] C. Song, B. Zhang, L. Hao, J. Min, N. Liu, R. Niu, J. Gong, T. Tang, Converting poly(ethylene terephthalate) waste into N-doped porous carbon as CO2 adsorbent and solar steam generator, Green Energy Environ. (2020). https://doi.org/10.1016/J.GEE.2020.10.002.

[191] T. Morishita, Y. Soneda, T. Tsumura, M. Inagaki, Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors, Carbon N. Y. 44 (2006) 2360–2367. https://doi.org/10.1016/j.carbon.2006.04.030.

[192] Z. Xu, Z. Yuan, D. Zhang, W. Chen, Y. Huang, T. Zhang, D. Tian, H. Deng, Y. Zhou, Z. Sun, Highly mesoporous activated carbon synthesized by pyrolysis of waste polyester textiles and MgCl2: Physiochemical characteristics and pore-forming mechanism, J. Clean. Prod. 192 (2018) 453–461. https://doi.org/10.1016/J.JCLEPRO.2018.05.007.

[193] F. Hussin, M.K. Aroua, M.A. Kassim, Transforming Plastic Waste into Porous Carbon for Capturing Carbon Dioxide : A Review, (2021).

[194] C.F. Leitten, W.L. Griffith, A.L. Compere, J.T. Shaffer, High-Volume, Low-Cost Precursors for Carbon Fiber Production, SAE Trans. 111 (2002) 727–734. https://about.jstor.org/terms (accessed January 7, 2022).

[195] A.L. Compere, W.L. Griffith, C.F. Leitten, J.T. Shaffer, Low cost carbon fiber from renewable resources, in: 33rd Int. SAMPE Tech. Conf., Seattle, WA, 2001.

[196] S. Kubo, J.F. Kadla, Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties, J. Polym. Environ. 13 (2005) 97–105. https://doi.org/10.1007/s10924-005-2941-0.

[197] E. Svinterikos, I. Zuburtikudis, Carbon nanofibers from renewable bioresources (lignin) and a recycled commodity polymer [poly(ethylene terephthalate)], J. Appl. Polym. Sci. 133 (2016) 1–12. https://doi.org/10.1002/app.43936.

[198] E. Svinterikos, I. Zuburtikudis, M. Al-Marzouqi, The nanoscale dimension determines the carbonization outcome of electrospun lignin/recycled-PET fibers, Chem. Eng. Sci. 202 (2019) 26–35. https://doi.org/10.1016/j.ces.2019.03.013.

[199] W. Qu, X. Bai, Thermal treatment of pyrolytic lignin and polyethylene terephthalate toward carbon fiber production, J. Appl. Polym. Sci. 137 (2020) 1–10. https://doi.org/10.1002/app.48843.

[200] W.F. Carroll, R.W. Johnson, S.S. Moore, R.A. Paradis, Poly(Vinyl Chloride), Appl. Plast. Eng. Handb. (2011) 61–76. https://doi.org/10.1016/B978-1-4377-3514-7.10005-4.

[201] S. Ōtani, On the carbon fiber from the molten pyrolysis products, Carbon N. Y. 3 (1965) 31–38. https://doi.org/https://doi.org/10.1016/0008-6223(65)90024-2.

[202] W.M. Qiao, S.H. Yoon, I. Mochida, J.H. Yang, Waste polyvinylchloride derived pitch as a precursor to develop carbon fibers and activated carbon fibers, Waste Manag. 27 (2007) 1884–1890. https://doi.org/10.1016/J.WASMAN.2006.10.002.

[203] E.O. Elakesh, T.R. Hull, D. Price, P. Carty, Thermal decomposition of chlorinated poly(vinyl chloride) (CPVC), J. Vinyl Addit. Technol. 9 (2003) 116–126. https://doi.org/10.1002/VNL.10073.

[204] J. Kim, J. Lee, C. Jo, C. Kang, Development of low cost carbon fibers based on chlorinated polyvinyl chloride(CPVC) for automotive applications, Mater. Des. 204 (2021) 109682. https://doi.org/10.1016/J.MATDES.2021.109682.

[205] M.H. Lehr, Method and composition for improved melt processibility of chlorinated polyvinyl chloride, 0189873B1, 1991. https://patentimages.storage.googleapis.com/6c/93/86/84dc07f861fc5a/EP0189873B1.pdf.

[206] M. Kowalik, C. Ashraf, B. Damirchi, D. Akbarian, S. Rajabpour, A.C.T. Van Duin, Atomistic scale analysis of the carbonization process for C/H/O/N-based polymers with the ReaxFF reactive force field, J. Phys. Chem. B. 123 (2019). https://doi.org/10.1021/acs.jpcb.9b04298.

[207] M.W. Hyer, Stress Analysis of Fiber-Reinforced Composite Materials, 1998.

[208] K. Naito, Y. Tanaka, J.M. Yang, Y. Kagawa, Tensile and flexural properties of single carbon fibres, ICCM Int. Conf. Compos. Mater. (2009).

[209] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, W.G. J.F Kadla, S Kubo, R.A Venditti, R.D Gilbert, A.L Compere, Lignin-based carbon fibers for composite fiber applications, Carbon N. Y. 40 (2002) 2913–2920. https://doi.org/10.1016/S0008-6223(02)00248-8.

[210] Y. Luo, W. Qu, E. Cochran, X. Bai, Enabling high-quality carbon fiber through transforming lignin into an orientable and melt-spinnable polymer, J. Clean. Prod. 307 (2021) 127252. https://doi.org/10.1016/j.jclepro.2021.127252.

[211] J. Jin, Carbon Fibers with Enhanced Mechanical Properties Derived from Lignin-Based Precursors, Clemson University, 2018. https://tigerprints.clemson.edu/all_dissertations/2256/.

[212] M. Culebras, M.J. Sanchis, A. Beaucamp, M. Carsí, B.K. Kandola, A.R. Horrocks, G. Panzetti, C. Birkinshaw, M.N. Collins, Understanding the thermal and dielectric response of organosolv and modified kraft lignin as a carbon fibre precursor, Green Chem. 20 (2018) 4461–4472. https://doi.org/10.1039/C8GC01577E.

[213] M. Xiaojun, Z. Guangjie, Preparation of carbon fibers from liquefied wood, Wood Sci. Technol. 44 (2010) 3–11. https://doi.org/10.1007/s00226-009-0264-3.

[214] X. Liu, C. Zhu, J. Guo, Q. Liu, H. Dong, Y. Gu, R. Liu, N. Zhao, Z. Zhang, J. Xu, Nanoscale dynamic mechanical imaging of the skin-core difference: From PAN precursors to carbon fibers, Mater. Lett. 128 (2014) 417–420. https://doi.org/10.1016/j.matlet.2014.04.176.

[215] M. Zhang, A.A. Ogale, Carbon fibers from dry-spinning of acetylated softwood kraft lignin, Carbon N. Y. 69 (2014) 626–629. https://doi.org/10.1016/j.carbon.2013.12.015.

[216] D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, J. Appl. Polym. Sci. 130 (2013) 713–728. https://doi.org/10.1002/app.39273.

[217] F. Torres-Canas, A. Bentaleb, M. Föllmer, J. Roman, W. Neri, I. Ly, A. Derré, P. Poulin, Improved structure and highly conductive lignin-carbon fibers through graphene oxide liquid crystal, Carbon N. Y. 163 (2020) 120–127. https://doi.org/10.1016/j.carbon.2020.02.077.

[218] L.M. Steudle, E. Frank, A. Ota, U. Hageroth, S. Henzler, W. Schuler, R. Neupert, M.R. Buchmeiser, Carbon Fibers Prepared from Melt Spun Peracylated Softwood Lignin: an Integrated Approach, Macromol. Mater. Eng. 302 (2017) 1600441. https://doi.org/10.1002/mame.201600441.

[219] Z. Gao, J. Zhu, S. Rajabpour, K. Joshi, M. Kowalik, B. Croom, Y. Schwab, L. Zhang, C. Bumgardner, K.R. Brown, D. Burden, J.W. Klett, A.C.T.T. van Duin, L. V. Zhigilei, X. Li,

Graphene reinforced carbon fibers, Sci. Adv. 6 (2020) 1–11. https://doi.org/10.1126/sciadv.aaz4191.

[220] Y. Zhang, B. Zhu, X. Cai, X. Yuan, S. Zhao, J. Yu, K. Qiao, R. Qin, Rapid In Situ Polymerization of Polyacrylonitrile/Graphene Oxide Nanocomposites as Precursors for High-Strength Carbon Nanofibers, ACS Appl. Mater. Interfaces. 13 (2021) 16846–16858. https://doi.org/10.1021/acsami.1c02643.

[221] O.K. Park, S. Lee, H.I. Joh, J.K. Kim, P.H. Kang, J.H. Lee, B.C. Ku, Effect of functional groups of carbon nanotubes on the cyclization mechanism of polyacrylonitrile (PAN), Polymer (Guildf). 53 (2012) 2168–2174. https://doi.org/10.1016/j.polymer.2012.03.031.

[222] X. Li, X. Ji, A. Qin, C. He, The plasticized spinning and cyclization behaviors of functionalized carbon nanotube/polyacrylonitrile fibers, RSC Adv. 5 (2015) 52226–52234. https://doi.org/10.1039/C5RA05696A.

[223] A. Owen, Assisted development of mesophase pitch with dispersed graphene and its resulting carbon fibers dispersed graphene and its resulting carbon fibers, University of Kentucky, 2018. https://doi.org/10.13023/etd.2018.454.

[224] M. Chung, Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber, US Department of Energy, Crystal City, VA, 2019. https://www.hydrogen.energy.gov/pdfs/review19/st147_chung_2019_o.pdf (accessed May 14, 2021).

[225] D. Kun, B. Pukánszky, Polymer/lignin blends: Interactions, properties, applications, 2017. https://doi.org/10.1016/j.eurpolymj.2017.04.035.

[226] N.A. Mohamad Aini, N. Othman, M.H. Hussin, K. Sahakaro, N. Hayeemasae, Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review, Front. Mater. 6 (2020) 329. https://doi.org/10.3389/fmats.2019.00329.

[227] P.J. Bissett, C.W. Herriott, Lignin/polyacrylonitrile-containing dopes, fibers, and methods of making same, US20120003471A1, 2010.

[228] M. Ozgür Seydibeyoglu, A Novel Partially Biobased PAN-Lignin Blend as a Potential Carbon Fiber Precursor, J. Biomed. Biotechnol. 2012 (2012). https://doi.org/10.1155/2012/598324.

[229] X. Dong, C. Lu, P. Zhou, S. Zhang, L. Wang, D. Li, Polyacrylonitrile/lignin sulfonate blend fiber for low-cost carbon fiber, RSC Adv. 5 (2015) 42259–42265. https://doi.org/10.1039/c5ra01241d.

[230] H.C. Liu, A.T. Chien, B.A. Newcomb, A.A. Bakhtiary Davijani, S. Kumar, Stabilization kinetics of gel spun polyacrylonitrile/lignin blend fiber, Carbon N. Y. 101 (2016) 382–389. https://doi.org/10.1016/j.carbon.2016.01.096.

[231] X. Jiang, Q. Ouyang, D. Liu, J. Huang, H. Ma, Y. Chen, X. Wang, W. Sun, Preparation of low-cost carbon fiber precursors from blends of wheat straw lignin and commercial textile-grade polyacrylonitrile (PAN), Holzforschung. 72 (2018) 727–734. https://doi.org/10.1515/hf-2017-0191.

[232] M. Al Aiti, A. Das, M. Kanerva, M. Järventausta, P. Johansson, C. Scheffler, M. Göbel, D. Jehnichen, H. Brünig, L. Wulff, S. Boye, K. Arnhold, J. Kuusipalo, G. Heinrich, Dry-jet wet spinning of thermally stable lignin-textile grade polyacrylonitrile fibers regenerated from chloride-based ionic liquids compounds, Materials (Basel). 13 (2020). https://doi.org/10.3390/MA13173687.