ISOTROPIC CARBON FIBRES FROM ANTHRACENE OIL DERIVATIVES

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Introduction

Anthracene oil is a low value distilled fraction of coal tar, largely made up of polycyclic aromatic hydrocarbons of 3-5 rings. The anthracene oil can be transformed into pitch by means of oxidative thermal treatment, whose main properties are their high aromaticity and a total absence of solid particles, making them excellent candidates for the preparation of carbon fibres[1,2,3]. In the present work a detailed study of the different variables involved in the processing of the anthracene oil-based pitch for the preparation of isotropic fibres is carried out. Aspects such as the temperature, the spinning speed and the nitrogen pressure used in the spinning of the fibre are optimized in accordance with 6the characteristics of the parent isotropic pitch in order to obtain isotropic carbon fibres with a homogeneous surface devoid of defects.

Experimental

The isotropic pitch used as raw material (IP upplied by Industrial Química del Nalón, S.A.) was obtained by subjecting an air-treated anthracene oil to thermal treatment/distillation. The softening point (Mettler standard) was determined as 247 °C. A laboratory scale stainless-steal apparatus fitted with either a 45 µm mesh or a stainless-steel spinneret (500 or 300 µm) was used to filter and melt-spin the precursor.

The precursor is heated to 260 °C and then a nitrogen pressure of 5bar was applied in order to filter the melted pitch through the mesh.

The filtered pitch is introduced in the reactor and heated up to the spinning temperature (260, 265, 270, 275, 280 and 285 °C). The melted pitch is extruded through the spinneret hole into carbon fibres by applying nitrogen pressures from 1 to 5 bar and different winding speeds (49, 98, 147, 196 y 245 cm/s).

The as-spun fibres were stabilized in air at a heating rate of 1°C/min following a multistep temperature program (150 °C 4 h, 160 °C 4 h, 180 °C 1 h, 200 °C 1 h, 220 °C 1 h, 250 °C 1 h, 270 °C 1 h).

The stabilized fibres were then carbonized at 900 °C for 30 minutes under nitrogen flow in a tube furnace at a heating rate of 2 °C /min.

The precursor is characterized by elemental analysis, softening point determination, thermogravimetric analysis in nitrogen and solubility tests.

The fibres were observed under a scanning electron microscope (SEM) to study the diameters obtained and the appearance of the surface.

Results and Discussion

The main properties of the IP pitch are shown in Table1.

Table 1. Properties of the Anthracene Oil-Based Pitch.

	SP	Solubility wt %		H/C	Elemental wt %				
	(°C)	TI	NMPI		C	H	N	O	S
IP	247	58.0	23.0	0.53	93.2	4.1	1.4	0.8	0.5

This isotropic pitch is mainly composed of carbon (> 93 %) and, to a lesser extent, hydrogen, nitrogen and oxygen. Sulphur accounts for less than 0.5 % of the total mass. The pitch does not contain solid particles (e.g. primary IQ), which makes it an excellent precursor for carbon fibres preparation.

Determination of the optimum spinning temperature.

Sample can be continuously spun at temperatures of 270 °C. However, at spinning temperatures lower than 280 °C, the fibres exhibit defects on their surface (Figure 1, position A). Therefore, a minimum spinning temperature at 280 °C can be defined for this pitch. This implies that the sample must be spun using an overheating of 33°C over its softening point.

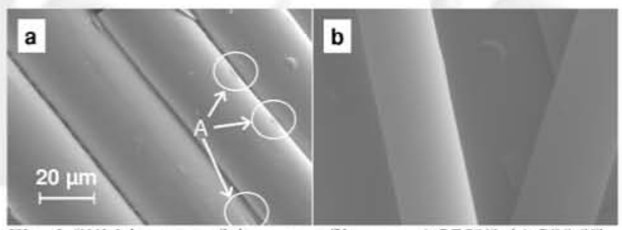

Fig. 1 SEM images of the green fibres at a) 275°C, b) 280 °C

Fig. 2 shows the TGA curves of the parent, filtered and as-spun pitch obtained at 280 °C. The carbon residue at 1000 °C increased in each step due to the gradual loss of volatiles during the filtration and spinning steps.

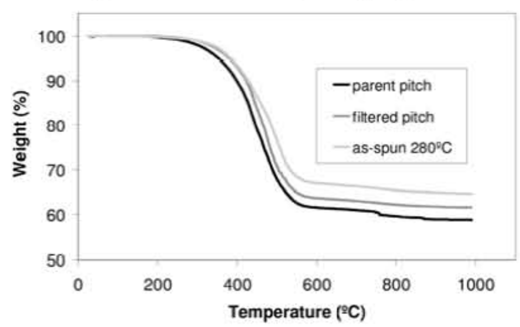

Fig. 2 TGA curves of parent, filtered and as-spun (280 °C) pitch.

Influence of winging speed and nitrogen pressure.

The diameter of the green fibres can be optimized by modifying the variables involved in the spinning process. The parameters that mostly influence these diameters are nitrogen pressure, the size of the spinneret hole and the winding speed.

Fig. 3 shows the variations of fibre diameter with different winding speeds obtained by melt-spinning at 280 ºC and different nitrogen pressures. As observed, lower nitrogen flow (that causes lower flow of the extruded pitch) and higher winding speed lead to lower green fibre diameters.

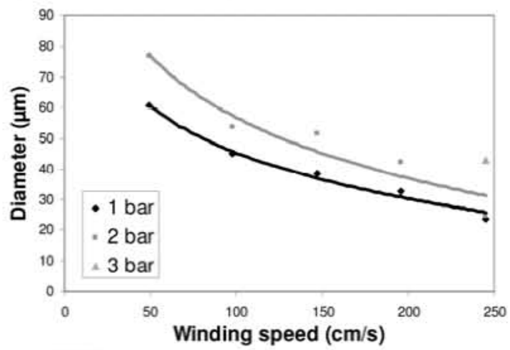

Fig. 3 Variations in diameter of the green fibres (500 µm spinneret) with winding speed for different nitrogen pressures.

Spinning conditions of 3 (or higher) bar of pressure and a winding speed lower than 245 cm/s do not allow winding the pitch into the fibre due to the excess of sample on the spool. At 1 bar and 245 cm/s the thinnest fibres with are obtained, exhibiting average diameters of 20 µm.

Influence of the spinneret hole size.

The precursor is also melt-spun at its optimum spinning temperature through a 300 µm spinneret. As shown in Fig. 4, a minimum nitrogen pressure of 3 bar is required to extrude the melted pitch into a continuous fibre. Increments in the nitrogen pressure do not exert a significant influence on the diameter of the extruded fibres.

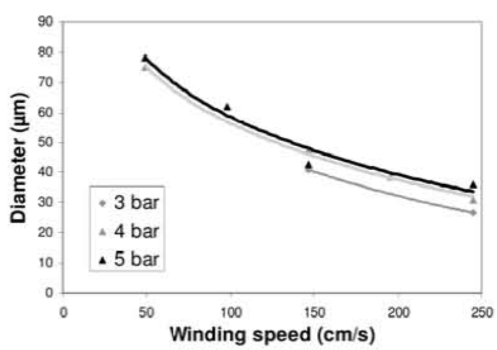

Fig. 4 Variations in diameter of the green fibres (300 µm spinneret) with winding speed for different nitrogen pressures.

In general it is observed that the average fibre diameters obtained with the 300 µm spinneret (spinning conditions of 3 bar of nitrogen pressure and 245 cm/s of winding speed) are slightly higher (≈ 10 µm) that those obtained with the 500 µm spinneret (Fig. 3). This could be related with the required increase of pressure to extrude the pitch.

Stabilization and carbonization.

The green fibres are stabilized in air and finally carbonized under nitrogen. As shown in Fig. 5, the carbon fibres retain their shape and lack of surface defects after carbonization.

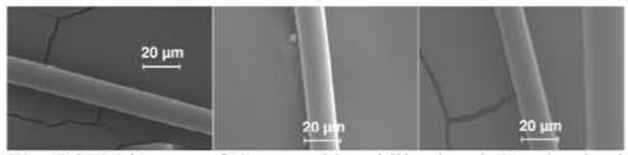

Fig. 5 SEM images of a) green, b) stabilized and c) carbonized fibres.

Conclusions

Anthracene oil based-pitch can be easily transformed into carbon fibres by melt-spinning. There is an optimum spinning temperature, defined as the lowest temperature that produces carbon fibres with no apparent surface defects.

Winding speeds of 245 cm/s and nitrogen pressures of 1 bar lead to fibres in the range of 20 microns.

In general, the use of a 300 µm spinneret instead of the 500 µm lead to carbon fibres with slightly higher average diameters, possibly due to the higher pressures required to extrude the pitch.

The fibres maintained their shape after stabilization and carbonization.

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