Characterisation and feasibility as carbon fibre precursors of isotropic pitches derived from anthracene oil

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Abstract

This work describes the preparation of isotropic carbon fibres from three anthracene oil-derived pitches of different softening points. The total absence of solid particles (e.g., primary quinoline insoluble (QI) particles) and the high aromatic composition turn these precursors into a promising raw material for the preparation carbon fibres, as they can be used without any pre-treatment. The carbon fibres were prepared by a melting process that involved the spinning of the pitches and subsequent oxidative stabilization with air and carbonisation. Scanning electron microscopy was used to monitor the surface appearance and diameter of the fibres.

The results showed that softening point by itself cannot explain the spinning behaviour of the pitches. Therefore, detailed characterisation of the samples by means of size exclusion chromatography, UV–fluorescence spectroscopy, and laser desorption time-of-flight mass spectrometry was used to elucidate the composition of the pitches, especially their molecular weight distributions. The combination of the characterisation of the precursors with the characterisation of the fibres provides an overall vision of the carbon fibre preparation from the pitches and will certainly permit a pre-selection of the most appropriate precursor for this application.

Keywords: Carbon fibres; Melt spinning; Anthracene oil; LDI–MS; UV–F

1. Introduction

Carbon fibres are applied in many fields where excellent mechanical, thermal or electrical properties are required. The consumption of carbon fibres is central to several highly-technological sectors, such as aerospace, aeronautics, and renewable energies (e.g., eolic energy) among others, to the point where it can be considered a socio-economic indicator of the development of a country. These industries consume significant amounts of carbon fibre, especially PAN-based carbon fibres [1], [2], [3], [4]. Despite stagnation in many sectors of the economy, the global demand for carbon fibre is expected to rise from 32,000 tonnes in 2008 to 70,800 tonnes by 2014 [5]. It is also foreseen that new markets for carbon fibres of moderate performance will arise (car manufacturing, civil construction, etc.). General purpose carbon fibres (GPCFs) might be considered as the ideal candidate to fill this gap in the market. However, the use of traditional fibres, e.g., PAN-based carbon fibres, for these applications is not possible due to both their low volume of production and prohibitive cost. The use of synthetic pitches from a low cost carbon-rich source such as anthracene oil has been proposed as an alternative for the production of this kind of fibres [6].

Anthracene oil-derived pitches can be obtained by a multistep sequential procedure that involves oxidative thermal condensation of anthracene oil and subsequent thermal treatment/distillation to reach the desired softening point of the pitch [7]. This type of pitch exhibits a consistency of quality and has a chemical composition free from solid particles, i.e., primary quinoline insolubles (QIs) and metals, which is guaranteed by the distilling technology employed in anthracene oil production [7]. Their highly aromatic composition makes them a promising raw material for obtaining carbon fibres.

The principal steps in the production of GPCF from isotropic pitches involve firstly the removal of entrained particulates and elevation of the softening points by distillation in order to make the precursor adequate for melt-spinning. Further stabilization and carbonisation of the obtained green fibres produce the final fibres. In the case of carbon fibres produced from anthracene oil–derived pitches, the removal of solid particles is not a requirement, since they are solid-free samples. Moreover, the production of these pitches is a versatile process and different high softening point fibre precursors can be obtained by merely changing operating conditions, in particular during the thermal treatment/distillation step.

Several studies have focused on determining the effect of the viscosity of the pitches on its spinnability [1], [2], [4] in particular in mesophase carbon fibres in which the liquid crystal theories can predict the spinnability conditions. For the preparation of GPCF, in which isotropic pitches exhibit Newtonian flow properties, the measurement of the softening point is very commonly used as one of the main characterisation parameters [8] and provides satisfactory indications about optimum spinning conditions for a certain pitch. The operational melt-spinning parameters, mainly the spinning temperature and winding speed, have to be optimised for each pitch. However, up to date no link has been established between molecular structures in the pitches and their spinning behaviours. This approach is of particular interest for the preparation of spinnable anthracene oil derived pitches because their versatile preparation method allows the preparation of pitches with on demand properties as a result of a full control of the pitch composition during all the steps. Composition is, therefore, the control parameter in this procedure.

In the present work, three anthracene oil-derived pitches of different softening point, obtained under controlled operational conditions, have been examined to ascertain their suitability for carbon fibre production. Operational parameters of the melt-spinning process have been controlled in order to evaluate their effect over the diameters of the green fibres.

This study also presents a detailed chemical analysis of the pitches and discusses their chemical features in relation to the fibre characteristics and the process conditions needed in their preparation. Several complementary analytical techniques have been used in order to glean information about molecular mass distributions, chemical structures and compositions [9], with a particular emphasis on the characterisation of the heavier fractions in the pitch, which mostly contain compounds above the mass range amenable to analysis by gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Raw materials

Three anthracene oil-derived pitches of increasing softening points (AOP1: 218 °C; AOP2: 235 °C; AOP3: 247 °C) were used as precursors for the preparation of the carbon fibres. The main characteristics of the pitches are summarised in Table 1.

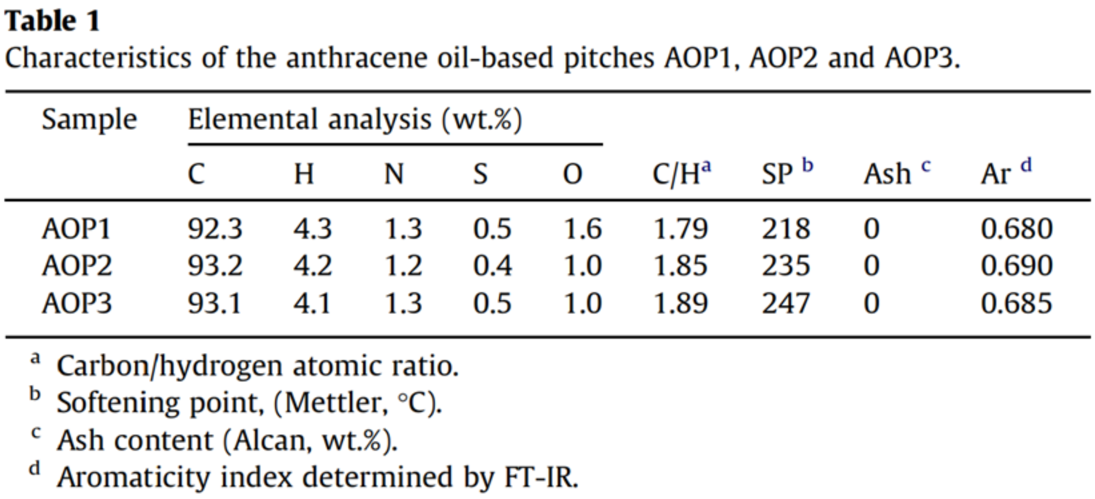


Table 1
Characteristics of the anthracene oil-based pitches AOP1, AOP2 and AOP3.

Sample	Elemental analysis (wt.%)								
	C	H	N	S	O	C/H[a]	SP [b]	Ash [c]	Ar [d]
AOP1	92.3	4.3	1.3	0.5	1.6	1.79	218	0	0.680
AOP2	93.2	4.2	1.2	0.4	1.0	1.85	235	0	0.690
AOP3	93.1	4.1	1.3	0.5	1.0	1.89	247	0	0.685

[a] Carbon/hydrogen atomic ratio.
[b] Softening point, (Mettler, °C).
[c] Ash content (Alcan, wt.%).
[d] Aromaticity index determined by FT-IR.

2.2. Green carbon fibre preparation

Green carbon fibres were prepared by the melt-spinning procedure. For this, a stainless steel laboratory scale apparatus (Fig. 1) with capacity for 25 g of sample was used to extrude the precursors through a monohole spinneret of 500 μm of diameter. In a typical experiment, the precursor (AOP1, AOP2 or AOP3) was heated to different temperatures (260–280 °C) and then extruded by applying a nitrogen pressure of 1 bar. The green fibres were then wound on a roller able to work at different winding speeds (from 49 to 245 cm s−1).

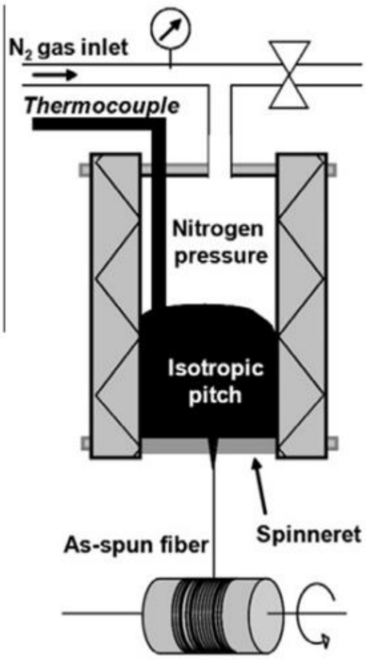


Fig. 1. Schematic diagram of the melt-spinning apparatus.

2.3. Characterisation of pitches and fibres

2.3.1. Elemental analysis

The carbon, hydrogen, sulphur and nitrogen contents of the samples were determined with a LECO-CHNS-932 micro-analyzer. The oxygen content was obtained directly using a LECO-VTF-900 furnace coupled to the micro-analyzer. The analyses were performed with 1 mg of sample ground and sieved to <0.2 mm. The results were quoted as the mean of values from four determinations. In all cases, the experimental error was <0.5% of the absolute value.

2.3.2. Softening point

The softening points of the pitches were determined according to the American Society for Testing and Materials (ASTMs) D3104 standard.

2.3.3. Pitch fractionation

The pitches were fractionated by solvent solubility, following a sequential fractionation with acetone, toluene and pyridine. The pitches (10 g) and acetone (450 ml) were refluxed for 2 h and cooled to room temperature. The mixture was filtered using a membrane filter with a pore diameter of 0.8 µm. After the first filtration the solid residue was refluxed with 450 ml of acetone following the same procedure. The acetone soluble fraction (AS) was dried under N2. The extraction procedure was repeated with toluene and pyridine, producing the pitch toluene soluble–acetone insoluble (TS) fraction, the pitch pyridine soluble-acetone–toluene insoluble (PS) fraction and the pitch pyridine insoluble (PI). Finally, the samples were dried under vacuum (10−3 mBar) at about 90 °C until a constant weight was achieved.

2.3.4. Size exclusion chromatography (SEC)

The method and calibration have been described elsewhere [10]. A 300 mm long, 7.5 mm i.d. polystyrene/polydivinylbenzene-packed Mixed-D column with 5 μm particles has been used (Polymer Laboratories, Church Stretton, UK). The column was operated at 80 °C at a flow rate of 0.5 ml min−1 of N-methyl 2 pyrrolidinone (NMP) as the mobile phase. Detection was carried out using a Perkin–Elmer LC290 variable wavelength UV-absorbance detector. As NMP is opaque at 254 nm, detection of standard compounds and samples was performed at 270 and 300 nm respectively, where NMP is partially transparent. All sample solutions in NMP were prepared to a similar concentration, which was in a range of 0.1–0.3 mg mL−1. A total of 20 μL of solution was injected into the SEC system.

2.3.5. UV–fluorescence spectroscopy

A Perkin Elmer LS55 luminescence spectrometer was used to obtain emission, excitation and synchronous spectra of the crude oil samples, using NMP as solvent in all cases (only synchronous spectra are shown in this work). The procedure has been described elsewhere [11], [12]. The spectrometer was set with a slit width of 5 nm, to scan at 500 nm min−1; synchronous spectra were acquired at a constant wavelength difference of 20 nm. A quartz cell with 1 cm path length was used. Solutions were diluted with NMP to avoid self-absorption effects: dilution was increased until the fluorescence signal intensity began to both decrease in intensity and the relative intensities of the different maxima in the spectra ceased to change.

2.3.6. Laser desorption/ionization–mass spectrometry (LDI–MS)

A Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer was used for LDI–MS analysis. Since the samples under investigation absorb the nitrogen laser wavelength of 337 nm, no matrix was used and only positively charged ions were analyzed. A high-mass detector operating in the linear time of flight (TOF) mode was used to investigate the higher molecular mass region. In linear mode the conditions used included a delayed ion extraction (DIE) time of 600 ns and a mass range of m/z 0–300,000. The detector high mass accelerator (HMA) voltage was reduced as the laser power was increased to avoid overloading. The extraction voltage was set to 20 kV.

For the analysis of the pitches and pitches fractions, the samples were placed directly onto the metal surface of the LDI–MS target without the use of a solvent. In all cases, 10 spectra were summed using the pulsed ion extraction (PIE) method on the same sample spot.

2.3.7. Scanning electron microscope (SEM)

Observations of the diameter and surface appearance of the fibres were carried out on a Zeiss DSM 942 microscope.

3. Results and discussion

3.1. Preparation of carbon fibres by melt spinning

As mentioned above, carbon fibres were prepared by the melt spinning procedure from three anthracene oil-derived pitches of different softening points (AOP1: 218 °C, AOP2: 235 °C and AOP3: 247 °C). These pitches show a total absence of solid particles (ash free samples, Table 1) and low sulphur content which make them suitable for their use as precursors of isotropic carbon fibres.

There are several parameters to optimise in the carbon fibre preparation process (winding speed, spinning pressure, cross flow air, quench temperature, etc.) [13], [14]. One of the most critical ones is the spinning temperature. In general terms, if the melt temperature is too low, the extrusion of the pitch through the spinneret does not take place. On the other hand, if the melt temperature is too high, the extruding jet of the material can break up into drops. The use of the minimum temperature that allows adequate spinning is therefore of interest.

To study the effect of the spinning temperature of each anthracene oil-derived pitch on the green fibre morphology, the spinning process was carried out at several temperatures above the softening point of each pitch. Nitrogen extrusion pressure of 1 bar and spinneret hole of 500 µm were kept constant in all the experiments.

A minimum spinning temperature (Tms) could be determined at which green carbon fibres with a smooth surface, as shown by SEM (Fig. 2), are obtained. Table 2 shows the Tms temperature for AOP1, AOP2 and AOP3 and the difference between this temperature and the softening point of each pitch (Tms-SP). Tms of each pitch, as expected, follows the same trend as their softening points, that is AOP1 < AOP2 < AOP3. Interestingly, Tms values were found to be 32–33 °C above the softening point for the three pitches studied.

Fig. 2. Scanning electron micrographs of green carbon fibres obtained from (a) AOP1, (b) AOP2 and (c) AOP3.

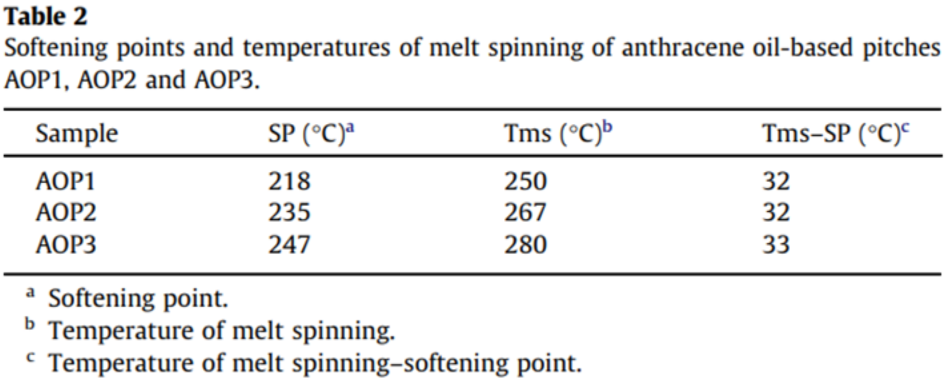


Table 2
Softening points and temperatures of melt spinning of anthracene oil-based pitches AOP1, AOP2 and AOP3.

Sample	SP (°C)[a]	Tms (°C)[b]	Tms–SP (°C)[c]
AOP1	218	250	32
AOP2	235	267	32
AOP3	247	280	33

[a] Softening point.
[b] Temperature of melt spinning.
[c] Temperature of melt spinning–softening point.

3.2. Influence of the winding speed on the diameters of the green fibres

The diameter of the green fibres is a parameter of special interest for carbon fibre production. Among the variables that control the diameter, the winding speed is probably the most relevant. If the winding speed is too low for a certain amount of extruded material, the required tensile stress of the filament is not reached and this may lead to the formation of drops of material. On the other hand, if the tensile stress within the filament exceeds the tensile strength of the material at a point along the threadline, the filament will break due to cohesive fracture.

The effect of winding speed on the diameter of the filament obtained from anthracene oil-derived pitches was studied in the range of 49–245 cm s−1 (Fig. 3). Some similarities in the trends obtained with each pitch are observed. For all pitches higher winding speed leads to smaller fibre diameters. Thus, it was possible to obtain green fibres with diameters close to 20 μm for a winding speed of 250 cm s−1 in the case of AOP3. However, the spinning behaviour of the pitches, measured in terms of variations in fibre diameter with winding speed, does not follow the trend of the softening point of the pitches. Although at winding speeds of 49 cm s−1 the diameters of the green fibres decrease with the increase in the softening point (or with Tms) of the pitch, that is AOP3 < AOP2 < AOP1, for higher winding speeds the variations in the diameter of the fibres follow the order AOP3 < AOP1 < AOP2.

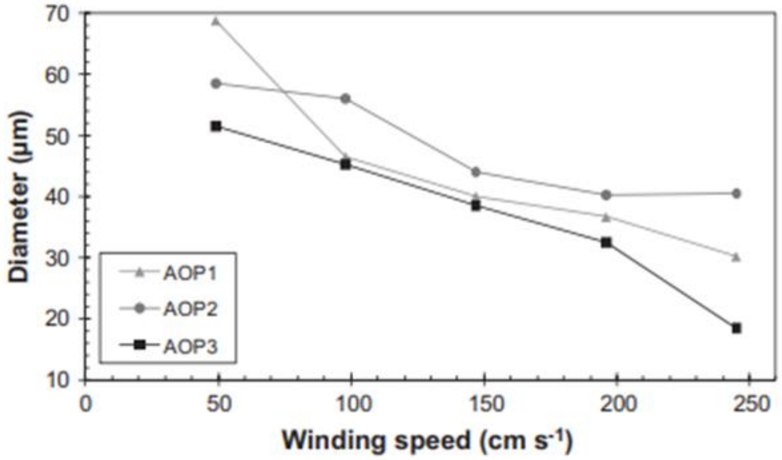
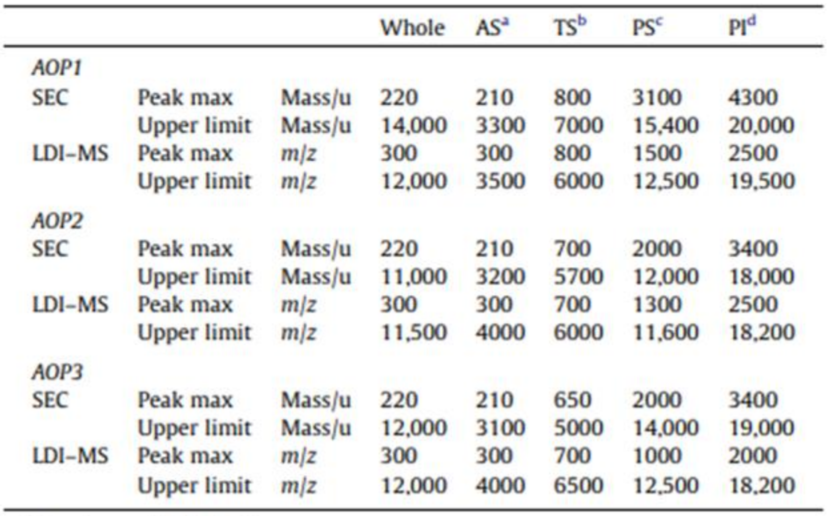


Fig. 3. Variations in diameter of the green fibres with winding speed for pitches AOP1, AOP2 and AOP3 spun at 250, 267 and 280 °C, respectively.

Table 3
Molecular weight estimations of anthracene oil based pitches AOP1, AOP2 and AOP3 calculated by SEC and LDI–MS.



			Whole	AS[a]	TS[b]	PS[c]	PI[d]
AOP1							
SEC	Peak max	Mass/u	220	210	800	3100	4300
	Upper limit	Mass/u	14,000	3300	7000	15,400	20,000
LDI–MS	Peak max	*m/z*	300	300	800	1500	2500
	Upper limit	*m/z*	12,000	3500	6000	12,500	19,500
AOP2							
SEC	Peak max	Mass/u	220	210	700	2000	3400
	Upper limit	Mass/u	11,000	3200	5700	12,000	18,000
LDI–MS	Peak max	*m/z*	300	300	700	1300	2500
	Upper limit	*m/z*	11,500	4000	6000	11,600	18,200
AOP3							
SEC	Peak max	Mass/u	220	210	650	2000	3400
	Upper limit	Mass/u	12,000	3100	5000	14,000	19,000
LDI–MS	Peak max	*m/z*	300	300	700	1000	2000
	Upper limit	*m/z*	12,000	4000	6500	12,500	18,200

[a] Acetone soluble fraction.
[b] Acetone insoluble, toluene soluble fraction.
[c] Acetone insoluble toluene insoluble and pyridine soluble fraction.
[d] Acetone, toluene and pyridine insoluble fraction.

These results clearly indicate that, for anthracene oil-derived pitches, the softening point is not the only parameter that determines their spinnability and, more specifically, the fibre diameter. Therefore, a more detailed characterisation of the pitches is needed in order to establish potential relationships between the pitch composition and its spinning behaviour.

3.3. Molecular weight determination of anthracene oil-derived pitches and their solvent solubility fractions

Molecular weight distributions of the pitches and their solubility fractions were obtained by SEC and LDI–MS. An initial analysis of the whole samples does not show clear differences in terms of molecular weight among the three pitches (Table 3) by either technique. In samples with large polydispersity like these pitches, signal from higher molecular weight materials is overshadowed by that of the more abundant lighter species. Fractionation allows then a more accurate determination of the range of molecular weights present in the sample [6].

As described in the experimental section, the anthracene oil-derived pitches were fractionated according to their solubility in acetone, toluene and pyridine. In order to gain more information about the composition of these fractions, a detailed molecular weight determination of each sample was carried out. The SEC chromatograms are shown in Fig. 4 (left) and the LDI–MS spectra in Fig. 4 (right). Table 3 summarises the most relevant features in the data from the pitches and their fractions.

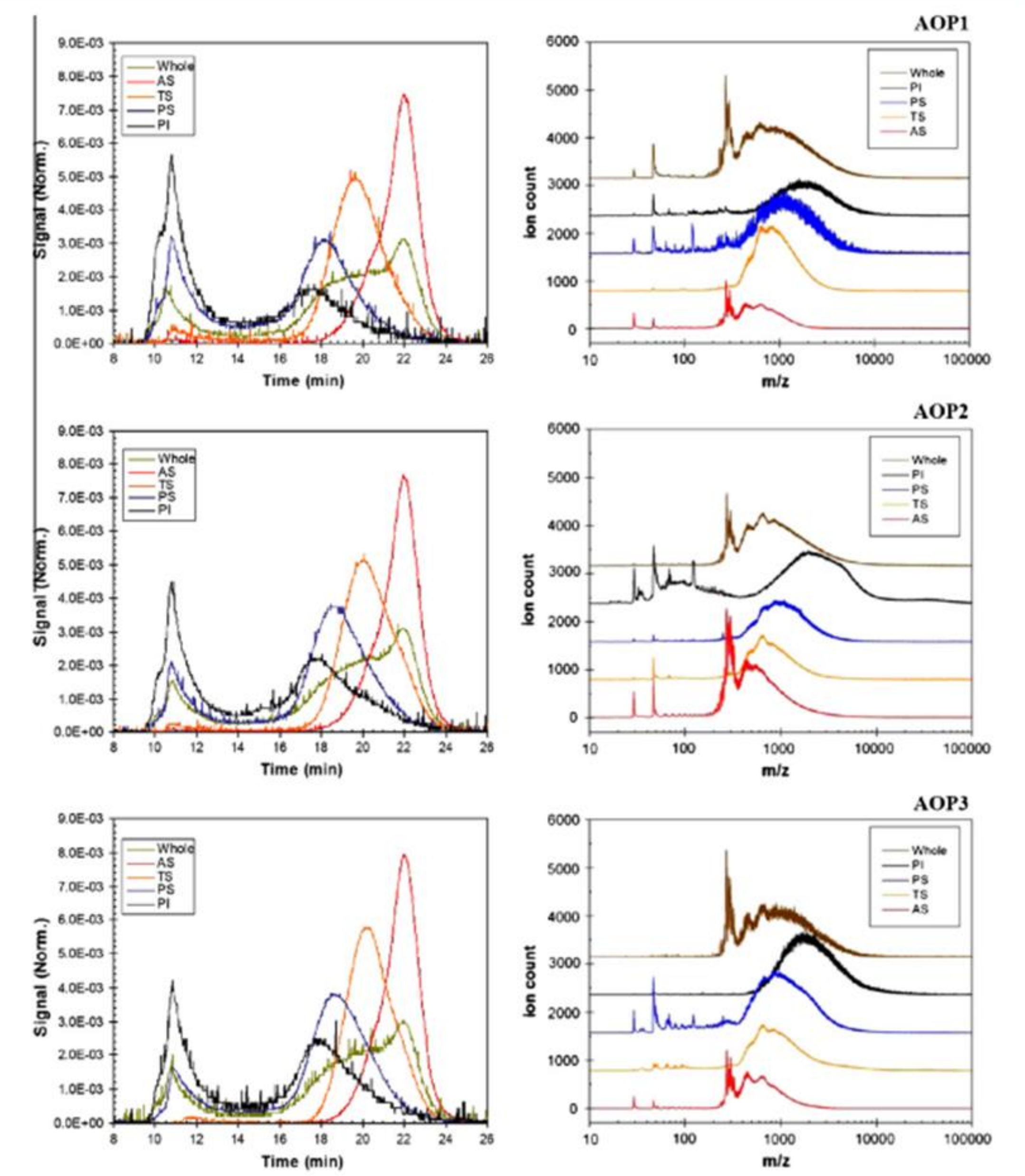


Fig. 4. SEC chromatograms (left) and LDI-MS spectra (right) of anthracene oil-derived pitches AOP1, AOP2 and AOP3.

All SEC chromatograms show a bimodal distribution, the earlier-eluting peak corresponding to material of molecular size unable to penetrate the porosity of the column packing, and referred to as “excluded” from the column porosity. The later-eluting peak corresponds to the material able to penetrate the porosity of the column packing. The exclusion limit of the column is about 200,000 u, according to a calibration based on the elution times of polystyrene standards. However, molecular conformation rather than molecular weight [10] is considered to be the factor that causes molecules to become excluded from the column porosity.

In all the cases the chromatograms of the pitch fractions are shifted to shorter elution times (higher apparent MW) with decreasing solubility (from AS to PI). Additionally, the excluded peak of the chromatograms is more prominent for the less soluble fractions. Estimates of the MW ranges of the retained peaks, calculated from a calibration with polystyrene standards and polycyclic aromatic hydrocarbon (PAH) standards are listed in Table 3.

Comparing equivalent fractions from different pitches, it can be noticed that they present similar MW distributions. The most significant differences appear for AOP1 toluene soluble (TS) and pyridine soluble fractions (PS), which showed a distribution shifted to higher MWs (maxima at 800 and 3100 u respectively) in comparison to AOP2 (700 and 2000 u for the TS and PS respectively) and AOP3 (650 and 2000 u for the TS and PS respectively). Variations in pitch MW distributions are a consequence of the conditions during the thermal treatment/distillation step, which is used in pitch production to adjust the softening point. It is clear that this adjustment gives rise to complex changes in compositions [7].

As any estimation of MW distributions by SEC relies on the polystyrene-based calibration accurately describing the elution behaviour of these samples, the SEC results were contrasted with those obtained by an independent technique such as LDI–MS. For the LDI–MS analysis, a combination of different laser powers and high-mass detector voltages was used (not shown). The optimum conditions for the analysis were selected taking into account the absence of significant fragment ions, the absence of any cluster ion distribution at very high mass and the stability of the shape of the ion distribution with no significant shifts to low or high masses with increasing laser power [15]. As observed in Fig. 4 and Table 3, the results show a good general agreement with those obtained by SEC, with the same trends and similar values in all cases.

The high mass limits were determined using a criterion of a 1° angle between the smoothed spectrum/chromatogram and baseline. The slope was determined by a “least-squares” calculation over a data interval corresponding to 2% of the whole data set [16], [17].

The upper limits obtained by LDI–MS are slightly lower than the corresponding SEC values for the less soluble fractions (PS and PI fractions), which could obey to the difficulty of ionizing high molecular weight compounds by LDI–MS. According to previous studies, this difficulty in the ionization is more acute in highly polydisperse samples, which seems to be the case in these fractions [9], [15]. This effect is particularly noticeable when comparing the LDI–MS upper limit for the whole samples (around 12,000 m/z) with the upper limit of the PI fractions (about 20,000 m/z).

Synchronous UV–fluorescence spectra in NMP (Fig. 5) shows that the aromatic chromophore sizes increased from the acetone-soluble to the pyridine-insoluble. The fluorescence intensity decreased in the same order, although the figures do not show this effect since the spectra have been height-normalised to make the comparison easier. The spectra of the pitch fractions show shifts to longer wavelengths in the order AS < TS < PS < PI, pointing towards higher concentrations of larger polynuclear aromatic groups as the fractions become more insoluble. Comparing the spectra of the samples, the more relevant differences appear again for AOP1 PS and PI fractions, which present a shift towards longer wavelengths (of about 30 and 20 nm correspondingly) in relation to the AOP3 and AOP2 corresponding fractions. These conclusions are in agreement with the SEC and LDI–MS results shown above.

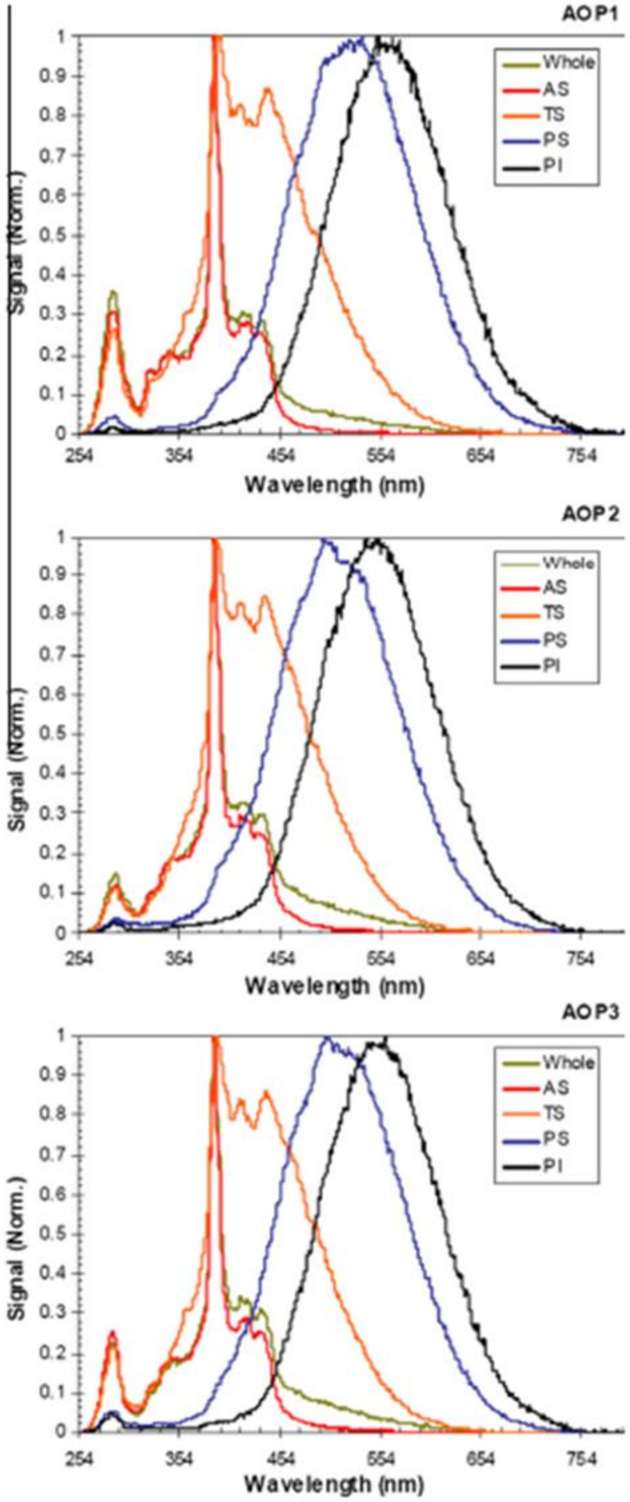


Fig. 5. UV-F spectra of anthracene oil-derived pitches AOP1, AOP2 and AOP3.

The mass balances of the fractionations are shown in Table 4. There is a decrease in the proportion of the two lower MW fractions, acetone soluble and toluene soluble, with the increase in the softening point of the pitches (AS and TS decrease along the series AOP1 > AOP2 >

AOP3). This is accompanied by a large increase in the pyridine insoluble fraction from AOP1 to AOP3 (pyridine insoluble fraction -PI- of 21, 34 and 36 wt.% for AOP1, AOP2 and AOP3 respectively), showing a consistent increase in the content of heavier fractions in samples with higher softening points. However, the pyridine soluble fraction follows a different trend. A higher value of PS (25 wt.%) was obtained for AOP1 in comparison with 20 and 22 wt.% for AOP2 and AOP3 respectively.

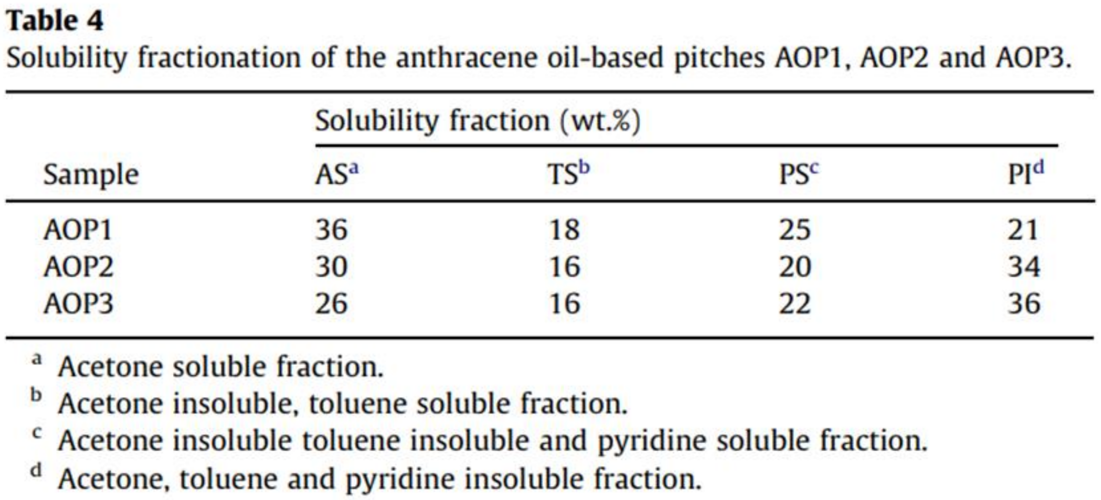


Table 4
Solubility fractionation of the anthracene oil-based pitches AOP1, AOP2 and AOP3.

Sample	Solubility fraction (wt.%)			
	AS[a]	TS[b]	PS[c]	PI[d]
AOP1	36	18	25	21
AOP2	30	16	20	34
AOP3	26	16	22	36

[a] Acetone soluble fraction.
[b] Acetone insoluble, toluene soluble fraction.
[c] Acetone insoluble toluene insoluble and pyridine soluble fraction.
[d] Acetone, toluene and pyridine insoluble fraction.

In summary, a good correlation was observed between the amount of soluble, low MW fractions in the pitches and their softening point with AOP3, the heavier pitch, showing the higher softening point. AOP3 also yields smaller-diameter fibres throughout the entire winding speed range. However, the relationship between softening point and spinning behaviour breaks down when AOP1 and AOP2 are compared. Despite its lower softening point and higher concentration of lighter fractions, AOP1 yields smaller fibre diameters than AOP2 for all winding speeds except the lower. Analysis by SEC and LDI–MS shows a shift towards upper MW limits in the PS and PI fractions (Table 3) of AOP1 in comparison with the corresponding fractions of AOP2 and AOP3. The presence of slightly heavier MW materials together with the larger amount of PS in AOP1 than in the two other samples could have some significant incidence on the spinning behaviour of AOP1 at higher winding speeds (Fig. 3), which produces fibres of intermediate diameters between AOP2 and AOP3.

4. Conclusions

Anthracene oil-derived pitches of high softening point can be used as precursors for preparation of isotropic carbon fibres by melt spinning. Analysis of the whole pitches by LDI/MS, UV–F and SEC demonstrated a relationship between higher softening point from AOP1 to AOP3 and the increasing presence of a heavier fraction in the pitch.

All three pitches tested proved suitable for the production of carbon fibres. Optimisation of the spinning temperature for each pitch (30–32 °C above the corresponding softening point) led to green carbon fibres with diameters as low as 20 μm. Variations in the fibre diameter with winding speed showed that at lower winding speeds (49 cm s−1), the diameters of the fibres decreases with increasing the softening point of the pitches. However, at higher winding speeds (up to 245 cm s−1) this trend is not observed when the two pitches with lower softening points are observed, indicating that the spinnability of the anthracene oil-derived pitches is not only dependent upon their softening point.

Variations in the spinning behaviour may reflect slight changes in pitch composition. A detailed analysis of these samples by solvent fractionation indicated that not only the relative proportions between solubility fractions but also the MW distributions in each fraction may have a critical effect in the spinning behaviour of the pitch. An improved understanding of the effect of MW distributions on the behaviour of the pitches during carbon fibre preparation could allow compositions to be tuned for the "on demand" preparation of anthracene oil-derived pitches.

Acknowledgments

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