

# **OPTIMIZATION OF THE MELT-SPINNING OF ANTHRACENE**

## **OIL-BASED PITCH FOR ISOTROPIC CARBON FIBRE**

Noel Díez, Patricia Álvarez, Ricardo Santamaría, Clara Blanco, Rosa Menéndez and

Marcos Granda

Instituto Nacional del Carbón, CSIC. P.O. Box 73. 33080-Oviedo, Spain

Author to whom correspondence should be addressed:

Dr. Patricia Alvarez

Instituto Nacional del Carbón, CSIC

Department of Chemistry of Materials

P.O. Box

33080-Oviedo, Spain

Tel.: +34 985 11 89 78

Fax: +34 985 29 76 62

e-mail: [par@incar.csic.es](mailto:par@incar.csic.es)

# OPTIMIZATION OF THE MELT-SPINNING OF ANTHRACENE OIL-BASED PITCH FOR ISOTROPIC CARBON FIBRE PREPARATION

Noel Díez, Patricia Álvarez, Ricardo Santamaría, Clara Blanco, Rosa Menéndez and  
Marcos Granda

Instituto Nacional del Carbón, CSIC. P.O. Box 73. 33080-Oviedo, Spain

**Abstract.** This paper demonstrates the suitability of a new environmentally friendly pitch, obtained from anthracene oil, for the preparation of isotropic carbon fibres. The pitch also exhibits adequate thermal behaviour and is free of solid particles. Green carbon fibres were prepared by means of a melt-spinning process with, no filtering step, and subsequent stabilization and carbonization. For the optimization of the melt-spinning process, the influence of the spinning temperature, extrusion pressure, spinneret hole size, winding speed and the interrelationship of these factors upon the microstructure and diameters of the fibres was studied. High winding speeds ( $250 \text{ cm s}^{-1}$ ), in combination with a high spinneret hole size ( $500 \text{ }\mu\text{m}$ ) and low extrusion pressures (1 bar), led to high quality isotropic carbon fibres with diameters as low as  $\sim 15 \text{ }\mu\text{m}$  and a tensile strength of  $> 1100 \text{ MPa}$  which fulfil the requirements for their application as standard isotropic carbon fibres.

**Keywords:** anthracene oil, isotropic pitch, carbon fibre, melt-spinning.

## 1. INTRODUCTION

Pitch-based carbon fibres are versatile materials that, depending on the precursor used and the properties exhibited, can be classified into two kinds; (i) the high performance carbon fibres (mesophase pitch-based carbon fibres) exhibit superb properties, such as an enhanced thermal behaviour, and are used for high-tech performance applications [1-3] and (ii) the carbon fibres for general applications (isotropic pitch-based carbon fibres), exhibit more modest properties such as those required for reinforcement composites or as raw material for the preparation of highly porous materials [4-7]. In terms of volume of production, isotropic pitch-based carbon fibres are produced on a wide scale, due to the comparatively low cost of manufacturing. Furthermore, it is predicted that the production of isotropic carbon fibres will increase in the future in order to satisfy the increasing demand.

Isotropic pitch-based carbon fibres are usually produced by melt-spinning [8]. One of the most important factors to be taken into account in their preparation is the specific characteristics of the precursors, in particular their softening point, carbon yield or the presence of solid particles including mesophase spheres [5,9]. The use of commercial pitches (coal-tar pitches and petroleum pitches) as carbon fibre precursor usually requires certain pre-treatments in order to adjust some of their characteristics [10]. This is because these pitches are mainly produced for use as binder and impregnating agents in aluminium and graphite industries.

In this context, we recently reported the preparation of new pitches with enhanced properties from coal-liquids (i.e. anthracene oil). Industrial anthracene oil, obtained as a distillation fraction from coal tar, can be employed as raw material for the preparation of pitches on an industrial scale, since it is readily available (it represents ~ 30 wt. % of

coal tar) and chemically consistent (all anthracene oils are composed of polycyclic aromatic hydrocarbons of 3-5 rings[11]). This raw material is considered nowadays a good alternative for producing pitches, with a controllable softening point, a high carbon yield and no solid particles [12]. Among the unique characteristics of these pitches is their low environmental impact, derived from the low content in polycyclic aromatic hydrocarbons (PAH) catalogued as potential carcinogenic. Furthermore, the preparation process (oxidative thermal condensation followed by thermal treatment) is highly versatile as it enables parameters such as the softening point of the pitch, to be easily controlled during the final steps of the preparation procedure [13]. This allows direct adjustment of the precursor characteristics during the process, making it unnecessary to apply the additional pre-treatments that are usually required when standard coal-tar pitch and petroleum pitches are used as carbon fibre precursors. Thus, the versatility of anthracene oil processing allows the preparation of isotropic pitches with different softening points and mesophase pitches with a suitable plasticity and a controlled microstructure from the same precursor [14,15]. All these reasons explain the interest in anthracene oil-based pitches as a new precursor for carbon fibre preparation, which, to the best of our knowledge, has not yet been studied.

In the present work, we have studied the feasibility of using novel anthracene oil-based pitches for the preparation of isotropic carbon fibres at lab scale. The main goals of the study are: (i) To characterize the anthracene oil-based pitch in order to determine the parameters that are relevant to its subsequent transformation into a carbon fibre (e.g., composition and pyrolysis behaviour) and (ii) to determine and optimize the main variables (spinning temperature, extrusion pressure, spinneret hole size and winding speed) that most affect the melt-spinning process. After stabilization and carbonization, the mechanical properties of the fibres (i.e., tensile strength) are determined.

## **2. EXPERIMENTAL**

### ***2.1. Raw materials***

The carbon fibre precursor used in this work was an isotropic anthracene oil-based pitch (AOP) supplied by Industrial Química del Nalón, S.A. This pitch was obtained from anthracene oil [12] by oxidative thermal condensation and then to thermal treatment until the desired softening point was reached (~ 250 °C).

### ***2.2. Characterization of the carbon fibre precursor***

The anthracene oil-based pitch was characterized in terms of elemental composition (using a LECO-CHNS-932 micro-analyzer and a LECO-VTF-900 furnace coupled to the micro-analyzer), softening point (ASTM D3104 standard) and Fourier-transformed infrared spectroscopy (using a Nicolet Magna IR-560 spectrometer equipped with a mercury–cadmium telluride detector operating at  $4\text{ cm}^{-1}$  at an average of 256 scans) [16,17]. The toluene insolubles (TI) were calculated according to the Pechiney B-16 (series PT-7/79 of STPTC) standard. The N-methyl-2-pyrrolidinone insolubles (NMPI) were determined following the ASTM D2318 standard for quinoline insolubles, but using N-methyl-2-pyrrolidinone (NMP) instead of quinoline.

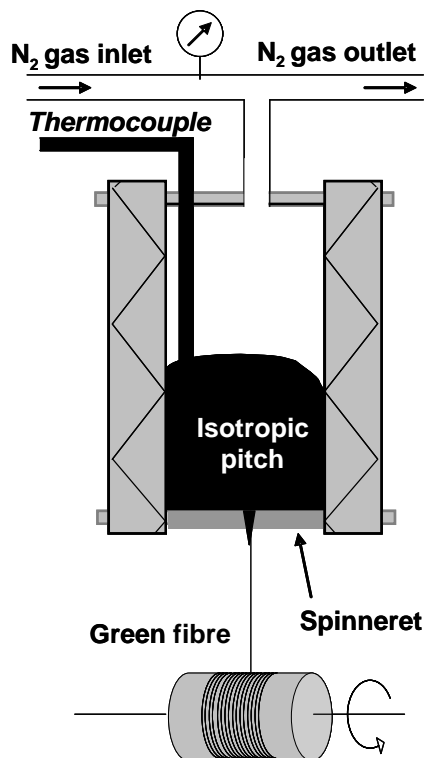
The PAH analysis was determined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) following standard procedures described elsewhere. Quantitative analyses were performed in an HP chromatograph fitted with an HP-1 capillary column (cross-linked methyl siloxane column) and an FID detector. 1  $\mu\text{l}$  volume of sample was injected in splitless mode and the oven temperature was increased from 50 to 280 °C at  $4\text{ }^{\circ}\text{Cmin}^{-1}$ . Hydrogen was used as the carrier gas at a flow rate of  $35\text{ ml min}^{-1}$ . The injector and detector temperatures were 315 and 300 °C,

respectively. The 16 PAH species catalogued as U.S. Environmental Protection Agency (EPA) priority pollutants were analysed and the benzo[a]pyrene equivalents (BaP<sub>eq</sub>) calculated according to the procedure described elsewhere [13].

The thermal stability of the pitch was studied by means of a standard industrial test. The pitch was heated up to 45 °C above its softening point for 20 h in an airtight device. The softening point of the product was then measured and compared with that of the parent pitch.

### ***2.3. Carbon fibre preparation***

Carbon fibres were prepared using anthracene oil-based pitch (AOP) as precursor. The fibres were melt-spun in a stainless steel reactor, equipped with stainless steel spinnerets of diameter 300 and 500 μm (Figure 1). The spinning temperatures chosen ranged within the range of 260 to 285 °C. Once the spinning temperature was optimized, different nitrogen extrusion pressures (from 1 to 5 bar) and winding speeds (from 50 to 250 cm s<sup>-1</sup>) were used to obtain fibres of different diameters.



**Figure 1.** Schematic diagram of the melt-spinning apparatus

The green fibres were stabilized in an oven under an air flow of  $20 \text{ L h}^{-1}$ , using the following multi-step program: heating at  $1 \text{ }^{\circ}\text{C min}^{-1}$  from room temperature to  $150 \text{ }^{\circ}\text{C}$ , maintaining this temperature for 4 h, and then heating at  $1 \text{ }^{\circ}\text{C min}^{-1}$  to 160, 180, 200, 220, 250 and  $270 \text{ }^{\circ}\text{C}$ , with 1 h of residence time at each of these temperatures. The stabilized fibres were then carbonized in a horizontal furnace, under a nitrogen atmosphere, at  $1 \text{ }^{\circ}\text{C min}^{-1}$  to  $900 \text{ }^{\circ}\text{C}$  and 30 min of residence time at this temperature.

#### **2.4. Carbon fibre characterization**

The texture and the diameter of the green, stabilized and carbonized fibres were studied by scanning electron microscopy (SEM). The tensile strength of the carbon fibres was measured according to the ASTM D3379-75 Standard for single-filament materials.

### 3. RESULTS AND DISCUSSION

#### *3.1 Suitability of anthracene oil-based pitch as a carbon fibre precursor*

The preparation of carbon fibres from pitches usually involves a melt-spinning procedure, followed by the stabilization and carbonization of the green fibres. An initial pre-treatment of the parent pitch is usually required in order to tailor the properties of the pitch prior to melt-spinning. A detailed characterization of the pitch is therefore required in order to determine whether any adjustment is necessary. This is of special interest in the case of this new anthracene oil-based pitch (AOP) which is produced from anthracene oil by means of an original synthetic procedure (an initial step of oxidative thermal condensation to form an intermediate product that is subsequently subjected to thermal treatment).

This anthracene oil-based pitch comprises a series of characteristics that makes it highly suitable as a precursor for the preparation of carbon fibres (Table 1). The pitch is totally ash free due to its origin (a coal tar distillation fraction) [17]. Therefore, its toluene and N-methyl-2-pyrrolidinone insoluble contents (TI and NMPI, respectively) are due exclusively to the presence of molecules with a high grade of condensation, which makes them insoluble in these solvents. Moreover, we have recently shown that the procedure developed for these pitches was designed to allow a certain control of their properties (e.g., softening point). Taking advantages of this fact, it was now adjusted the second step of the procedure to produce a pitch with a high softening point (~ 250 °C), enabling it to reach similar values to those of standard isotropic pitches used as carbon fibre precursors without further pre-treatments.



**Table 1.** Main characteristics of the anthracene oil-based pitch AOP.

Sample	Elemental Analysis (wt.%)					I <sub>Ar</sub> <sup>1</sup>	Ash <sup>2</sup>	TI <sup>3</sup>	NMPI <sup>4</sup>	SP <sup>5</sup>
	C	H	N	O	S					
AOP	93.3	4.1	1.4	0.8	0.4	0.65	0.0	58	23	247

<sup>1</sup> Aromaticity index determined by FTIR.

<sup>2</sup> Ash content ( wt. %).

<sup>3</sup> Toluene insoluble content ( wt. %).

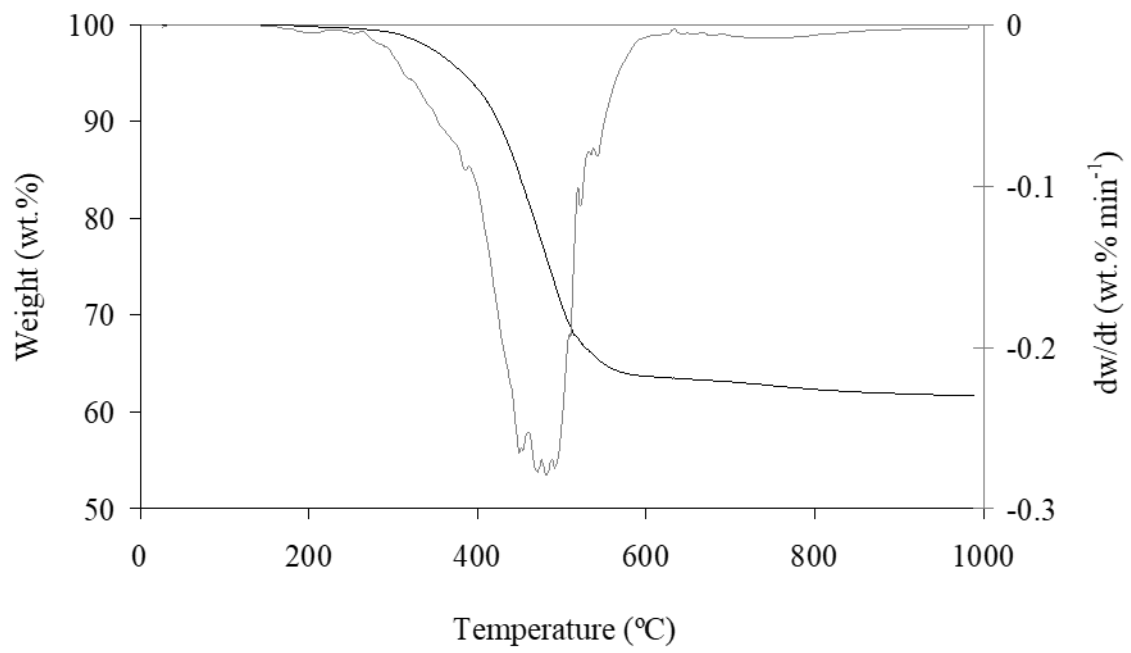
<sup>4</sup> N-methyl-2-pyrrolidinone insoluble content ( wt. %).

<sup>5</sup> Mettler softening point (°C)

The resultant pitch (AOP) is mainly composed of carbon (> 93%) and, to a lesser extent, hydrogen, nitrogen and oxygen. The hydrogen is mainly aromatic, as indicated by the high aromaticity index of the pitch components. The low oxygen content (0.8 wt.%) proves that the oxygen groups introduced during the oxidative thermal condensation step were successfully removed during the subsequent thermal treatment. Another important feature is the low sulphur content of this pitch (less than 0.4 wt.%).

The low toxicity is also one of the main characteristic of the AOP. The amount of the 16 PAH's catalogued as genotoxic by the EPA (US Environmental Agency [13]) accounts for 197 g kg<sup>-1</sup> in AOP. Its relative carcinogenicity (which is known to be a better estimation of the potential toxicity on human health) was determined in terms of the amount of benzo[a]pyrene in pitch (7.78 g kg<sup>-1</sup>) and benzo[a]pyrene equivalents (BaPeq, 16.98 g kg<sup>-1</sup>). Compared to those obtained for a standard pitches [12] (Benzo[a]pyrene of 10.8 g kg<sup>-1</sup> and BaPeq of 28.2 g kg<sup>-1</sup>) it can be concluded that the industrial use of this anthracene oil-based pitch as carbon fibre precursor is highly interesting not only due to its inherent characteristics (e.g., absence of particles) but also due to environmentally concerns [18], [19], [20].

Thermogravimetric analysis is a useful technique that provides relevant information about the most suitable spinning and stabilization conditions for the production of the green fibres. An example is the carbonaceous residue that the pitch generates through carbonization and the temperature range within which the pitch loses weight. The results of this analysis are shown in Figure 2. It can be seen that below ~ 350°C, weight loss is negligible (< 3 wt.%) which is to be expected of a pitch with a low volatiles content. Weight loss which mainly occurs between ~ 350 and ~ 600 °C yields a carbonaceous residue at 1000°C of 62 wt. %. These results indicate that the pitch could be heated above its softening point (required step for melt-spinning the pitch) up to ~ 350°C without undergoing any significant loss of volatiles. In addition, the high carbon residue obtained at 1000°C indicates that this pitch has the capability to retain carbon at high temperatures.



**Figure 2.** Thermogravimetric curves of the anthracene oil-based pitch.

The thermal stability of the precursor was studied according to the industrial procedure described in the experimental section. After 20 h at 292 °C, the softening point of the pitch increased by only 0.5 °C. Furthermore, the thermogravimetric curve of the pitch after the test exhibited virtually the same pattern than that of AOP (shown this later in Figure 2) indicating that the pyrolysis behaviour of the pitch had not undergone any significant change during the experiment.

From these results it can be inferred that this anthracene oil-based pitch would be especially suitable for use as a carbon fibre precursor.

### ***3.2. Optimization of the melt-spinning of anthracene oil-based pitch***

Having established that anthracene oil-based pitches do not require any pre-treatment prior to melt-spinning, we next set out to evaluate the feasibility of melt-spinning this pitch. For this purpose, a laboratory-scale apparatus that uses nitrogen pressure to extrude the pitch through a mono-hole spinneret (Figure 1) was employed.

Among the parameters involved in the pitch melt-spinning process, spinning temperature, extrusion pressure, winding speed and spinneret hole size are the most important, requiring optimization and will be analyzed in detail [18,19].

#### ***3.2.1. Effect of spinning temperature***

The first parameter to be optimized was the spinning temperature, which is directly related to the softening point of the pitch [18]. When the spinning temperature is too low, extrusion of the pitch through the spinneret cannot take place. On the other hand, if the spinning temperature is too high, the extruding jet of material may break up into

drops. Establishing the minimum temperature for correct spinning (carbon fibres free of surface defects) is therefore of the utmost importance.

Spinning was carried out at different temperatures (Table 2) using a 300  $\mu\text{m}$  monohole spinneret, a nitrogen extrusion pressure of 5 bar and a winding speed of 250  $\text{cm s}^{-1}$ .

**Table 2. Spinning temperatures and surface appearance of green fibres observed by means of SEM.**

<b>Th<sup>1</sup></b>	<b><math>\Delta</math>Th<sup>2</sup></b>	<b>Surface<sup>3</sup></b>
260	13	-
265	18	Defects
270	23	Defects
275	28	Defects
280	33	No defects
285	38	No defects

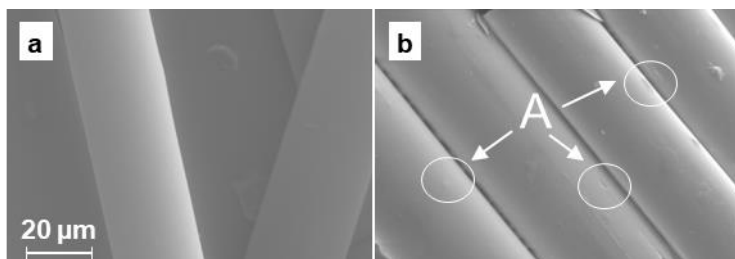
<sup>1</sup> Spinning temperature (°C).

<sup>2</sup> Difference between the spinning temperature and the pitch softening point (°C).

<sup>3</sup> Surface appearance of the green fibre observed by SEM.

The results show that extrusion of the pitch only occurs at temperatures above 260 °C, and that spinning temperatures higher than 265 °C are necessary to achieve a continuous flow of pitch through the spinneret.

Examination of the green fibres by SEM (Figure 3) revealed that only spinning temperatures higher than 280 °C (~30 °C above their softening point) lead to green fibres with smooth and defect-free surfaces (Figure 3a). Below this temperature (Figure 3b, position A) the presence of defects on the surface of the fibres was detected.



**Figure 3.** SEM images of green fibres spun at (a) 280 and (b) 275 °C.

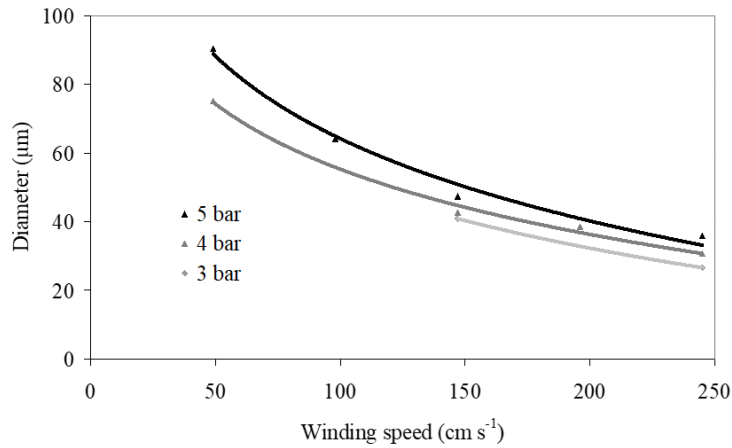
### ***3.2.2. Effect of extrusion pressure and winding speed on the diameter of the green fibres***

The amount of sample that is extruded through the spinneret hole per unit of time was determined by the nitrogen pressure applied (at a fixed hole size). The diameter of the green fibres obtained is affected by this nitrogen pressure and by the winding speed applied. If the winding speed is too low for a certain extruded amount of pitch, the

required tensile stress of the filament is not reached and this may lead to the formation of drops of pitch [18]. On the other hand, if the winding speed is too high for a certain extruded amount of pitch, the internal tensile stress of the filament exceeds the tensile strength of the material and the filament will break as a result of cohesive fracture.

In order to study the effect of these two parameters (extrusion pressure and winding speed) on the diameter of the green fibres, several experiments were carried out using different nitrogen pressures (3 to 5 bar) and winding speeds (50 to 250 cm s<sup>-1</sup>), while the spinning temperature (280 °C) and spinneret hole size (300 µm) were kept constant (Figure 4).





**Figure 4.** Variation in diameters with winding speed for green fibres spun at different extrusion pressures (spinning temperature 280 ° C, spinneret hole size 300 µm).

The results show that only nitrogen pressures between 3 and 5 bar allow a continuous flow of pitch resulting in correctly spun fibres. Thus, whereas nitrogen pressures lower than 3 bar fail to produce extrusion of the pitch, pressures higher than 5 bar do not allow the pitch to be stretched and wound correctly.

Variation in the diameter of the green fibres with the winding speed confirms that the fibre diameter decreases with the increase in winding speed, possibly because the filament is more easily stretched. It was also observed that an increment in extrusion

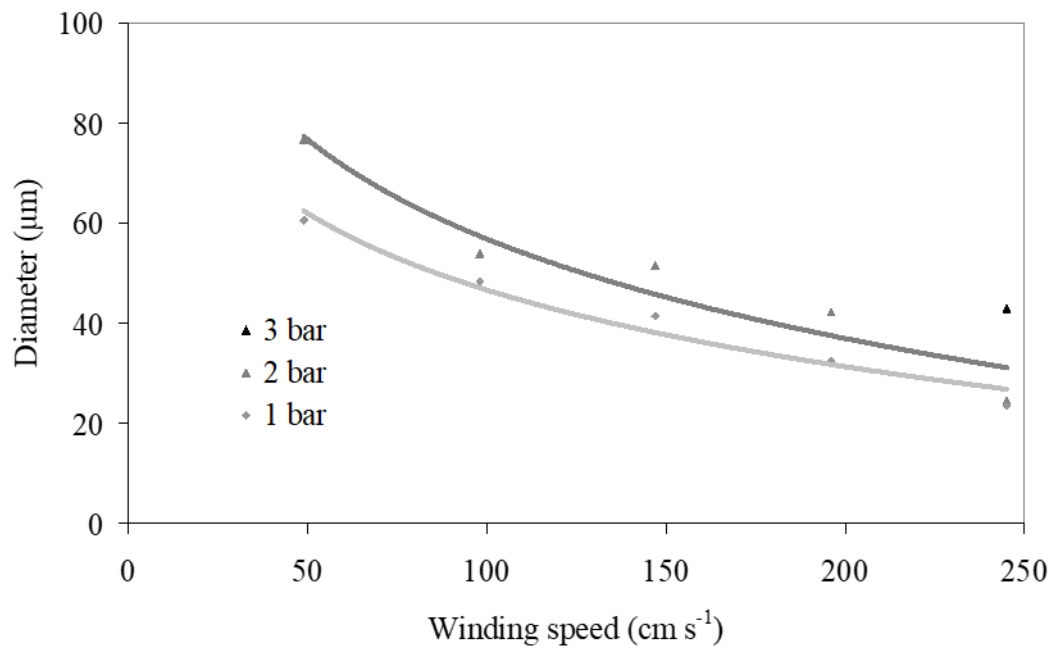
pressure does not exert any significant influence on the average diameter of the extruded fibres.

The thinnest fibres (average diameter of  $\sim 25 \mu\text{m}$ ) were obtained at a nitrogen pressure of 3 bar and a winding speed of  $250 \text{ cm s}^{-1}$ .

### ***3.2.3. Effect of spinneret hole size***

The spinneret hole size exerts a great influence not only on the diameter of the fibre but also on the nitrogen pressure that must be applied to extrude the pitch. It is known that greater the size of the spinneret, the lower the pressure needed to extrude the pitch under the same winding speed conditions. This explains why in the experiments carried out with a spinneret of  $500 \mu\text{m}$ , the nitrogen pressures give rise to successfully spun fibres under a continuous and homogeneous flow of pitch ranged between 1 and 3 bar. Pressures above 3 bar and a winding speed lower than  $250 \text{ cm s}^{-1}$  do not result in a successfully wound pitch due to an excess of sample around the spool. On the other hand, pressures lower than 1 bar does not allow the extrusion of the pitch.

In general, the average diameter of the fibres obtained with the  $500\mu\text{m}$  spinneret (under a nitrogen pressure of 3 bar and a winding speed of  $250 \text{ cm s}^{-1}$ ) is slightly higher than that achieved with the  $300\mu\text{m}$  spinneret (Figures 4 and 5). Thus, at 3 bar and  $250 \text{ cm s}^{-1}$  the pitch that is spun through the  $500 \mu\text{m}$  spinneret shows an average diameter of  $\sim 30 \mu\text{m}$ ,  $\sim 10 \mu\text{m}$  larger than that spun with the  $300 \mu\text{m}$  spinneret diameter. However, when a spinneret of a larger size was used, green fibres with diameters as low as  $\sim 20 \mu\text{m}$  were obtained because it was possible to apply lower extrusion pressures (up to 1 bar).

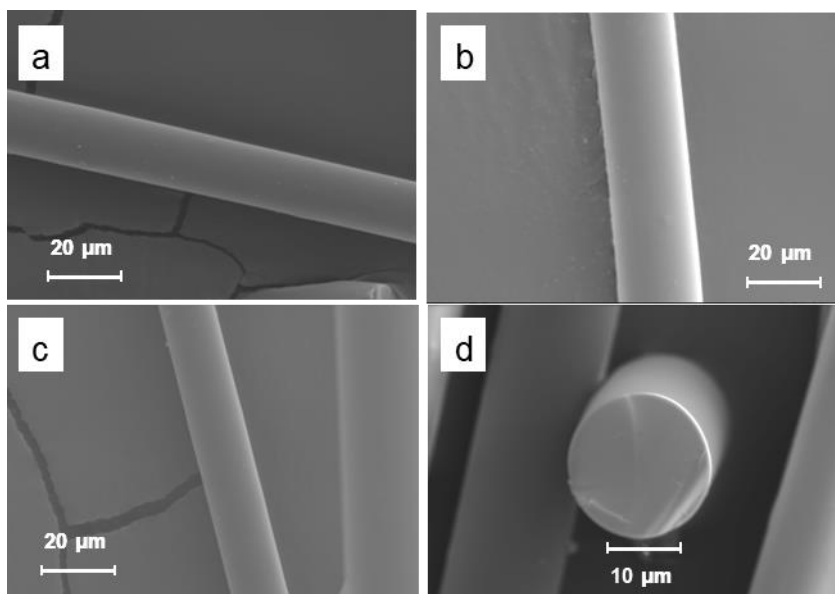


**Figure 5.** Variation in diameters with winding speed for green fibres spun at different extrusion pressures (spinning temperature 280 °C, spinneret hole size 500 µm).

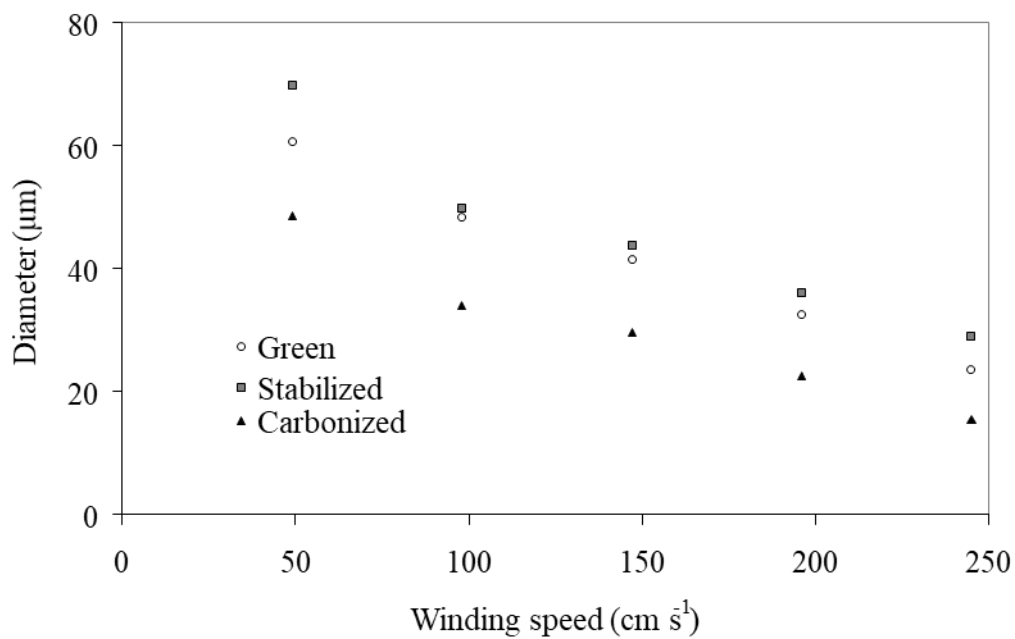
### ***3.3. Stabilization and carbonization***

Once spun, the green carbon fibres must be stabilized prior to carbonization in order to render the fibre infusible. The green fibres obtained at a spinning temperature of 280 °C, a nitrogen pressure of 1 bar and a spinneret hole size of 500 µm (conditions that led to the green fibres with the smallest diameters) were stabilized, using the temperature/time program given in the experimental section, and then carbonized at 900 °C for 30 min.

SEM observations showed that neither stabilization nor carbonization produced any defect on the surface of the fibres (Figure 6). Moreover, the microstructure of the carbon fibre remains completely isotropic (Figures 6d) whereas the morphology of the fibres, especially their diameter, undergoes substantial changes (Figure 7). Thus, stabilization causes a slight increase in the diameter of the fibres, which may be related to the uptake of oxygen during the process. Subsequent carbonization produces shrinkage that results in a decrease in the diameter of the fibre (Figure 7). This shrinkage leads to carbon fibres that have an even smaller diameter than that of the green fibre (~ 15 µm).

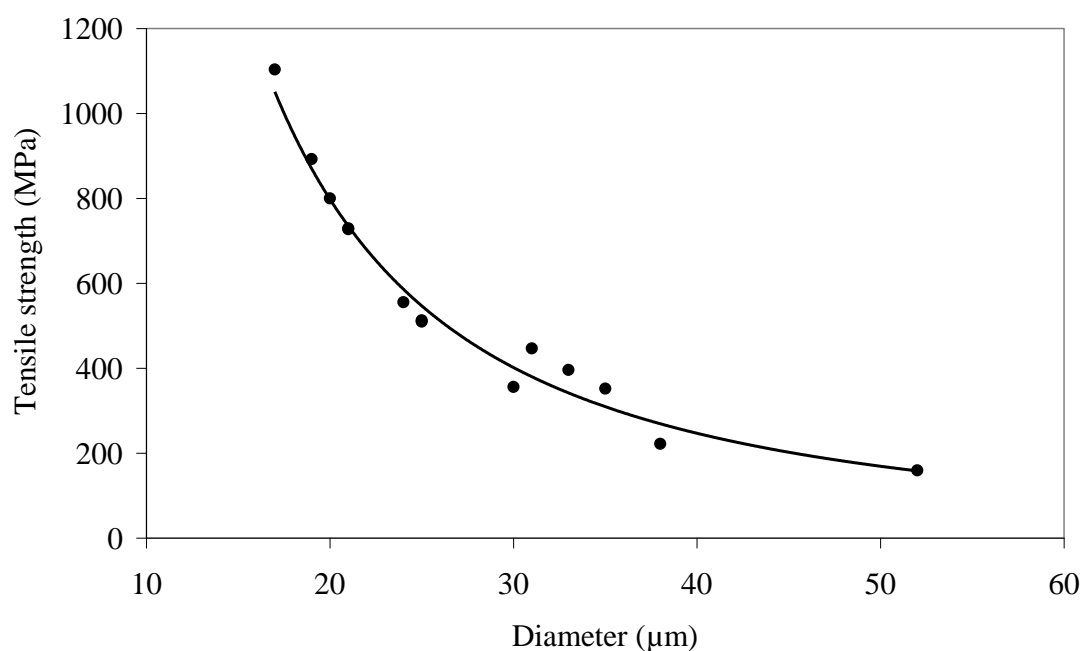


**Figure 6.** SEM images of (a) green, (b) stabilized and (c, d) carbon fibres.



**Figure 7.** Variation in diameters with winding speed for green, stabilized and carbon fibres (spinning temperature 280 °C, extrusion pressure 1 bar and spinneret hole size 500 µm).

The mechanical properties of the carbon fibres were evaluated in terms of tensile strength (Figure 8). As expected, tensile strength increases exponentially as the carbon fibre diameter decreases, from ~ 200 to > 1100 MPa (for carbon fibres with an average diameter of ~ 40 and 15  $\mu\text{m}$ , respectively). These values are comparable to those reported in the literature for isotropic carbon fibres [20].



**Figure 8.** Variation in tensile strength with carbon fibre diameter (temperature spinning 280°C, nitrogen pressure 1 bar and spinneret hole size 500  $\mu\text{m}$ ).

### 3. CONCLUSIONS

A novel anthracene oil-based pitch of high softening point was successfully transformed into isotropic carbon fibres by melt-spinning. Close examination of the pitch composition, thermal stability, and pyrolysis behaviour showed that this pitch can be used for this purpose as-produced (without the need for any additional post-treatment).

Furthermore, its low content in carcinogenic compounds, compared to other standard pitches, indicates that its use is highly recommended due to work place safety and environmental concerns.

The melt-spinning of the anthracene oil-based pitch requires temperatures of  $\sim 30$  °C above its softening point. By employing a spinneret with larger hole size, green fibres with diameters as low as  $\sim 20$   $\mu\text{m}$  can be obtained due to the fact that lower extrusion pressures can be applied.

Stabilisation of the green fibres produces an increase in the diameter of the fibres. However, this increase is subsequently reduced during carbonisation, resulting in carbon fibres with diameters smaller than those of the green fibres ( $\sim 15$   $\mu\text{m}$ ).

Analysis of the mechanical strength of the carbon fibres demonstrated that the isotropic precursor (anthracene oil-based pitch) and the procedure used in this study lead to carbon fibres with a tensile strength comparable to that of typical pitch-based isotropic carbon fibres produced from standard pitches (1100 MPa), showing that the production of carbon fibres from this novel precursor represents an alternative to the ones available nowadays in the market.

**5. ACKNOWLEDGEMENTS.-** The research leading to these results has received funding from the European Union's Research Fund for Coal and Steel (RFCS) research programme (under grant agreement N° RFCR-CT-2009-00004 and Ref. RFC-PR-08008) and from Spanish Science and Innovation Ministry (Ref. MAT2009-08587-



E/MAT). Dr. Patricia Alvarez also thanks the Spanish Science and Innovation Ministry for her Ramon y Cajal contract.

### **Figure captions**

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

Figure 2. Thermogravimetric curves of the anthracene oil-based pitch.

Figure 3. SEM images of green fibres spun at (a) 275 and (b) 280 °C.

Figure 4. Variation in diameters with winding speed for green fibres spun at different nitrogen extrusion pressures (spinning temperature 280 °C, spinneret hole size 300 µm).

Figure 5. Variation in diameters with winding speed for green fibres spun at different nitrogen extrusion pressures (spinning temperature 280 °C, spinneret hole size 500 µm).

Figure 6. SEM images of (a) green, (b) stabilized and (c, d) carbon fibres.

Figure 7. Variation in diameters with winding speed for green, stabilized and carbon fibres (spinning temperature 280 °C, extrusion pressure 1 bar and spinneret hole size 500 µm).

Figure 8. Variation in tensile strength with carbon fibre diameter (spinning temperature 280 °C, nitrogen extrusion pressure 1 bar and spinneret hole size 500 µm).

### **Table captions**

Table 1. Properties of the anthracene oil-based pitch.

Table 2. Spinning temperatures and surface appearance of green fibres observed by means of SEM.

## 6. REFERENCES

- [1] M.L. Greene, R.W. Schwartz, J.W. Treleaven , Short residence time graphitization of mesophase pitch-based carbon fibers, *Carbon* 40 (2002) 1217-1226.
- [2] F.Watanabe, S. Ishida, Y. Korai, I. Mochida, I. Kato, Y. Sakai, M. Kamatsu, Pitch-based carbon fiber of high compressive strength prepared from synthetic isotropic pitch containing mesophase spheres, *Carbon* 37 (1999) 961-967.
- [3] E. Mora, C. Blanco, R. Santamaría, M. Granda, R. Menéndez, Novel method to obtain a petroleum-derived mesophase pitch suitable as carbon fibre precursor, *Carbon* 41 (2003) 445-452.
- [4] X. Fu, W. Lu, D.D.L. Chung, Ozone treatment of carbon fiber for reinforcing cement, *Carbon* 36 (1998) 1337-1345.
- [5] S.M. Zeng, T. Maedaa, K. Tokumitsua, J. Mondoria, I. Mochida, Preparation of isotropic pitch precursors for general purpose carbon fibers (GPCF) by air blowing—II. Air blowing of coal tar, hydrogenated coal tar, and petroleum pitches, *Carbon* 31 (1993) 413-419.
- [6] J. Alcañiz-Monge, D. Cazorla-Amorós, A. Linares-Solano, S. Yoshida, A. Oya, Effect of the activating gas on tensile strength and pore structure of pitch-based carbon fibres, *Carbon* 32 (1994) 1277-1283.
- [7] X. Fu, W. Lu, D.D.L. Chung, Ozone treatment of carbon fiber for reinforcing cement, *Carbon* 36 (1998) 1337-1345.

- [8] F. Derbyshire, R. Andrews, D. Jacques, M. Jagtoyen, G. Kimber, T. Rantell, Synthesis of isotropic carbon fibers and activated carbon fibers from pitch precursors, *Fuel* 80 (2001) 345-356.
- [9] E. Mora, C. Blanco, V. Prada, R. Santamaría, M. Granda, R. Menéndez, A study of pitch-based precursors for general purpose carbon fibres, *Carbon* 40 (2002) 2719-2725.
- [10] J. Alcañiz, D. Cazorla, A. Linares Solano, A. Oya, A. Sakamoto y K. Hoshi. Preparation of General Purpose Carbon Fibres from coal tar pitches with low softening point, *Carbon* 35 (1997) 1079-1087.
- [11] J.J. Fernandez, M. Alonso, Anthracene oil-based pitches, *Light Metals* (2004) 449-450.
- [12] P. Álvarez, M. Granda, J. Sutil, R. Santamaría, C. Blanco, R. Menéndez, J. J. Fernández, J. A. Viña, Preparation of Low Toxicity Pitches by Thermal Oxidative Condensation of Anthracene Oil, *Environ. Sci. Technol.* 43 (2009) 8126–8132.
- [13] P. Álvarez, M. Granda, J. Sutil, R. Menéndez, J. J. Fernández, J. A. Viña, T. J. Morgan, M. Millán, A. A. Herod, R. Kandiyoti, Characterization and Pyrolysis Behavior of Novel Anthracene Oil Derivatives, *Energy & Fuels* 22 (2008) 4077–4086.
- [14] P. Álvarez, M. Granda, J. Sutil, R. Santamaría, C. Blanco, R. Menéndez, A unified process for preparing mesophase and isotropic material from anthracene oil-based pitch, *Fuel Processing Technology* 92 (2011) 421-427.
- [15] P. Álvarez, J. Sutil, R. Santamaría, C. Blanco, R. Menéndez, M. Granda, Mesophase from Anthracene Oil-Based Pitches, *Energy & Fuel* 22 (2008) 4146–4150.
- [16] C. Blanco, V. Prada, R. Santamaría, J. Bermejo, R. Menéndez, Pyrolysis behaviour of mesophase and isotropic phase isolated from the same pitch, *J. Anal. Appl. Pyrol.* 63 (2002) 251–265.

- [17] C. Blanco, R. Santamaría, J. Bermejo, R. Menéndez, Separation and characterisation of the isotropic phase and co-existing mesophase in thermally treated coal-tar pitches, *Carbon* 38 (2000) 1169–1176.
- [18] D.D. Eddie and M.G. Dunham, Melt spinning pitch-based carbon fibres. *Carbon* 27 (1989) 647-655.
- [19] S. Kase, in: A.Ziabicki and H. Kawai (Eds.), *High-Speed Fibre Spinning*, Wiley Interscience, New York, 1985, pp. 67-113.
- [20] K.S. Yang, D.J. Lee, S.K. Ryu, Y. Korai, Y.J. Kim, I. Mochida, Isotropic carbon and graphite fibres from chemistry modified coal-tar pitch, *Korean J. Chem. Eng.* 16 (1999) 518-524.