Original Article

Manufacturing carbon fibres from pitch and polyethylene blend precursors: a review

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ABSTRACT

Carbon fibres are one of the newer, emerging materials with multiple engineering applications, from automobiles to space vehicles. Carbon fibres have high mechanical strength, are lighter than metals with better chemical resistance.

There have been reports on the use of polyethylene and pitch precursors for the production of carbon fibres, but there are few reports of how these blends could be used for carbon fibre preparation. Bearing in mind the myriad of benefits that using carbon fibres could bring, this paper reviews recent advances published in the literature on how mesophase pitch and polyethylene could be suitable precursors for carbon fibres. It also provides an introduction to the development of precursor blends that allow the properties of carbon fibres to be tailored to specific applications, including processing techniques, fibre parameters, fibre properties and fibre structure.

1. Introduction

Carbon fibres are widely deployed in numerous industries including defence, aerospace, construction, and healthcare due to their combinations of superior mechanical, electrical, and thermal properties [1–5]. For example more than half the components of the Airbus A350 XWB are composites, with the A350 XWB's wing measuring 32 m long by 6 m wide possibly the largest single aviation part ever made from carbon fibres [6]. The carbon fibre market is projected to proliferate in both new industries such as wind energy to the more traditional such as the automotive [7–9].

However, rapid expansion of the application of carbon fibres in industry will continue only if they can be produced at low cost without compromising physical properties. The precursors of carbon fibres derived from poly-acrylonitrile (PAN), exhibit high tensile strength but are very expensive which contributes significantly to the cost of manufactured items which include carbon fibres.

Edison, inventor of the electric light bulb in 1870, was probably the first to use carbon fibres when he utilised cellulose (bamboo or cotton) as filaments. Carbon fibres using synthetic rayon as a precursor were developed beginning in 1960 [10,11], and pitch-based carbon fibres have been produced with high elastic modulus since 1963 [12].

Carbon fibres from pitch-based precursors are cheaper than carbon fibres produced from PAN-based precursors [13,14]. Carbon fibres derived from mesophase pitch show one of the highest tensile moduli of any man-made fibre, but they

are brittle with short strain-to-failure, and relatively low tensile strength compared to carbon fibres derived from PAN. Hence, the task with pitch-based carbon fibres is to manufacture carbon fibres with both excellent tensile strength and improved strain-to-failure (less brittle). Such carbon fibres would offer a highly desirable combination of mechanical properties and low cost, a breakthrough what would greatly enhance their use in industry [15–17].

Polyethylene fibres have been used as a relatively low-cost precursor for manufacturing carbon fibres with moderately good mechanical properties (tensile strength 2 GPa; tensile modulus 200 GPa) [18,19]. Polyethylene also is known to have the useful property of large strain-to-failure (above 500% strain at failure) [20]. Hence, polyethylene can potentially act as a material which can be blended with pitch fibres to produce less brittle, but lower cost fibres. The current review will focus on work carried out in the development of pitch fibre precursors, polyethylene-based precursors and blends of pitch and polyethylene precursors by previous researchers whose reports are in the public domain. We will also focus on challenges faced when mixing these two materials to produce a blend of pitch and polyethylene precursor fibres, potential solutions and innovations which can be implemented to produce a high-quality pitch/polyethylene blend precursor, followed by fabrication of inexpensive, high-quality carbon fibres with outstanding mechanical properties.

The review is divided into three parts: the first part will focus on explaining the type of pitch used to produce carbon fibre precursor, and the manufacturing process of pitch fibre precursors followed by a description of carbon fibres derived from pitch. The second part of the review will focus on the manufacture of polyethylene fibre precursors, resulting carbon fibres and their consequential mechanical properties. The third part of the review will collate previous work done on mixing/blending of pitch with polyethylene to produce pitch/polyethylene blend precursor fibres, the resulting physical properties, and potential improvements which can be made to the properties of the blended precursors fibres for manufacturing high performance, low-cost carbon fibres.

2. Pitch-based carbon fibres

Pitch is a general term used for a thick viscoelastic, dark substance usually obtained from coal and petroleum-based products [2]. Natural pitch was historically used for shipbuilding in, for example, ancient Egypt (Fig. 1) to waterproof boats made of wooden planks joined by wooden pegs [21]. In this article, we focus on the pitch-derived from petroleum products because they are low-cost alternatives to pitch derived from coal tar which having comparable physical properties [22].

Pitch has a higher elastic modulus than PAN because pitch is more graphitisable than PAN [13]. Pitch-derived from petroleum can be defined as a thick black bituminous elements obtained during fractionation and distillation of crude oil, see Fig. 2 [23]. Coal pitches are broadly more aromatic than petroleum pitches, the main reason being the solid carbon particles have the ability to expedite coke deposition through extrusion and thermal handling. Even though

petroleum pitches are less aromatic, they are attractive as precursors for carbon fibres.

2.1. Petroleum pitch: structure and composition, softening point of different types of pitches

Pitch is a residue of distillation of coal tar and petroleum. It is a convoluted mixture of several thousand aromatic hydrocarbons [24,25]. The composition of petroleum pitches is evaluated primarily by processing temperature and distillation time to which it is subjected to during its purification. The aromatic fraction and the viscosity of the pitch generally increase with increase in temperature and processing time. There are four main components in petroleum pitch [3].

1. Asphaltene: is the highest molecular weight component in pitch with high aromaticity and is quite suitable for the formation of carbon fibres.
2. Polar aromatic compounds: the heterocyclic aromatic and high molecular weight components.
3. Aromatic compounds based on naphthalene: low molecular weight saturated ring structures with aromatic ring structures.
4. Saturated chemical compounds: the aliphatic low molecular weight chemicals.

Referring to Table 1 it is evident that the softening point of pitch increases with increasing asphaltene content. The high molecular weight aromatic structure of asphaltene is responsible for the increase in the aromatic content of pitch and its softening point. Due to its highly aromatic structure, asphaltene rich pitch is an appropriate precursor for carbon fibres. The composition of asphaltene is mainly poly-aromatic carbon ring complexes with nitrogen, sulphur, oxygen and traces of heavy metals. One example of the possible structure of asphaltene is shown in Fig. 3. The asphaltene molecules have a strong tendency to form nano-aggregates that assemble in the form of large colloidal particles (40–100 nm diameter) which contain thousands of individual asphaltene molecules [26].

Carbon fibres have been manufactured using isotropic and mesophase pitch. Isotropic pitch will result in general-purpose low strength/stiffness carbon fibres, while the mesophase pitch (made by polymerising isotropic pitch) is used to create more useful, stronger and stiffer carbon fibres [3]. Before we look into carbon fibre manufacture, it is imperative to grasp the rudiments of isotropic and anisotropic (mesophase) pitch as explained in the following section.

2.2. Isotropic and mesophase pitch as precursors for carbon fibres

Isotropic and mesophase (anisotropic and aligned phase) pitches are commonly used as precursors to create carbon fibres. Historically, pitch-based carbon fibres date back to the 1970s when the Kureha Corporation industrialised production of an isotropic carbon fibre using a method invented by Otani [27].

The isotropic phase of pitch lacks any form of alignment of the constituent aromatic chemical compounds. The isotropic pitch is known to produce relatively low strength/stiffness

Fig. 1 – (a) Ancient Egyptians used tar/pitch to join wooden plants for shipbuilding, (b) example of pitch being used to waterproof a boat constructed from wooden planks.
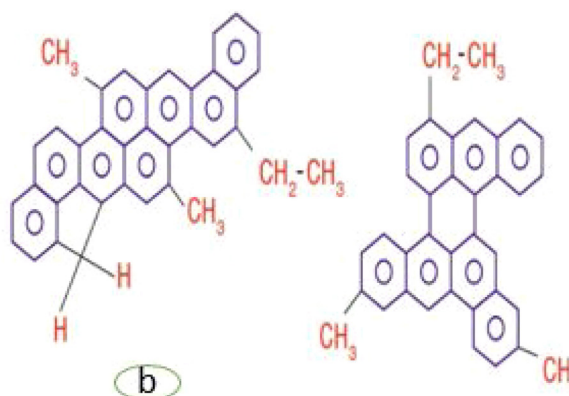

Fig. 2 – Pitch: (a) physical appearance, and (b) chemical components found in pitch-derived from crude oil/petroleum.

Table 1 – Composition of various petroleum pitches from different commercial suppliers [3].

Compound	Asphaltene (%)	Polar Aromatic (%)	Naphthene aromatic (%)	Saturate (%)	Softening point (°C)
EXXON (DAU) Bottoms (refinery sludge)	14.5	41.1	18.1	26.3	29
Ashland 240 petroleum pitch	64.4	8.6	25.4	1.6	119
Ashland 260 petroleum pitch	82.7	5.9	11.4	0.0	177

carbon fibres (mainly used for filtration and electrostatic dissipation applications) compared to mesophase pitch. Hence, we focus on the process of transforming isotropic pitch to mesophase pitch, and then describe the properties and structure of mesophase pitch [28–30].

Brook and Taylor first reported the formation of the mesophase in pitch (formed by the alignment of poly-aromatic chemical compounds present in the pitch) when pitch was heated and maintained at a temperature between 350–500 °C [31,32]. The poly-aromatic chemical compounds present in the pitch help form alignments in the liquid state (liquid crystals/mesophase), seen in Fig. 4 [33]. The alkyl side groups on the poly-aromatic chain act as a bridge between the adjacent poly-aromatic molecules which help increase the fusibility of these molecules as depicted in Fig. 5 [34,35]. The mesophase alignment of pitch can be changed by processes such as an external flow field, i.e., the extrusion process. Process flow of

production of isotropic and mesophase pitch is presented in Fig. 6.

In the initial part of the heating cycle, the mesophase will appear as small bright spheres. On heating further, these spheres collide and coalesce to form lamellas of the mesophase (Fig. 7) which has a nematic liquid crystal structure [36].

There are two commonly used methods of converting isotropic pitch into mesophase pitch. The first method is the production of mesophase by pyrolysis and the second is the production of mesophase pitch by solvent treatment. Manufacture of mesophase by pyrolysis involves heating it under an inert gas such as nitrogen for approximately 40 h. The optically isotropic material is transformed into an optically anisotropic liquid stage mesophase by the heat treatment. Heating Ashland 240 pitch at 400–410 °C for almost 40 h, caused approximately 50% to be transformed into an oriented
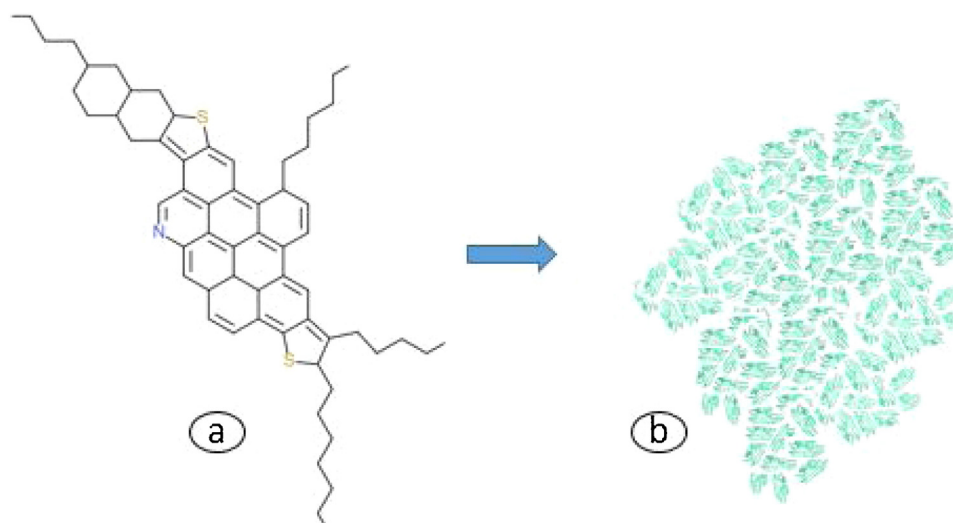
Fig. 3 – (a) An example of possible chemical structure found in asphaltene, (b) the nano-aggregates of asphaltene molecules (adapted from Moir [26]).
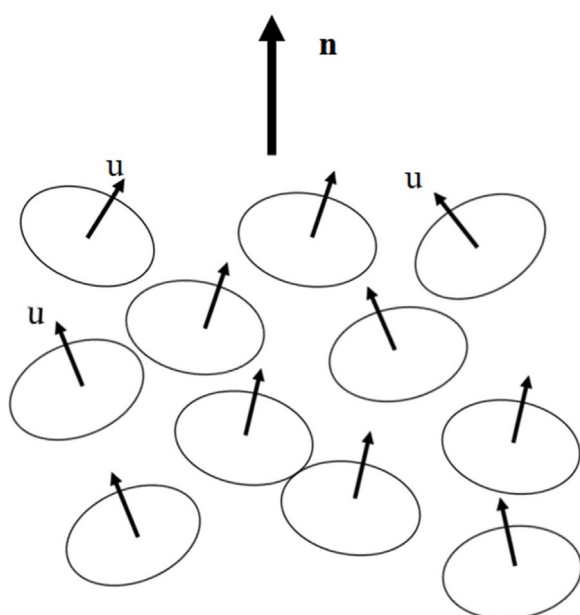

Fig. 4 – Directions of orientation of uniaxial discotic nematic liquid crystalline materials (*n* is the average orientation of unit normal to the disc-like molecules in a discotic nematic phase) adapted from Yan et al. [33].
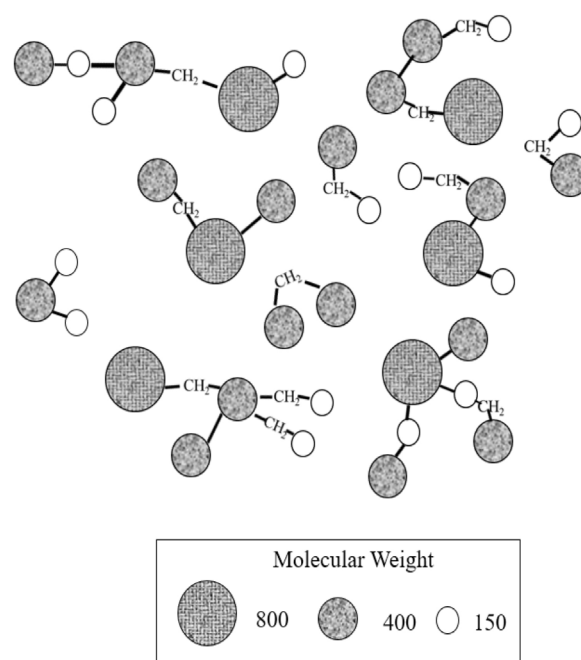

Fig. 5 – Spider wedge model of mesophase constituent molecules (adapted from Mochida et al. [34]).

phase (mesophase pitch) [30] mixed with the remaining 50% isotropic phase pitch. However, such a two-phase pitch mixture caused problems during fibre spinning [37].

The second method of manufacturing mesophase pitch is to extract the isotropic pitch using solvents. In the solvent extraction process, the higher molecular weight fraction of the pitch is concentrated in the insoluble fraction while the smaller, disordered molecules are removed. By heating in the range of 230–400 °C for 10 min, the insoluble portion can be polymerised to 100% anisotropic phase. This method can produce high molecular weight pitch, mainly mesophase pitch,

however the primary disadvantages of this method are the solvent cost and difficulties in ensuring 100% solvent trace removal from the mesophase pitch [38].

To overcome the difficulty of two-phase pitch (mesophase and isotropic pitch mixture), Chwastiak and Lewis carried out simultaneous agitation and heat treatment at a similar temperature as Lewis (380–440 °C) [37,39]. In this process, nitrogen was passed through the pitch to remove any highly volatile elements and cracked by-products. This process allowed the manufacture of mesophase with lower molecular weights (90% of the molecular weights being less than 1500) [30]. As

Fig. 6 – Basic steps required for the production of carbon fibres from pitch (isotropic, mesophase) (adapted from Inagaki [25]).

460 °C   500 °C

550 °C   700 °C

Fig. 7 – Mesophase nucleation and coalescence [27].

this process forms a single 100% mesophase pitch, it can avoid problems occurring during extrusion of two-phase pitch reported by Lewis [37]. Furthermore, this method seems to be advantageous compared to solvent extraction as there is no need to use additional solvents (quinoline and pyridine) which can increase the cost of mesophase pitch production [30].

Table 2 – Parameters described in the literature.

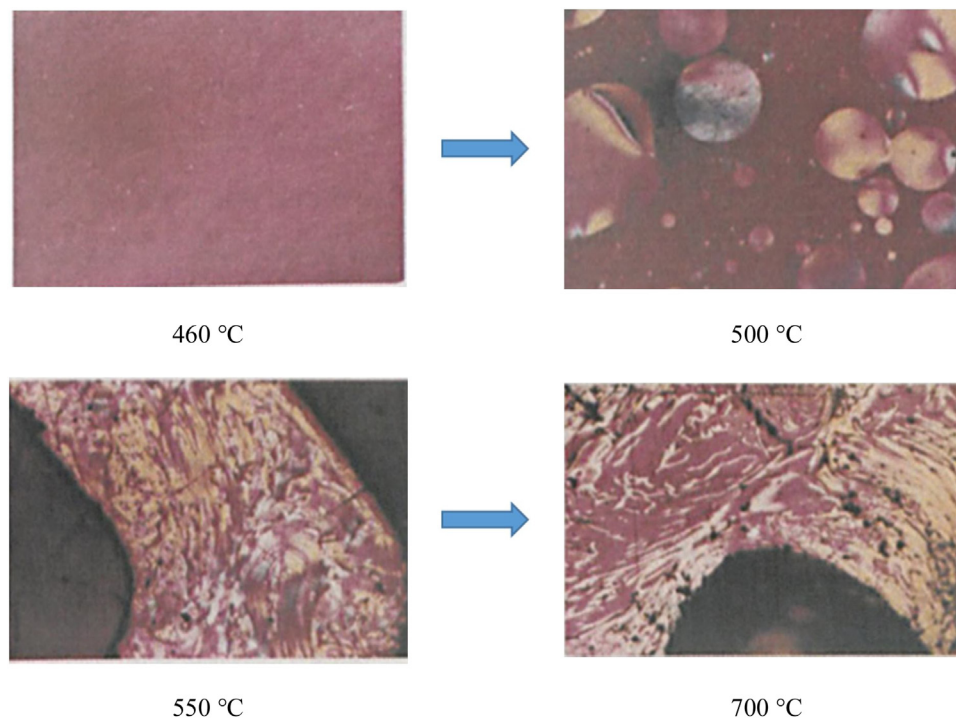| Research paper	Extrusion temp (°C)	Spinning speed (m/s)	Spinneret or extrusion temp (°C)
Edie et al. [44]	NA	8.575	363.45
Lim et al. [2]	340	NA	350
Jiang et al. [46]	NA	3.64	350
Lim et al. [45]	340	5.83	NA
Edie et al. [40]	343	5.33 to 10.33	351

2.3. Fibre spinning process for isotropic and mesophase pitch

The process of melt spinning produces pitch precursor fibres. As seen in Fig. 8 the pitch precursor is fed into a hopper purged with nitrogen [40], followed by extrusion of a solid block into the melting zone and passed through a sintered metal filter (5 μm nominal pore size) before being extruded from the holes of the spinneret. Four spinneretes were utilised: three spinneretes that had 12 rectangular capillaries (L = 0.5, 0.7, 0.9 mm; W = 0.1 mm) and one spinneret with 24 circular capillaries (D = 0.1 mm) [1,41]. The temperature of spinning not only affects fibre symmetry but also molecular orientation [42].

Mesophase pitch carbon fibres have an extensive change of interior structures, for example, radial, onionskin, random and flat-layer, see Fig. 9 [24,30]. Inspection of the different cross-section shapes of fibres revealed that the radial folded cross-section has highest tensile modulus and strength due to its ability to prevent crack propagation. An important finding was that random and onion cross-section fibres could be manufactured by manipulating the cross-sectional area of the spinneret capillary and tension imposed by fibre drawdown. In contrast, a line-origin shape, see Fig. 9 was a result of a deliberate non-circular spinneret capillary. The various cross-sectional shapes can be seen in Fig. 9 [30].

There have been numerous investigations concerning the mechanical properties of high-performance fibres [43]. Mesophase pitch extrusion and fibre spinning are most important in defining the properties of pitch fibre precursors. Corresponding and relevant process parameters, see Table 2, include extrusion temperature, fibre spinning temperature, fibre spinning speed, and material parameters such as pitch viscosity, all of which influence the spinning process and subsequent fibre properties. Below are findings from important previous studies on the extrusion of mesophase pitch and fibre spinning, including early studied that exhaustively presented results on a breadth of properties, especially non-circular cross-sections.

Edie et al. [44] investigated mesophase pitch prepared from Ashland Petroleum A-20. The winding speed was 8.575 m/s and spinneret temperature was 363.45 °C. To get unbroken filaments, they increased extrusion rate or decreased the speed of the winder. When they used warm air quenching, which allowed slower cooling of fibres after extrusion, they achieved improved spinnability.

Lim et al. [2] extruded mesophase pitch supplied by Tech Chem Korea at 340 °C under 1 bar gauge of nitrogen and produced aligned pitch fibres with a spinneret temperature of 350 °C (single hole of diameter of 0.5 mm, and L/D ratio of 5).

Compared to fibres produced by conventional batch process. the carbon fibres resulting from the pelletised pitch-based process had tensile strength and tensile modulus enhancement by 57.1% and 92.6% respectively, Because the filament pitch was not easy to wind due to its brittleness, Lim et al. [45] extruded mesophase pitch at a slower winding speed of 5.83 m/s, and spinning temperature of 340 °C through the same multi-holed spinneret.

Jiang et al. [46] extruded mesophase pitch under nitrogen at three pressures (3.5, 4 and 4.5 bar), through a single hole spinneret, diameter 0.3 mm and length 0.6 mm, with winding speed 3.64 m/s and spinning temperature 350 °C. They reported that the spinning should be carried out for at least 15 min to obtain steady-state fibre production with the specified processing conditions.

Edie et al. [40] produced ribbon-shaped pitch fibres from rectangular capillaries (L = 0.5, 0.7, 0.9 mm; W = 0.1 mm) using winding speeds from 5.33 to 10.33 m/s and spinning temperature 351 °C. The extruder was purged by nitrogen during spinning. Similar to their previous work [44] they found that manufacturing fibres with higher cross-sectional area allowed them to achieve more stable spinning conditions [40].

2.4. Manufacturing of pitch fibres

At the end of the mesophase pitch extrusion and fibre spinning process, the precursors obtained will soften at high temperatures, and eventually melt. Hence, in order to carbonise them at a high temperature, it is essential to first stabilise/oxidise them so they do not melt during the carbonisation process. The type of pitch precursor, the fraction of mesophase content, and the molecular weight determine the softening point of the pitch fibres. The stabilisation/oxidation process is carried out by heating the pitch fibre to a temperature which is below its softening point, typically mesophase pitch fibres are heated to between 275 to 350 °C for 5 to 60 min to reach stabilisation. Oxidation is performed in gases such as air, oxygen, oxygen-nitrogen mixture, ozone or sulphur dioxide [47]. The fibre is stabilised for carbonisation due to dehydrogenation, cyclisation and cross-linking.

2.4.1. Oxidation/stabilisation

The stabilisation/oxidation reactions result in an increase of mass due to the oxidation. This process will depend on many factors such as the composition of the pitch, local concentration of oxygen, rate of heating and temperature of the process, duration of oxidation process, and fibre diameter [48–53]. Oxidation results in an increase in oxygen present in the pitch fibre; e.g., an increase in oxygen/carbon ratio and a decrease in hydrogen/carbon ratio as the temperature of the oxidation/stabilisation process is increased [48]. Shen et al. [54] found that the optimum oxygen content in petroleum-based pitch fibres to attain maximum tensile strength of the final carbon fibre was 8%. The concentration of oxygen during the oxidation process may vary from the fibre surface to the fibre core. This gradient in oxygen content in the pitch fibre is shown in Fig. 10, and can lead to a skin-core effect in the final carbon fibre [55,56]. Hugh et al. [57] and Liu [58] reported that when the soak/dwell time for oxidation of petroleum-based pitch fibres was increased from 60 to 360 min at 360 °C,
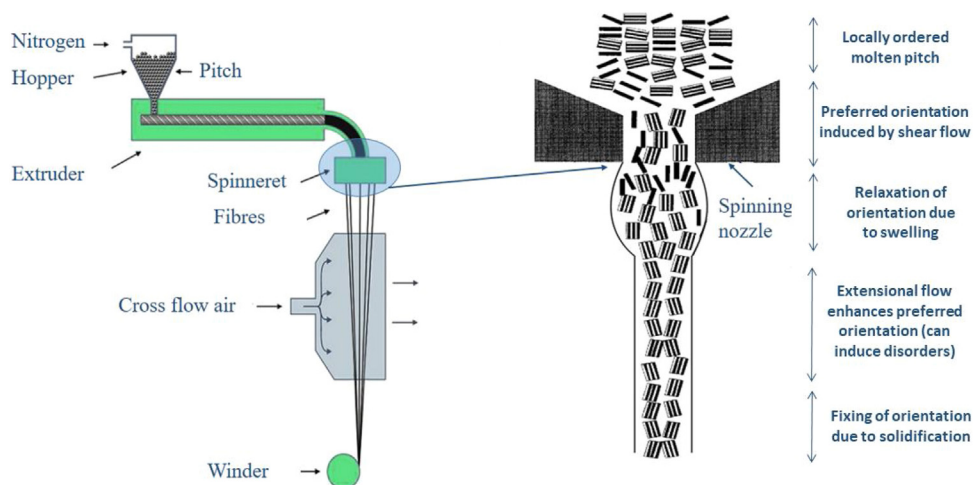
Fig. 8 – Schematic of spinning of melt produced pitch precursor fibres (adapted from Huson [48] and Yoon et al. [118]).
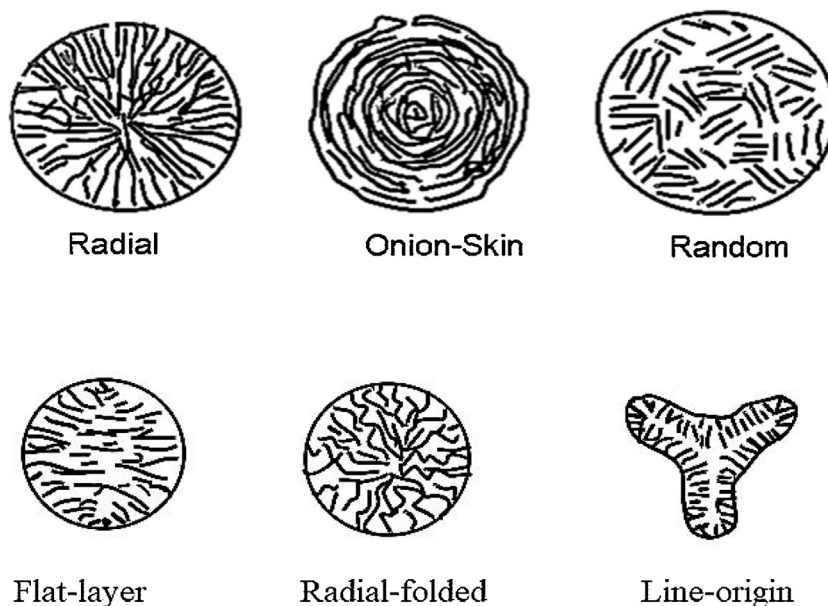

Fig. 9 – Transverse texture mesophase pitch carbon fibres (adapted from Edie [30]).

Table 3 – Average of mechanical properties of mesophase before/after stabilisation (250 °C for 2–3 h with 5 °C/min heating rate) [47].

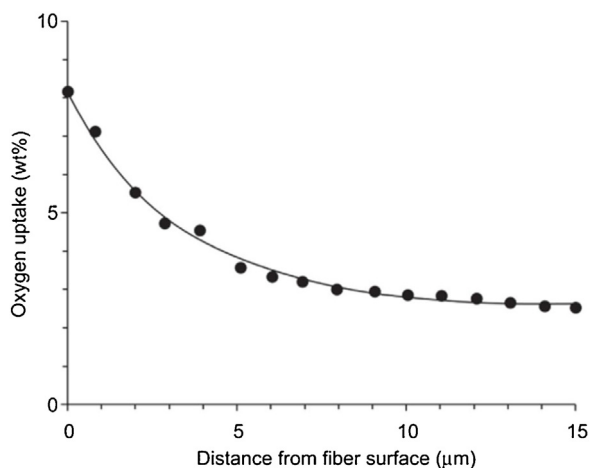| Mesophase fibre	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)
As-spun	0.04	4.7	0.85
Stabilised	2.06	216	0.95

the resulting carbon fibres displayed an increase of 163% and 46% in modulus and tensile strength respectively as shown in Table 3.

The stabilisation/oxidation reaction is a slow process. It is governed by oxygen diffusion from the surface of the pitch fibre to the core, though this process can be accelerated by increasing the temperature. However, the oxidation is also a highly exothermic reaction which can self-catalyse at a higher temperature, hence appropriate precautions must be taken to balance the reaction temperature and oxidation/stabilisation time as shown in Fig. 10 [56,59].

2.4.2. Carbonisation

Carbonisation is mostly completed at a temperature below 2000 °C and may include various phases. Ideal carbonisation in inert nitrogen may entail a heat treatment (0.5–5 min at 700 °C), followed by treatment at 900 °C for 0.5 min and finally in the temperature range 1500–2000 °C [47]. In the case when carbonisation is completed too quickly, the fast development of volatiles can bring about structural disturbances and imperfections, degrading the quality of the carbon fibre [60]. Jones et al. [60] confirmed the two leading causes for the misalignment of crystallite in carbon fibres during heat treatment as: liberation of CO and CO_2 at about 300 °C, and liberation of H_2

Fig. 10 – Oxygen uptake of mesophase pitch fibre stabilised in air at 300 °C for 15 min, as a function of radial distance [48].

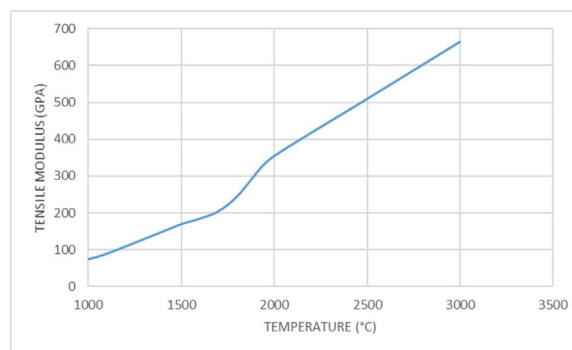**Fig. 11 – Impact on tensile strength of mesophase fibres of further heat treatment after carbonisation (adapted from Morgan [47]).**

Fig. 12 – Impact on tensile modulus of mesophase fibres of post carbonisation heat treatment (adapted from Morgan [47]).

Maintaining a temperature of 2000–3000 °C during graphitisation is an expensive process, and the time for graphitisation is minimised to reduce costs. Green et al. reported [65] that a graphitisation/heat treatment process as short as 0.7 s could achieve significant graphic graphitic crystal structural improvement [48].

2.5.   Structure and mechanical properties of carbon fibres derived from pitch

The mechanical properties of pitch-based carbon fibres compared to fibres from other sources (e.g., PAN, rayon/cellulose and polyethylene) are presented in Table 4. It is evident that the tensile modulus of mesophase pitch fibres can be superior to that of PAN fibres depending on the grade, however its tensile strength, as well as the strain-to-failure, expressed as elengation, is generally lower than PAN derived carbon fibres. In this and the following sections we will focus on the structure of pitch-derived carbon fibres, and understanding the cause of the relatively low strength of mesophase pitch-based carbon fibres in comparison to PAN-based carbon fibres.

2.6.   Intrinsic and extrinsic toughness in the context of carbon fibres

Properties of materials depend upon type of material, microstructure, and processing parameters. There have been many efforts to develop new materials for real-life applications which combine excellent toughness, strength and ductility. In this regard, interfaces have a vital role in the mechanical behaviour of polymer blends and composites. Currently, structures are selected based on their strength and toughness (resistance to fracture), both of which can be adapted in different ways. For example, high strength is a result of strong directional bonding and limited mobility (dislocation mobility in the case of crystalline solids and chain mobility in the case of polymers), with high strength leading to brittle failure and poor toughness, so much so, that toughness is considered inversely proportional to strength [66]. In polymeric materials, strength is defined as resistance to permanent (plastic) deformation, and is measured under

and CH_4 at about 500–600 °C. The gas molecules present in the fibres during carbonisation process damage the crystallites, proliferating the misorientation of the basic plane relative to the axis of the fibre. Beyond 1000 °C during carbonisation, H_2 gas reacts with the graphitic planes to give rise to the final turbostratic structure as graphite. Figs. 11 and 12 show how the tensile strength and tensile modulus, respectively, of pitch mesophase carbon fibre increased with treatment temperature [30].

2.4.3.   Graphitisation
Once every non-carbon based atom has been eliminated during carbonisation, the fibres form a backbone of carbon-based graphitic planes. The next step after carbonisation is graphitisation, to increase the size and perfection of the graphitic crystals. This improvement is achieved by heat treatment for 10 s to 5 min at a higher temperature in the range 2000–3000 °C [47,61,62]. Apart from the elimination of a few volatiles from the fibre, the majority of the changes promote the growth and orientation of graphitic crystals towards the fibre axis [63,64]. The precise duration and temperatures of the heat treatment depend on the type of pitch used in the precursors and conditions of fibre spinning and stabilisation.

Table 4 – Comparison between properties of PAN, Pitch and Rayon carbon fibres derived from various precursors ([5,16,58]9).

Precursor	Grade	Density (mg/m³)	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)	Electrical resistivity, μ (Ω m)
Rayon/cellulose	50S	1.67	1.9	390	0.5	10
	75S	1.82	2.5	520	0.5	–
PAN	T800	1.80	5.6	290	1.9	13
	M50	1.91	2.4	490	0.4	7.6
Polyethylene		0.955	2.0	200		
Single-crystal graphite		2.25	–	1000	–	0.4
Isotropic pitch	T101F	1.65	0.8	33	2.4	150
	T201F	1.57	0.7	33	2.1	50
Mesophase pitch	P25	1.90	1.4	160	0.9	13
	P120	2.18	2.2	830	0.3	2.2

uniaxial tension, compression or bending, and designated as yield strength or ultimate strength [66].

Both strength and toughness are crucial requirements for the majority of structural materials; however, in most materials the properties of strength and toughness are mutually exclusively. Research continues into attaining materials that are both stronger and harder, but these will have few applications as bulk structural materials if they do not possess the necessary fracture resistance. Materials having superior toughness are employed for many essential applications, where there has been a compromise required between strength and toughness of the materials, invariably in the form of a compromise between hardness and ductility. We see from studies of metallic glasses, natural and biological materials, and structural and biomimetic ceramics that extrinsic toughening is the primary means, often the only means of toughening brittle materials.

Examples from monolithic ceramics could be silicon carbide, silicon nitride and alumina, materials that can be toughened extrinsically by enhancing grain bridging and crack deflection much more easily that attempting intrinsic toughening. A number of natural materials are dependent on both intrinsic and extrinsic toughening and provide excellent examples of damage tolerant materials, one of which is seashells [67]. An important reason for this is the hierarchical structures of natural and biological materials, which combine structural features on multiple lengthscales from molecular to near-macroscopic. Currently, the interest in fracture toughness and strength of carbon fibres have been increased in the case of fracture behaviour of composites and their application in various fields. The fracture toughness of brittle matrix composites is strongly affected by the fibre fracture toughness as well as its interface toughness. Several kinds of notches with straight notch front have been used on carbon fibres monofilaments by taking the advantage of the focused ion beam machining system. The fracture of notched carbon fibres originated from notched tip with hackle pattern proves that this method is applicable for fracture toughness tests of the carbon fibre.

Toughness and strength may be exclusive properties but hardness and strength characterise the behaviour of a material under deformation. Toughness being the energy required to cause fracture, while the stress intensity, strain-energy release rate, or nonlinear elastic J-integral are used to evaluate toughness, which helps in the calculation of the initial force required to initiate a crack and/or propagate a pre-existing crack [67].

Toughness has also been defined as the property of a material to dissipate deformation energy without propagation of a crack. Improving the microstructural resistance by, for example, altering the interfacial structure, can enhance the toughness of materials. This can be done by embedding second-phase particles which reduces damage in the form of microcracking or microvoid formation in front of the crack tip. This mechanism is intrinsic toughening, and generally refers to ductile materials. Note that intrinsic toughness is considered as an inherent property of a material [68].

The idea of intrinsic fracture toughness was derived from the famous Griffith (1920) model based on the energy required to create the fracture surfaces. The intrinsic toughness at the interface is obtained as the difference between total fracture toughness and plastic dissipation, as in the following equation;

Intrinsic toughness = Total fracture toughness −

Plastic deformation

Several mechanisms have been used to explain intrinsic toughness; the traditional approach was to divide the surface energy, the energy required to generate unit surface area, into its components (e.g. interatomic and/or intermolecular bonds). Because intrinsic toughness is equal to total fracture toughness less the plastic dissipation, it is a measure of the work/energy required to form the fracture zone [69].

Microstructural mechanisms are mainly responsible for extrinsic toughening. In contrast to intrinsic toughening, extrinsic toughening acts behind the crack tip to suppress the crack-driving force at the crack tip, and is also known as crack-tip shielding [70]. Phase transformations, crack bridging and microstructure tuning help to provide extrinsic toughening which is the main determinant of crack growth toughness, but has very little effect on crack initiation behaviour. The toughening of materials is usually achieved by extrinsic toughening mechanisms [71]. For example, blending, alloying, developing of composites from combinations of brittle and ductile materials can help to achieve extrinsic toughening in brittle materials, while extrinsic toughening of epoxy can be

achieved by the blending of rubbers and other materials with the epoxy [72].

There are many mechanisms which can enhance extrinsic toughening to resist crack growth, these include crack bridging (sometimes referred to as wedging), zone and crack tip shielding and, particularly with composites, crack deflection or meandering [73].

The blending of polymers has gained in importance over the past few decades due to its success in achieving various desirable properties and microstructures; in particular (i) distribution of one polymer component in another; and (ii) a co-continuous two-phase microstructure [74]. The viscosity and proportion of blend partners, concentrations of blend partners, and type of blend partners are the aspects that govern the forms of microstructure which can be acquired in certain polymeric blends. Often, the toughening mechanisms associated with polymer blends are affected by the characteristics and properties of the blended polymers and the final microstructure of the blend. In particular, the optimisation of the interfacial adhesion within the blend will govern the development of materials with new properties, which will, of course, be associated with the blend partners [75].

Accordingly, good bonding at interfacial regions within the resultant blend and/or composite can enhance the material's properties, including delamination resistance, crack resistance, tensile strength, shear strength, fatigue and fracture resistance. The micro-mechanisms ultimately causing the plastic deformation lead to the debonding of blend components and composite phase (generating holes). Plastic deformation of the matrix areas, if large enough, leaves cavities between the blend component and composite phases. Generally, areas within the deformation zone expand up to rupture point due to the tearing occurring at particles of the dispersed component of the blend. Debonding is considered as a primary damage mechanism [76].

Researchers have investigated the fracture mechanism of styrene/butadiene block copolymer blends. They have mentioned the nanophase separated structure mechanism, which helps to modify the toughness by a particular morphology-toughness mechanism, wherein, long range lamellar structures are transformed into less ordered microstructures, which play an important role in providing toughness [77]. It has also been mentioned that the wormlike microstructure of styrene-butadiene block copolymers blend, allowed control of the toughness/stiffness ratio of the blends [78]. Fracture toughness of poly(lactic acid)/ethylene acrylate copolymer/wood-flour composite blends has been also reported, where a staggered microstructure conntributes one-third to its overall toughness [79].

Mesophase pitch-based carbon fibres are recommended for their fantastic thermal and electrical conductivities, excellent tensile modulus, moderate tensile strength, but nonetheless inferior compressive strength. All these properties contribute to the texture and crystalline structure (collectively known as microstructure) of the fibres [80]. Fibre microstructure is developed throughout processing due to the discotic character of the mesophase pitch precursor. Important criteria such as the size and shape of capillaries within the spinneret, spinning temperature and carbonization temperature have also

been varied to produce different types of fibres with distinctive microstructures and properties [81].

The close relations between the microstructure of mesophase pitch-based carbon fibres and their properties (mechanical, electrical, and thermal) have been mentioned by several investigators. The fibre structure is the basis for the process and type of mesophase precursor, with tensile strength decreasing as fibre diameter increased [55]. Tensile strength, however, seems to improve with the folding of graphite sheets within the fibre cross-section, as well as voids or other impurities.

The toughening mechanism associated with increased folding of the graphite planes also results in greater strain-to-failure. This is predicted to occur since increased folding of the graphitic planes enables a larger number of smaller cracks to form, thus permitting the fibre to stretch. However, these cracks are not of sufficient size for full-fibre fracture. Features which can include inter-crystalline disorder and crystallite size have been shown to influence compressive strength, but it is the general pattern of the sheet-like structure that determines a fibre's ability to maintain compressive stress [82]. The sheet-like structure of intense modulus mesophase pitch-based carbon fibres makes them more sensitive to crack propagation and fibre failure due to shearing of the graphitic planes. Also, the high modulus of mesophase pitch-based carbon fibres make them more sensitive to crack propagation due to the sheet-like structure, and it has been observed that fibre failure occurs due to shearing of the graphitic planes. Nonetheless, similar to tensile failure, a reduction in plate size and entire cross-sectional orientation (longitudinal axis alignment) makes it more difficult for cracks to propagate, toughening the fibre with respect to shear failure [83].

2.7.   Why pitch is brittle: structural analysis explanation

Open wedge cracks are frequently observed in the transverse direction of pitch-derived carbon fibres, due to its radial texture, and these contribute significantly to the decrease in the mechanical properties of pitch fibres [60]. Yoon et al. carried out an extensive study on transverse cracks in pitch-derived carbon fibres and factors affecting crack formation and growth during the manufacturing process [84,85]. They observed that transverse cracks can be present in carbon fibres at the embryo stage, from the pitch fibre precursor formation. The embryonic crack which is formed during pitch fibre manufacture extends further during successive heat treatments, during oxidation, carbonisation and graphitisation stages as shown in Fig. 13.

Yoon et al. [84] also studied the effect of the type of die used to extrude the pitch fibres and the temperature at which the fibres from the pitch precursors were spun, on the formation and development of transverse cracks in the precursor and during the carbonisation stage. They reported that temperature above 290 °C, with 0.5 mm diameter die (die length to diameter ratio = 3) did not show any crack formation during pitch fibre precursor manufacturing or after carbonisation, see Fig. 14. However, pitch fibres spun from a 0.3 mm diameter die crack formation unlike the fibres spun from 0.5 mm die.

They further explored the influence of the cross-sectional shape of the pitch fibre on the transverse crack initiation. They
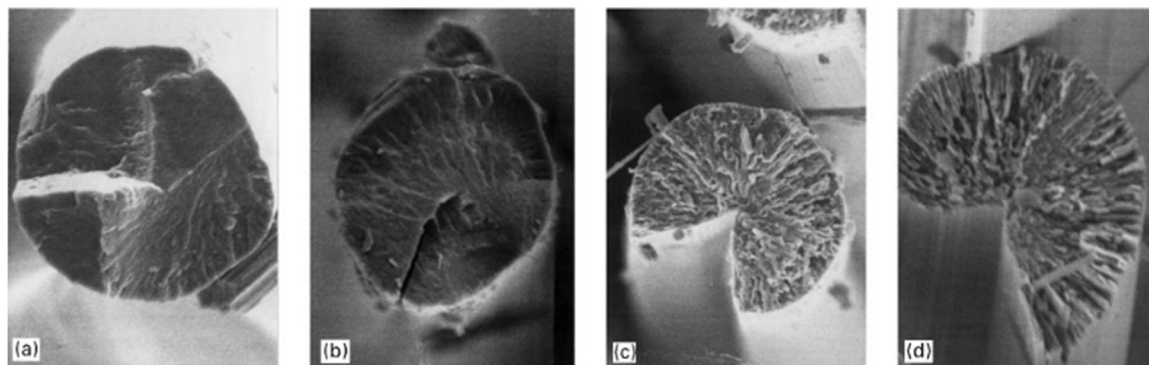
Fig. 13 – Propagation of open crack with increasing heat treatment temperature [84].
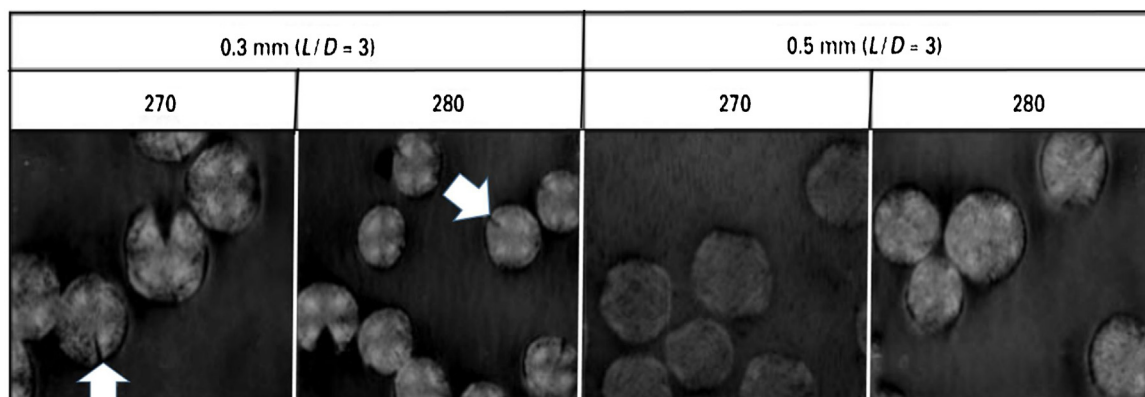

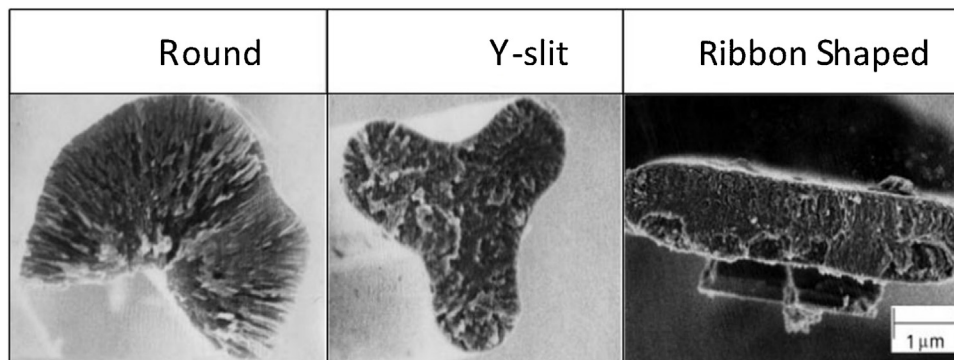**Fig. 14 – Optical micrographs of carbonised fibre at 600 °C of SUS-304 and graphite nozzles [84].**

Fig. 15 – Scanning electron microscope photographs of carbonised fibres spun through different shaped nozzles [84].

found that elliptical or ribbon-shaped cross-sections of the pitch fibres had a lower tendency to form transverse crack compared to circular cross-section pitch fibres, see Fig. 15.
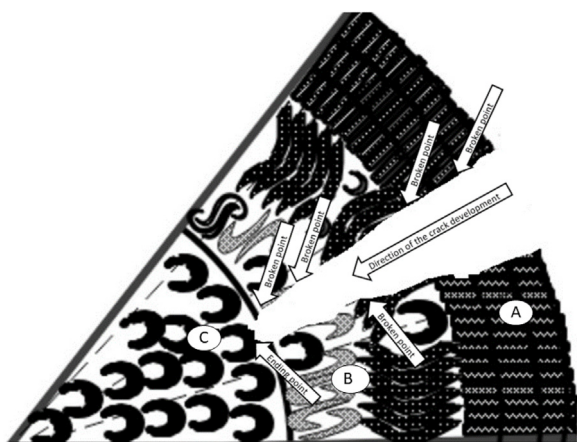
Yoon at al. [85] carried out further analysis of the effect of the graphitic microstructure formed in carbon fibre on transverse crack propagation. They used high-resolution scanning electron microscopy (HR-SEM) imaging to extensively study the carbon fibre graphitic microstructure going from the outer layer of the fibre towards the centre (fibre core) as shown in Fig. 16.

Based on this analysis, they proposed a schematic model for the distribution of differently aligned graphitic planes starting from the fibre sheath and progressing to the core. Shown in Fig. 17 is the skin of the carbon fibre with linear graphitic plane alignment (section A). As we move from the skin towards the core, the graphitic plane alignment assumes a bent shape (section B). Finally, at the core of the fibre, the graphitic planes show a loop shaped microstructure (section C).

The authors also compiled a montage of HR-SEM images to study the transverse crack propagation in carbon fibres. Crack growth was shown to be governed by the distribution of graphitic plane domains/shapes which have different microstructures. The authors concluded that the intermediate and central parts of the carbon fibre which had bends and loop domains were able to impede crack progress into the central part, as shown by the schematic representation in Figs. 16 and 17 [85].

Fig. 16 – Shapes of domains on crack surface: (A) linear domains, (B) bent domains and (C) loop domains (adapted from Yoon et al. [85]).

The graphitic plate domains are major structural elements of a fibre and are of two main kinds: dense (representing prior mesophase) and those with microporosity (such as foam-like structures containing well-ordered carbon). Domain formation occurs during spinning. The rheology of a two-phase structure governs the dispersal and character of the domains. Heat treatment causes changes in the entire fibre and does not influence the domain structure so much [86].

2.8. *Change of process or precursor to avoid brittleness*

Yoon et al. [84] probed the spinning conditions and found that domain alignment affects the open-wedge crack, and to obtain crack-free pitch-based carbon fibres, Y-shaped and slit shaped nozzles were used and the spinning conditions for these are shown in Table 5.

Elevating the spinning temperature increased the preferred orientation, for both steel and graphite nozzles, and which increased up to 285 °C before degrading. However, the highest orientation at the uppermost spinning temperature was accompanied by largest cracks whereas lower spinning temperatures reduced the chances of crack formation.

Yuan et al. [87] also showed ribbon-shaped fibres have normal shrinkage after heat treatment, and therefore, the shrinkage cracking usually present in round-shaped fibres could be avoided.
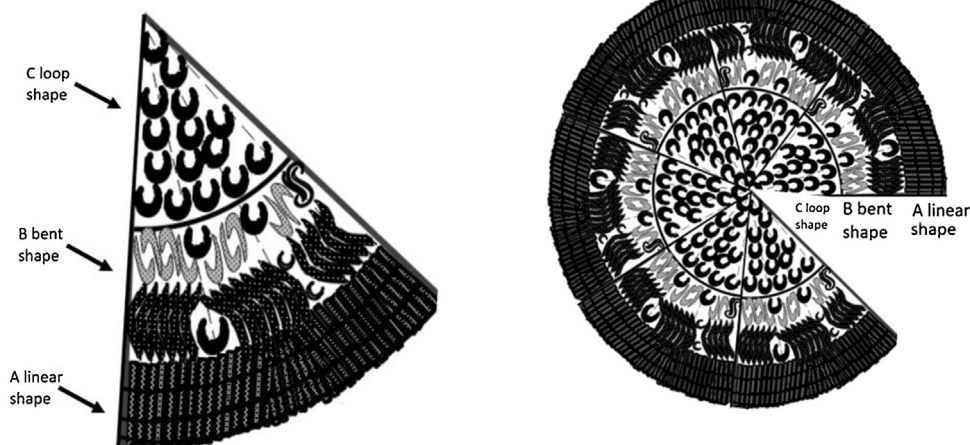
3. Polyethylene based carbon fibres

The technology of producing carbon fibres from polyethylene was first patented by Japanese inventor Shozo Horikiri in 1978 [88]. The first research on carbonisation of polyethylene (PE) began in 1972 when PE powder was chlorinated for stabilisation and carbonisation, and the study successfully demonstrated the conversion of PE into aromatic structures [19]. PE has characteristics which make it valuable as a carbon fibre precursor. It has high carbon content and can be simply weaved into fibres. Fibres from high molecular weight PE with high values for of tensile strength and elastic modulus are readily obtainable [89]. Textile grade polyethylene has a simple chemical composition, and is attractive as a precursor for carbon fibre production as it could decrease manufacturing cost by as much as 50% compared to PAN [18,90–93].

There are four main types of PE fibres used as precursors to manufacture carbon fibres: low density polyethylene (LDPE) [93], linear low density polyethylene (LLDPE) [20,94,95], high density polyethylene (HDPE) [18,90] and ultra high molecular weight polyethylene (UHMW PE) [89,96]. The fibre spinning of polyethylene precursors, oxidation/stabilisation, carbonisation and graphitisation are presented in the following section.

3.1. *Fibre spinning process for PE precursor fibres*

The preferred method of generating polymeric fibres is melt-spinning. Palmenaer et al. [18] melted commercial granular HDPE in an extruder at 200 °C, and pushed it through a spinneret with 72 capillaries, each of diameter 0.25 mm, with capillary $L/D = 2$. The molten filaments so formed were solidified via quenching in air, followed by drawing off and take-up at between 40 to 50 m/s with a 0.43 g/s mass throughput.

Fig. 17 – Typical structural domains within a carbon fibre (adapted from Yoon et al. [85]).

Table 5 – Melt spinning conditions to obtain crack-free fibres [84].

Spinning conditions	Material of nozzle			
	SUS-304			Graphite
Aspect ratio (*L/D*)	1	3	3	3
Diameter (mm)	0.3	0.3	0.5	0.3 and 0.5
Spinning temperature (°C)	Independent	>290	Independent	Independent
Transverse texture obtained	Radial-skin	Onion-skin	Radial	Kinds of radial

Postema et al. [95] also prepared the LLDPE fibres by melt spinning at 170 °C and draw-off speed of 0.06 m/s. A porous metal filter was used to make two kinds of fibres using different draw-down ratios (20 and 65). Both fibres were 40 microns thick, showed an increase in tensile properties up to a certain level of applied stress before deteriorating. The first fibre with the 20 draw-down ratio exhibited maximum tensile strength (0.55 GPa) and elastic modulus (25 GPa) at an applied stress of 0.1 MPa. The other fibre displayed higher maximum tensile strength (1.15 GPa) and elastic modulus (60 GPa) at an applied stress of 1.3 MPa.

Other research by Kim and Lee [94], involved spinning LLDPE fibres in distilled water at ambient temperature and then pumping it through a single hole spinneret die (hole diameter of 250 microns, spinneret pressure of 2 kg/cm^2) which was maintained at 170 °C. The fibres were taken-up at 0.26 m/s. Subsequently, the material was immersed in n-hexane for one day before washing in distilled water. Finally, the fibres were hot drawn (80 °C and draw ratio of 5) and cold drawn. Oak Ridge National Laboratory used a sophisticated spinning technique to produce the required PE precursor diameter; after spinning tetrahydrofuran (THF) at 50 °C, the PLA matrix was re-dissolved to obtain the remaining filaments [19].

Typical carbon fibres have circular cross-section. However, Hunt et al. [97] was able to produce PE-based carbon fibres with customised surface contours and cross-sections by integrated sulphonation and bi-component fibre melt-spinnings. The fibres produced had diameters from 0.5 to 20 microns. The process required meticulous modelling of the geometry and flow path of the spinneret. Despite these fibres not exhibiting enhanced mechanical properties, the tailored geometry has potential in many applications.

3.2. Manufacturing of PE fibres

3.2.1. Oxidation/stabilisation

PE-based precursors are thermoplastic and, hence, have low melting points. To avoid losing their form, they need to be stabilised by cross-linking to enable them to endure the temperatures required for carbonisation. There are four methods of stabilising, of these sulphonation has the merit of highest density of cross-linking, which can be tuned by temperature manipulation. Kim et al. [93] achieved cross-linking of LDPE in 98% fuming sulphuric acid at 130–170 °C, before rinsing in distilled water and drying at 60 °C for one day.

Zhang and Bhat [89] immersed the fibres in 95% H$_2$SO$_4$ at 130–140 °C contained in a stainless steel heater bath. In a continuation of this research Zhang [96] wound fibres around steel wires which were immersed into a sulphuric acid bath

Table 6 – Mass increment during stabilisation [89].

Stabilisation time (min)	Maximum temperature (°C)	Percentage increase in mass (%)
60	150	7.9
75	160	50.4
90	170	61.0
105	180	74.6
120	190	84.1

at 200 °C. Running tap water was used to rinse the fibres before oven-drying at 60 °C for 1.5 h. An increase in mass was observed with simultaneous increase in stabilisation time and maximum temperature, see Table 6. This is attributed to the addition of sulphur and oxygen to the polymer.

Palmenaer et al. [18] and Wortberg et al. [90] used a reaction vessel with inner and outer borosilicate glass walls with a feed and an outlet for silicon oil (thermofluid) to allow temperature control of the sulphuric acid contained in the inner vessel. A PTFE coated magnetic stirrer was used to maintain a uniform temperature distribution of the acid. The precursors were fastened to stirring rods using PTFE tape and heated to 140 °C before drying. Colour change of the fibres was an indication of complete sulphonation. The fibres transformed from white to brown and finally black. A study by Zhang and Bhat [89] also showed a similar pattern of change of fibre colour at frequent intervals throughout the stabilisation step, see Table 7.

While the previous researchers used one sulphuric acid bath, Barton et al. [20] used two baths for stabilisation. The first bath contained 20% fuming H$_2$SO$_4$ (1 h) and the second bath contained 96% acid (1 h) at 120 °C. Then the fibres were immersed in a room temperature water bath for 1 h. Kim and Lee [94] used a rate of heating of 8 °C/min to attain different temperatures throughout the stabilisation process (130, 140, 150 and 160 °C). This was coupled with weights on each precursor to vary the stress (0.09, 0.18 and 0.26 MPa). Kim et al. [93] performed TGA on the LDPE prepared from the three stabilisation temperatures (130, 150 and 170 °C), the results are shown in Table 8.

It was observed that carbon yield rose with increasing stabilisation temperature. The rinsing and drying process used by Behr et al. [98] was slightly different; fibres were rinsed in deionised water and dried overnight in a vacuum.

Besides sulphonation, there are three other commonly used methods for crosslinking stabilisation of polyethylene fibres [93].

1. Radiation based crosslinking methods: when the polymer chain is exposed to ionising radiation it can lead to chain scission or a reaction between chain free radicals to form

Table 7 – Colour change during stabilisation of PE fibres [89].

Time (min)	Maximum stabilisation temperature (°C)							
	130	140	150	160	170	180	190	200
15	Yellow							
30	Grey	Grey						
45	Grey	Grey	Black					
60	Black	Black	Black	Black				
75	Black	Black	Black	Black	Black			
90	Black	Black	Black	Black	Black	Black		
105	Black	Black	Black	Black	Black	Black	Black	
120	Black	Black	Black	Black	Black	Black	Black	Black

Table 8 – Thermographic analysis (TGA) results for sulphonated LDPE [93].

TGA	Polymer decomposition temperature (°C)	Max. temp (°C)	Carbon yield (%)	Fibrous form
As received	447.32	472.80	2.78	Failed to form
PE-S-130	462.29	483.26	10.44	Failed to form
PE-S-150	454.33	477.58	26.82	Surface fractured fibre
PE-S-170	238.43	492.32	50.27	Stable fibre

crosslinking between the neighbouring polymer chains. Some researchers have used different forms of ionising radiation for enhanced crosslinking: gamma irradiation [99,100], electron beam irradiation [101], and ion beam irradiation [102]. The crosslinking obtained from ion beam irradiation was shown to be more effective for HDPE than LDPE [103].

2. Peroxide based crosslinking methods: this technique is based on a free radical decomposition technique. Typically, thermally decomposed peroxides come into contact with the melted PE bonds, and cross-linking can happen via radical formation and recombination, as shown in Fig. 18 [104,105].

3. Abundant research can be found which has utilised peroxides to initiate chemical cross-linking [106–111].

Peroxides have advantages compared to radiation-based crosslinking. For instance, radiation cross-linking induces the crosslinking process only on the surface of a polymer, whereas peroxide-based crosslinking can induce the crosslinking process both on the surface and inside the bulk of the polyethylene sample [91].

3.2.2. Carbonisation

Stabilisation is followed by carbonisation under tension and higher temperatures than used for stabilisation. In the initial attempts, cross-linked carbon fibres were carbonised at a temperature of 1200 °C in an argon environment. A tension of 2.05 MPa was applied [112]. This yielded 76% carbon content in the final carbon fibre. To achieve higher carbon content, Zhang [75], and Zhang and Sun [92] fastened the fibres to a carbon fibre leader, which was gradually sent into the central zone of a preheated ceramic furnace for 4 min at 1150 °C in a nitrogen environment. The general range for carbonisation is 900–1300 °C, but Andreas et al. [18] carbonised at the lower temperature limit of 900 °C. The fibres shrank 30–50%. Barton et al. [20] performed carbonisation of LLDPE in a nitrogen atmosphere at 1000 °C for 15 min with a tension of 0.5 N, a process which yielded the properties listed in Table 9.

Table 9 – Fibre properties after carbonization of LLDPE in a nitrogen atmosphere at 1000 °C for 15 min [20].

Property	LLDPE
Tensile strength (GPa)	1.5
Modulus (GPa)	90
Strain (%)	1.7
Density (g/cm^3)	2–2.1

Postema et al. [95] carbonised in an externally heated glass tube. The nitrogen used for the atmosphere was dried with anhydrous $CaCl_2$ and deoxygenated over Cu at 450 °C. The author varied the time, temperature and stress on the fibre and determined the optimum carbonisation temperature was 900 °C, besides a desirable elongation to failure of 3% and carbon yield of 72–75%. The research done by Kim and Lee [94] on LLDPE investigated the carbonisation with rate of heating 6.2 °C/min to achieve 950 °C, which was maintained for 5 min, before cooling to ambient temperature with a quenching rate of 3.1 °C/min. Weight was added during carbonisation to evaluate the influence of stress (0.15, 0.2, 0.25 and 0.3 MPa) on cross-linked fibres. It was found that increasing the applied stress up to 0.25 MPa improved the tensile strength. Applying stress during carbonisation can render the molecular orientation similar to that of PAN-based carbon fibres.

3.2.3. Graphitisation

Subjecting the fibres to higher temperatures than those at carbonisation, can enhance mechanical properties as reported by Barton et al. [20]. It was observed that graphitising the fibres at 2400 °C in an UHT tube furnace purged by nitrogen, improved elongation by more than 5% and raised the elastic modulus from 90 GPa to 200 GPa.

3.3. Structure and mechanical properties of carbon fibres derived from PE

Zhang [75], and Zhang and Sun [92] used highly oriented UHMWPE fibres to fabricate carbon fibres with good mechani-
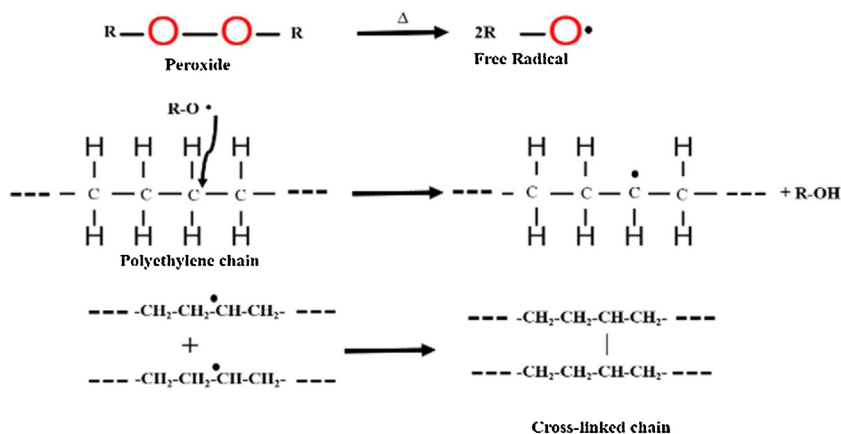
Fig. 18 – Peroxide cross-linking of PE [91] (where Δ is thermal decomposition).
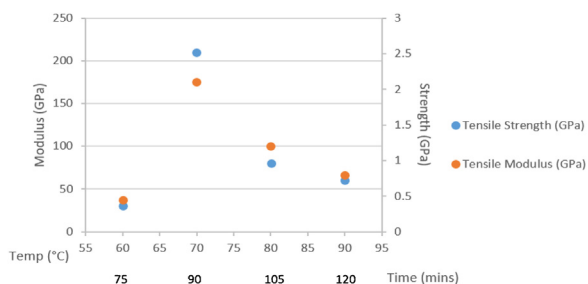

Fig. 19 – Tensile properties of fibres for various stabilisation times and temperatures (adapted from Zhang et al. [89]).

cal properties. The fibres showed an elastic modulus of 210 GPa and tensile strength of 2.1 GPa, however, the fibres were quite brittle with strain-to-failure of less than 1%. This research also produced fibres with properties that depended on stabilisation temperature and stabilisation time, as shown in Fig. 19. This process had a respectable carbon yield of 75–80%.

The research also emphasised the importance of tension during stabilisation. A higher level of tension did not allow the relaxation induced kink bands that formed in fibres subjected to lower tension during stabilisation. Kinked and non-kinked fibres can be seen in Fig. 20.

Stress during carbonisation and heating rate also impacted the mechanical properties as shown in Fig. 21.

Further, Penning et al. [113] demonstrated the significant influence that the diameter of LLDPE-derived carbon fibres had on their mechanical properties, possibly due to fibres having a skin-core structure. Fibres were produced with diameters in the range 13–57 microns by increasing the maximum attainable draw-down ratio. It was found that the diameter effect was more prominent for thinner fibres. Thinner precursors led to stronger carbon fibres that had a modulus of 130 GPa, strength of 2.16 GPa, high strain-to-failure of 3% and enhancement of maximum achievable draw-down ratio. Influence of diameter on the fibre properties is shown in Fig. 22.

Horikiri et al. [94] reported that PE-based carbon fibres with appropriate properties can be manufactured at a temperature of 1200 °C, which confirms reports in the literature that fibre modulus increases with heating temperature until it reaches a maximum value, followed by property degradation. Kim and Lee [94] manufactured a more ductile PE fibre with 110 GPa modulus and 1.65 GPa tensile strength. It was also reported
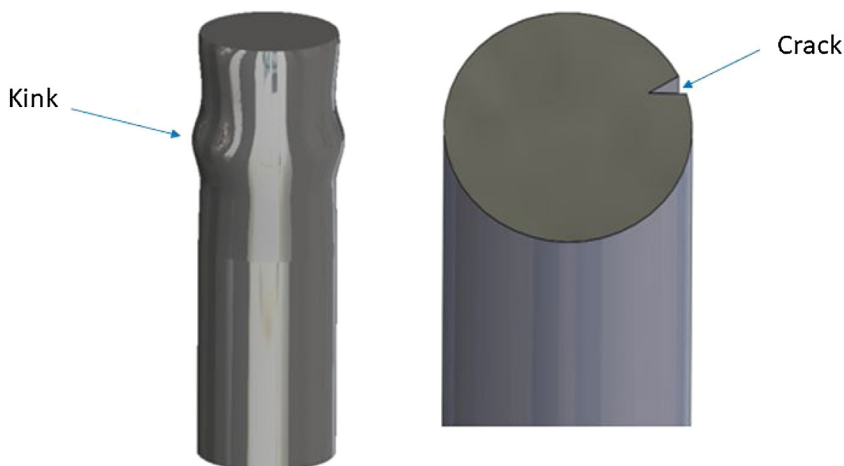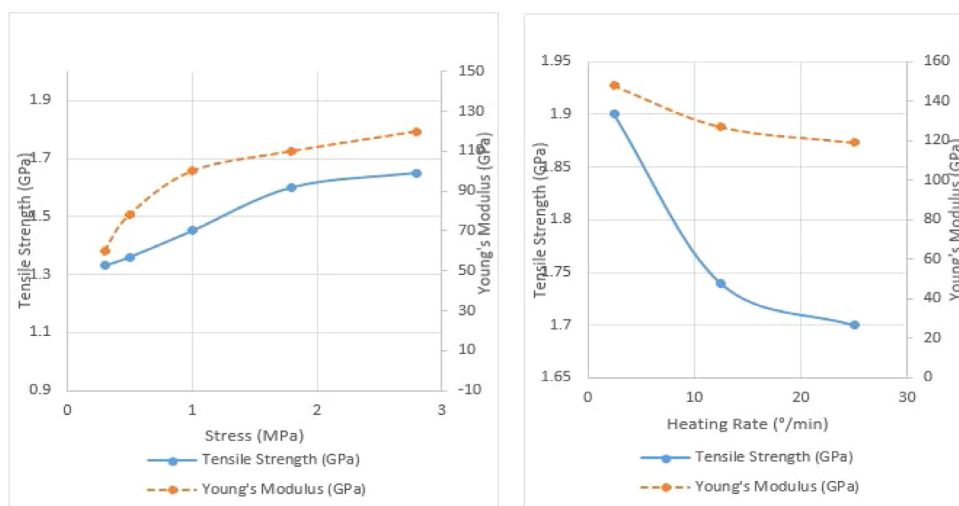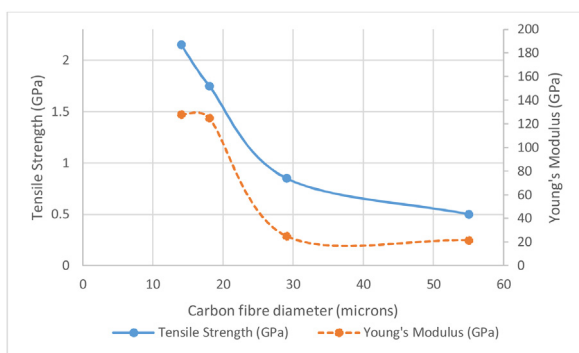

Fig. 20 – Schematic representation of kinked and not-kinked fibres (adapted from Zhang and Bhat [89]).

Fig. 21 – Effect of stress and heating rate on mechanical properties of fibres after carbonisation (adapted from Penning et al. [113]).

Fig. 22 – Tensile strength and modulus as a function of fibre diameter (adapted from Penning et al. [113]).

that the modulus can be lowered by stressless carbonisation of fibres.

Table 10 outlines the properties of different PE-based carbon fibres.

3.4. Advantages and disadvantages/weakness of the carbon fibres produced from PE

PE is cheaper than PAN because 50–65% of production costs are due to the synthesis of the PAN precursor. These costs can be ascribed to convoluted solvent spinning and preparation, and generate a high final market price of 2–5 €/kg. PE production via melt spinning is considerably cheaper, swifter, more energy-efficient and eco-friendly. Besides, PE has higher carbon content, carbonisation ratio availability and is a congruent precursor [16,18,68,70,72–75,77,93]. Sulphonation of the PE precursor makes it easier to carbonise at higher temperatures in an oxygen-deficient atmosphere. Sulphonation is a diffusion-driven process so, by regulating the reaction time, the degree of sulphonation, the wall thickness and cross-section of the fibre can be customised [97].

The fundamental demerit of PE precursors is that, despite being highly oriented, they are thermoplastic in nature. Hence, they melt at low temperatures and have to be stabilised by cross-linking. Stabilisation via sulphonation can take a shorter or longer time depending on the temperature, however, longer times make the process uneconomical and shorter times mean a reactively violent process that can degrade fibre properties [88]. UHMWPE, in the absence of a sufficient number of branches attached to main chain, can yield unfavourable properties due to swelling and axial crack propagation [68,72,73,75].

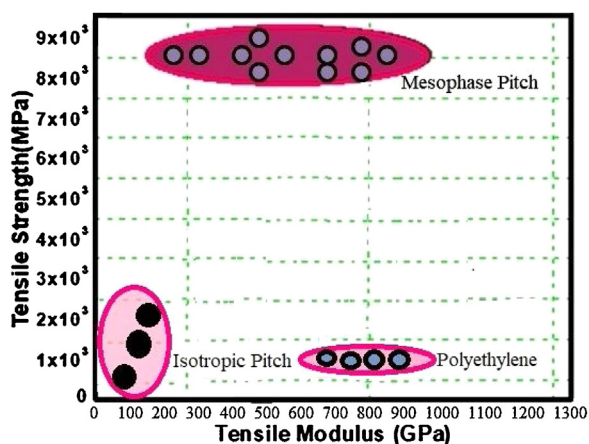## 4. Blends of pitch and polyethylene precursors

Pitch precursors have a lower cost compared to PAN-based precursors [13,14]. They show a better elastic modulus, but an extremely low failure strain and inferior tensile strength compared to PAN-based carbon fibres. However, PE-based precursors are inexpensive and produce carbon fibres with moderate mechanical properties and favourable strain-to-failure [18,19]. As shown earlier in this review, both pitch and PE-based carbon fibre production, through meticulous manipulation of process parameters, can impede the crack propagation observed in carbon fibres derived from pitch precursors with customised cross-sections and non-linear morphology. The crack deterrent morphology is seen in 16 showing the bent and loop domains that can obstruct crack development.

Carbon fibre costs could be reduced if PE and pitch could be blended to produce carbon fibres that offer a combination of better ductility, lower cost, and greater modulus and strength. Higher draw-down ratios and easier fracture-free winding are possible during carbon fibre production from PE/pitch precursors. Hence, this section focuses on the development of new carbon fibre precursors which can be blended with pitch precursors to enhance fibre spinning.

Table 10 – Properties of PE-based carbon fibres.

Property	LLDPE	HDPE	UHMWPE
Tensile strength (GPa)	≤2.160	≤2.673	≤2.100
Modulus (GPa)	≤148	≤139	≤210
Strain (%)	0.7–3	–	<1
Diameter (μm)	9–17	8	–
Density (g/cm^3)	2–2.1	0.97	0.97
Carbon yield (%)	72–75	70–76	75–80
Source	[95,113]	[88]	[68,96]

Fig. 23 – Tensile strength plotted against tensile modulus for isotropic pitch, polyethylene and blend pitch and polyethylene.

Fig. 23 represents an Ashby plot for mesophase pitch, mesophase/polyethylene blend, polyethylene and isotropic pitch for a range of tensile strength and tensile modulus stiffness as has been reported in previous studies [114]. It is noted that that tensile strength and modulus is dependent upon the type of sample. Interestingly, the mesophase pitch shows a greater value of tensile strength and tensile modulus than the isotropic pitch.

In 2017, Oak Ridge National Laboratory and Pennsylvaniya State University formulated a PE-pitch hybrid precursor [115]. Two years previously, Xi'an University of Technology and Petrochina Liaoyang Petrochemical Company had blended low-cost petroleum pitch with waste PE to manufacture mesophase pitch [116]. These first steps sufficiently successful to indicate that this was a fruitful area of development.

4.1. Blending techniques of PE and pitch

Oak Ridge formed two reactive PE co-polymers, poly(ethylene-co-divinylbenzene) and poly(ethylene-co-vinyldiphenylacetylene) by metallocene-driven co-polymerisation reactions. Both co-polymers were individually blended with pitch in the ratio 1:5 (co-polymer to pitch) by weight. The reactive side groups of the co-polymer were involved in cyclo-addition and ring fusion with poly-aromatic pitch. Appropriate reaction conditions (comparatively low temperature) were identified due to the availability of several PE co-polymers. The PE/pitch blend could then be subjected to melt fibre spinning to produce PE/pitch-based carbon fibres [115].

Cheng et al. [116] integrated waste PE (from discarded milk bags) and inexpensive pitch to manufacture a modified pitch (mesophase pitch). Waste PE was cleaned, dried, melted and transformed into particles. The petroleum pitch was warmed in an iron vessel with a shearing speed of 3750 rpm. After 5 min, several weight fractions of waste PE (0–5 wt%) were added to the vessel while the temperature was held constant. Every 30 min, the sample was swelled in the die for 10 min. The resulting modified pitch was heated at 1.5 °C/min in an atmosphere of nitrogen with a shearing speed of 1000 rpm. The sample was held for some time before quenching to room temperature.

4.2. Structure and mechanical properties of carbon fibres derived from pitch/PE blends

Chung [115] investigated the rheological properties of PE/pitch mixtures and found crucial information for the subsequent melt-spinning step in CF production: trends in the melt viscosity and viscoelastic properties of PE/pitch precursors influenced their melt-processability, and carbon and mass yields. Chung performed only the first step of CF production: melt fibre spinning.

A modified (mesophase) pitch precursor was produced by Cheng et al. [116] by adding weight fractions of waste PE (again from discarded milk bags) to inexpensive pitch. At 1 wt% waste PE, the mesophase content in pitch, initially quite small, increased with temperature and achieved 100% mesophase at 450 °C. The loading of waste PE also impacted the mechanical properties of the modified pitch which acquired a streamline mesophase structure with addition of the waste PE up to a limit of 2 wt%. Further addition of waste PE hindered mesophase development and may even induce isotropy and hence, deterioration of mechanical properties. This trend also holds good for carbonisation yield and regularity of the carbon layers.

Neither study attempted to manufacture final carbon fibres from the PE/pitch precursors. It remains to be seen what properties and structure the carbon fibres will have after fibre spinning, stabilisation, carbonisation and graphitisation. More studies need to be performed to investigate the initiation of phase separation after a threshold PE/pitch ratio.

5. Future direction and recommendations

PAN-based precursors have the largest market share in carbon fibre production. Despite their associated production costs,

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they have been more extensively used than pitch or PE-based CF, on account of their relatively high ductility. Research is needed into cost reduction and improvement of mechanical properties by investing in pitch and PE-based carbon fibre research and development.

To exploit the full potential of the mechanical properties of PE/pitch-based carbon fibres to avoid catastrophic failures, it is proposed based on the above review that PE/pitch morphology is the key to arresting crack propagation and, hence, reducing the likelihood of brittleness observed in pitch fibres.

There have been a few reports of PE/pitch blends. In one such study [116], the author recommends using weight fractions in the range 1 wt% PE to 4.5 wt% PE in petroleum pitch to determine the optimum concentration and produce the final carbon fibres. While some workers did report the successful manufacture of hybrid precursors, there were no reports of carbon fibres manufactured from these hybrids. There are essential requirements on the specification of the fibre for carbonisation, primarily the carbon yield must be at least 50%, which signifies that the backbone of carbon chains must not suffer significant splits, and the residual carbon must form textured crystallites [117]. This entails exploring the individual steps of stabilisation, carbonisation and graphitisation of PE/pitch precursors, and exploring the possibility of producing ductile carbon fibres for numerous and diverse applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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