THE INFLUENCE OF MELT-SPINNING CONFIGURATION ON THE MICROTEXTURE OF PETROLEUM PITCH-BASED CARBON FIBERS[1]

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Abstract

Carbon materials are normally used in applications that demand high mechanical properties and low density. In that context, carbon fibers produced from polyacrylonitrile or pitch play a major role. In the present work, a petroleum pitch was produced from an aromatic residue from the petroleum industry, to evaluate the influence of the spinning configuration on the final microtexture of pitch-based carbon fibers. The petroleum pitch was spun using 48 different spinning configurations, varying the diameter and length of the spinning hole and with or without a filter. The obtained structures were analyzed by polarized light optical microscopy and by scanning electron microscopy. For reduced diameters and higher lengths of the spinning hole, it was necessary to use filters. For reduced spinning hole diameters and filters of smaller mesh, the obtained structures showed a more homogeneous distribution. The random microtexture was obtained in the great majority of the considered configurations.

Key words: Petroleum pitches; Carbon fibers; Optical microscopy.

INFLUÊNCIA DA CONFIGURAÇÃO NO PROCESSO DE FIAÇÃO A QUENTE SOBRE A MICROTEXTURA DE FIBRAS DE CARBONO PRODUZIDAS A PARTIR DE PICHE DE PETRÓLEO

Resumo

Os materiais de carbono são normalmente utilizados em aplicações que demandam elevadas propriedades mecânicas e baixa densidade. Nesse contexto, as fibras de carbono produzidas a partir de poliacrilonitrila ou de piche se destacam. No presente trabalho, um piche de petróleo foi produzido a partir de um resíduo aromático oriundo da indústria do petróleo, com o objetivo de se avaliar a influência da configuração de fiação sobre a microtextura final de fibras de carbono de piche. O piche de petróleo foi fiado utilizando-se 48 configurações de fiação distintas, variando-se o diâmetro e comprimento do orifício de fiação e utilizando-se ou não filtros. As estruturas obtidas foram analisadas por microscopia ótica com luz polarizada e por microscopia eletrônica de varredura. Para diâmetros reduzidos e elevados comprimentos do orifício de fiação, se fez necessário o uso de filtros. Para diâmetros do orifício de fiação reduzidos e filtros de menor malha, as estruturas obtidas apresentaram uma distribuição mais homogênea. A microtextura aleatória foi obtida na grande maioria das configurações avaliadas.

Palavras-chave: Piches de petróleo; Fibras de carbono; Microscopia ótica.

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1 INTRODUCTION

Carbon fibers are among the most important composite reinforcement materials. Carbon fibers application is growing in a variety of areas, including aerospace, sporting goods, and also in ordinary commercial/industrial applications.(1)

There are two main carbon fiber precursors: polyacrylonitrile (PAN) and pitch.(1) Pitch is a complex mixture of aromatic hydrocarbons and it can be made from petroleum or coal tar.

Restrictive environmental legislation concerning the emission of toxic and carcinogenic fumes at work and the closing of numerous coke plants in some countries have led to the search for new pitches capable of replacing, at least in part, the coal-tar pitches. In this respect, petroleum pitches could be a good alternative to the competition in a market which, until now, has been exclusively dominated by coal-tar pitches.(2) Petroleum feedstocks are essentially composed of large polycyclic molecules with different levels of aromaticity and aliphatic side-chains.(3)

The melt-spinning process, normally used to convert anisotropic pitch into carbon fibers, is similar to those used for many thermoplastic polymers. Briefly, the pitch is melted in an extruder and forced to pass through a spinnerette.

The production of a high quality carbon material, such as continuous pitch- based carbon fiber, is directly related with the type of mesophase generated inside the pitch during the heat treatment. The filament production and subsequent production steps parameters are critical to the fiber costs and its mechanical properties and these parameters are completely dependent on the type and characteristics of the anisotropic pitch precursor. (3)

The relationship between the fiber strength and the anisotropic structures of pitch-based carbon fibers has been studied(4) and discussed, according to Matsumoto,(5) based on observations in two different scales: macroscopic and microscopic.(5)

Radial distorted (5), radial, flat-layer and random(6) structures are the usual patterns observed at the transverse section of the pitch-based carbon fibers by the optical microscope or scanning electron microscope (SEM) (Figure 1). These patterns describe, as stated by Matsumoto,(5) the structure of the carbon fibers in macroscopic scale.

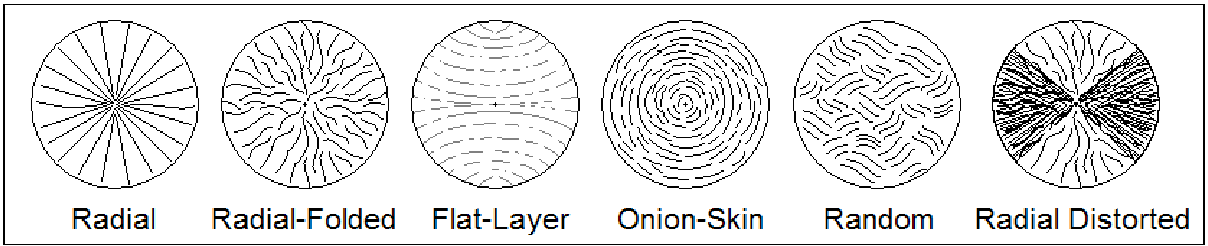

Figure 1. Transverse textures of mesophase pitch-based carbon fibers.(5,6)

Polarized light optical microscopy produces different colors for the different areas of the sample. The isotropic areas exhibit a purple color, which is independent of the rotation angle of the sample, while the anisotropic areas exhibit a yellow color that changes into blue, with the rotation of the sample.(7-9)

Carbon fiber texture and mechanical properties are related to each other and to its specific applications.

The objective of this work is to correlate different melt-spun configurations with the microtexture of carbon filaments using optical microscopy.

2 MATERIALS AND METHODS

2.1 Materials

In order to produce an anisotropic petroleum pitch, an aromatic heavy oil (sediments free decanted oil) obtained from fluid catalytic cracking of Brazilian crudes bottoms was used as feedstock. This pitch was obtained by a sequence of thermal treatments of this decanted oil(10) and its properties are summarized in Table 1.

Table 1. Anisotropic petroleum pitch properties

Properties/Material		Anisotropic Pitch
Elemental Analysis	C (%)	94.6
	H (%)	4.2
	N (%)	< 0.3
	S (%)	0.6 (dif)
	O (%)	0.3
Chemical and physico-chemical analysis	Melting Point (^{0}C)	334.2
	Anisotropy (%)	84.7
	Toluene Insoluble (%)	67.8
	Quinoline Insoluble (%)	56.2
	Density (g/cm^3)	1.364
	Coke value (%)	92.5

2.2 Carbon Filaments Production

Around 20 g of pitch were melt-spun through a 6 hole spinnerette to produce the carbon filaments using several L/D ratios, with or without filters.

The values of the capillary diameters ranged from 0.1 mm to 0.4 mm and the values of the capillary lengths ranged from 1 to 4 mm.

In addition to the variation of the capillary geometry, the absence and the use of filters with different openings, 40 µm and 100 µm, were also evaluated.

After spun, the filaments were thermally treated in a two-step process: stabilization around 250^{0}C – 300^{0}C and carbonization around 1,000^{0}C – 1,500^{0}C.

2.3 Optical Microscopy Analysis

The produced carbon filaments were mounted in epoxy resin and then grinded and polished to obtain a flat surface of the transversal section of the filaments. A LEICA optical microscope was used in this work, and a polarizer was used to distinguish between the anisotropic/isotropic portions by color.

The photographs of each spinning configuration were evaluated in two different magnifications, 200x and 500x and the textures of the carbon filaments were compared to those listed in the references (Figure 1).

2.4 Scanning Electron Microscopy Analysis

For the sample preparation, the carbon fiber filaments were fixed to an aluminum plate and the transversal sections of the filaments were evaluated. A Carl Zeiss FEG (field emission gun) microscope was utilized in the present work and the photos were obtained by the secondary electrons detector.

3 RESULTS

The texture obtained for each configuration analyzed is summarized in Table 2.

Table 2. Carbon filaments final structure for each configuration

Capillary Length (mm)	Capillary Diameter (mm)	Structures		
		no filter	filter (100 µm)	filter (40 µm)
1	0.1	NFO	NFO	radial distorted
1	0.2	NFO	random / flat-layer	flat-layer / radial distorted
1	0.3	random	random	random
1	0.4	random	random	random
2	0.1	NFO	NFO	NFO
2	0.2	NFO	random / radial distorted	random / radial distorted
2	0.3	random	random	random / radial distorted
2	0.4	random	random	random / radial distorted
3	0.1	NFO	NFO	NFO
3	0.2	NFO	random	random
3	0.3	random	random	random
3	0.4	random	random	random
4	0.1	NFO	NFO	NFO
4	0.2	NFO	random	random
4	0.3	random	random	random
4	0.4	random	random	random

NFO = No filaments obtained; Source: Authors

FiguresFigure 2 toFigure 7 exemplify the different types of carbon filaments structures observed by optical microscopy, using 200x and 500x magnifications only, to make the presentation easier to understand.

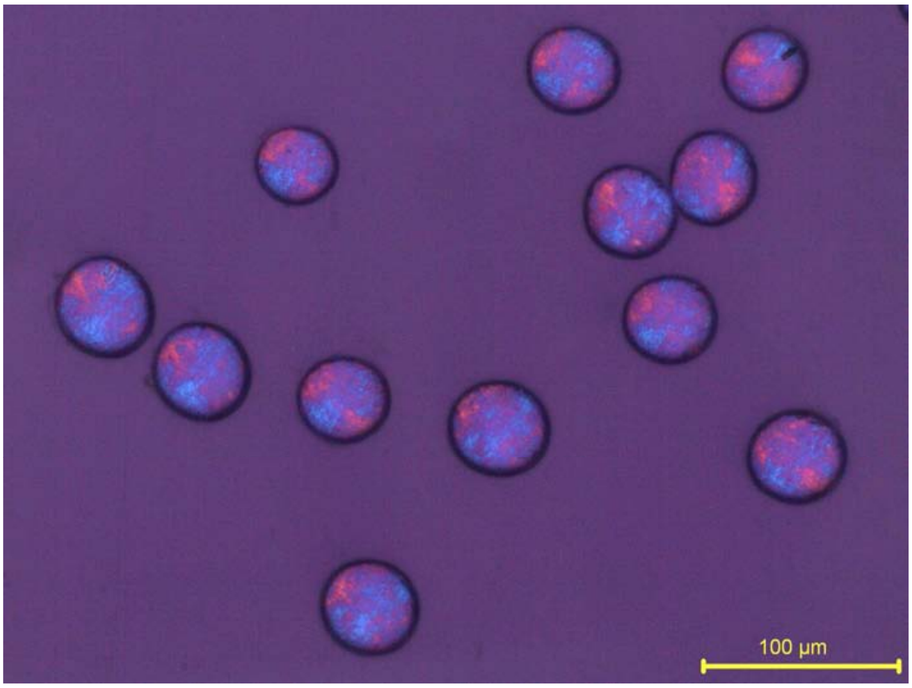

Figure 2. Optical microscopy photo of random structure samples, 200 x.

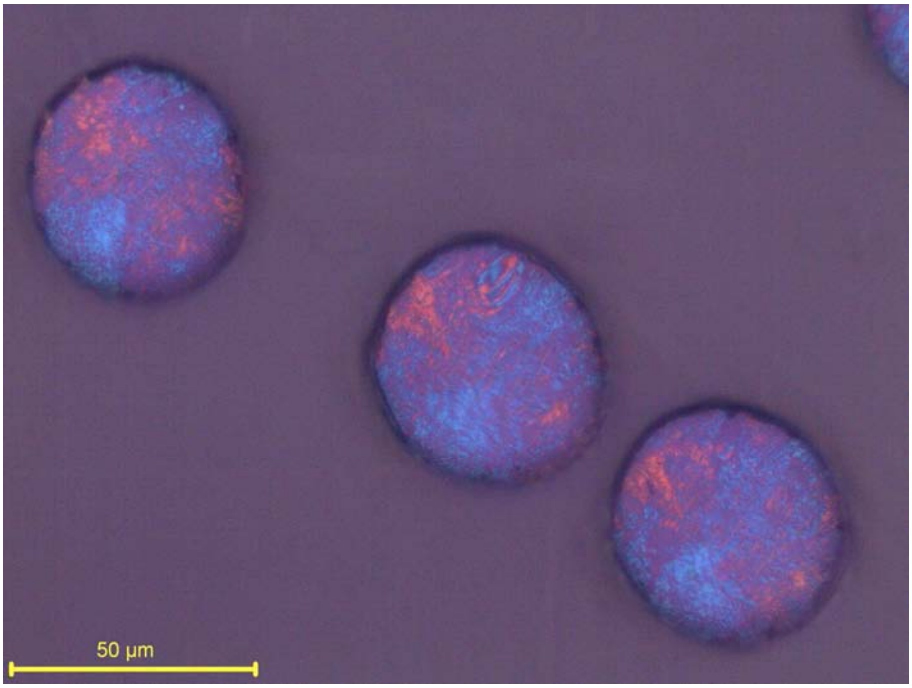

Figure 3. Optical microscopy photo of random structure samples, 500 x.

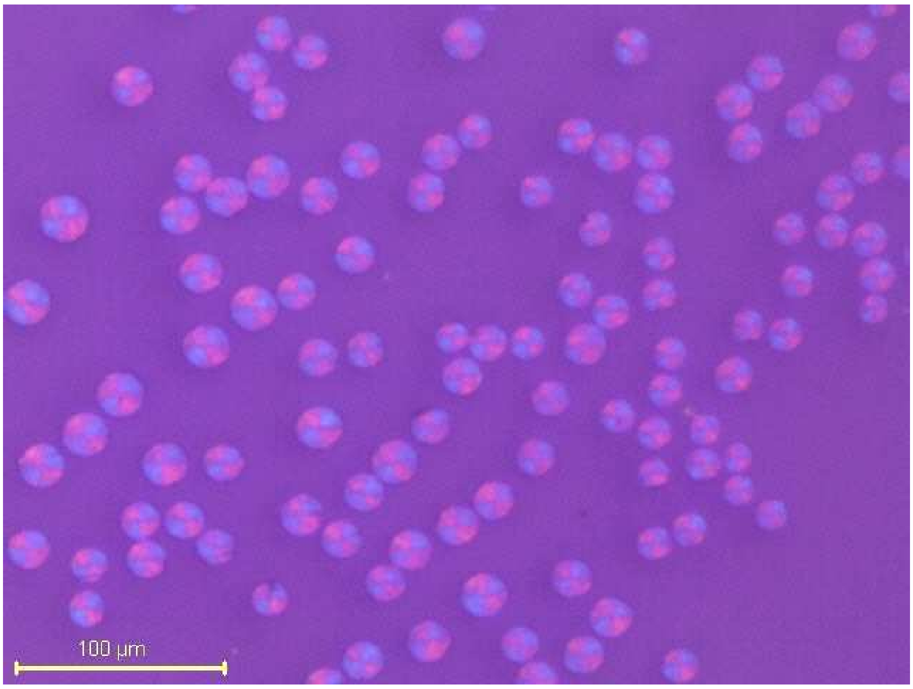

Figure 4. Optical microscopy photo of radial distorted structure samples, 200 x.

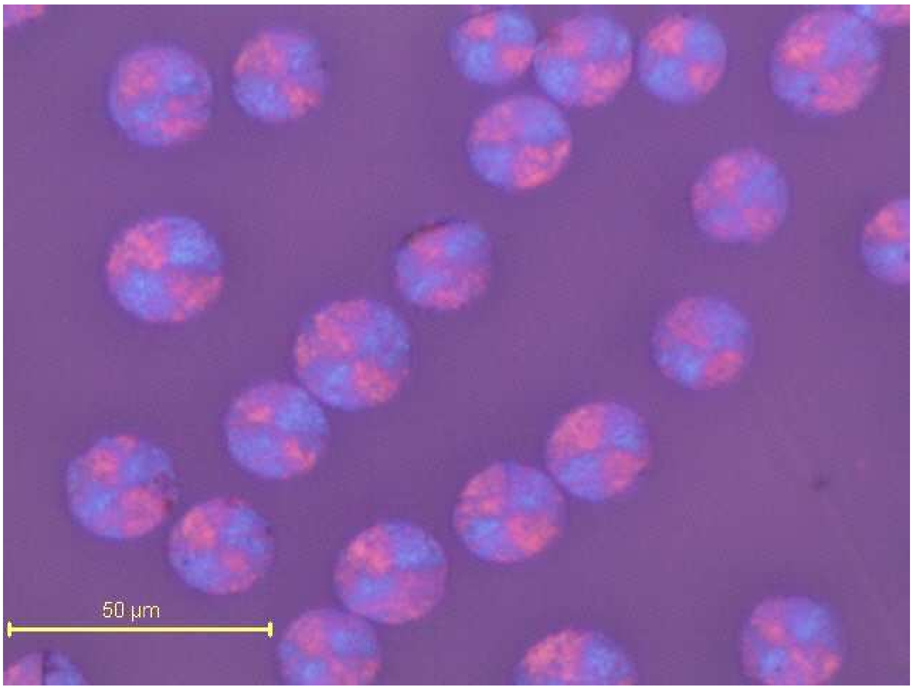

Figure 5. Optical microscopy photo of radial distorted structure samples, 500 x

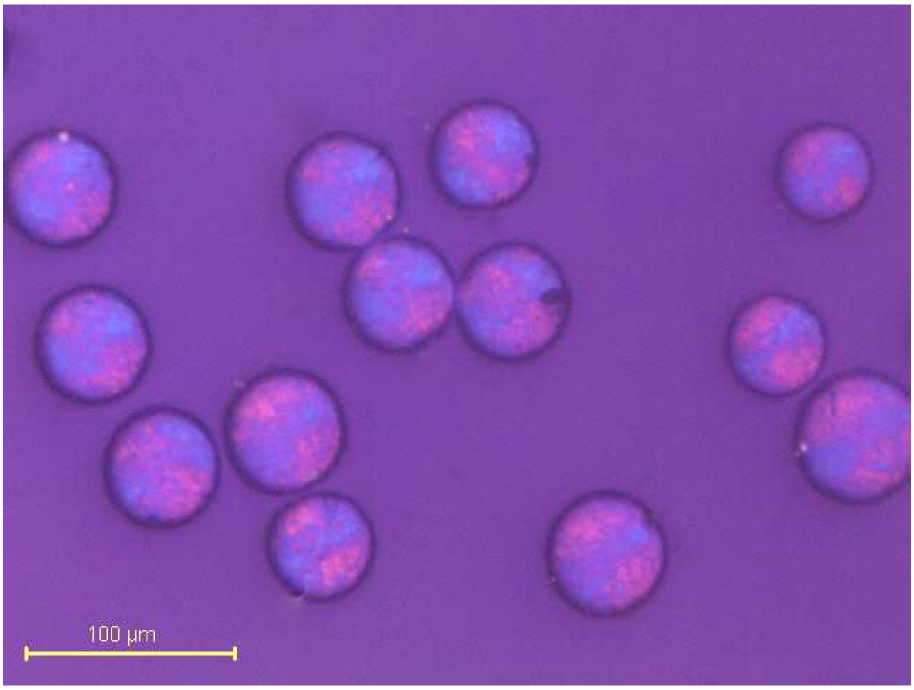

Figure 6. Optical microscopy photo of flat-layer structure samples, 200 x.

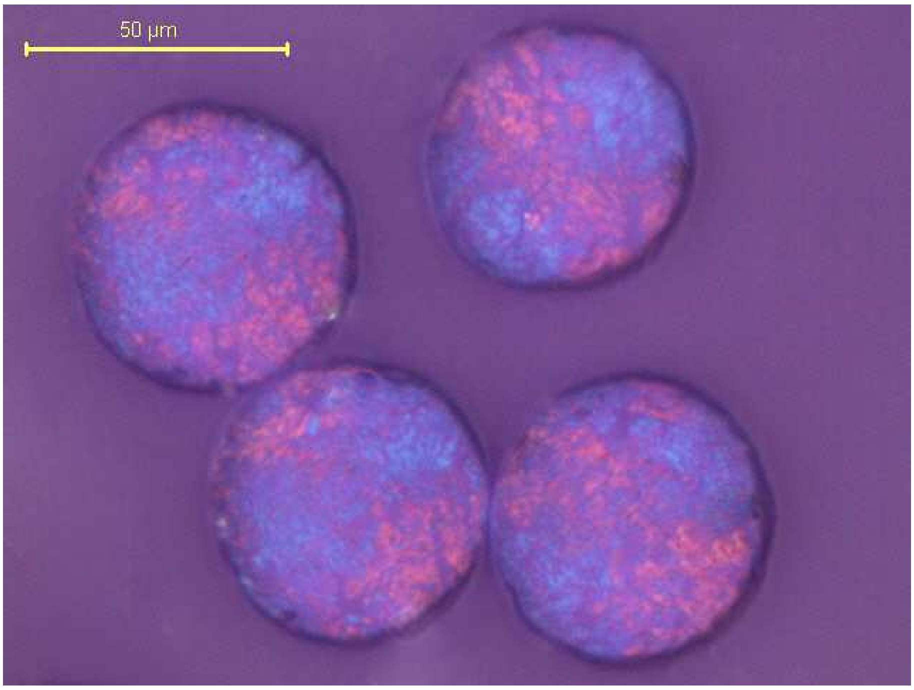

Figure 7. Optical microscopy photo of flat-layer structure samples, 500 x.

Figures 8 to 10 exemplify the different types of thermally treated carbon filaments structures observed by scanning electron microscopy.

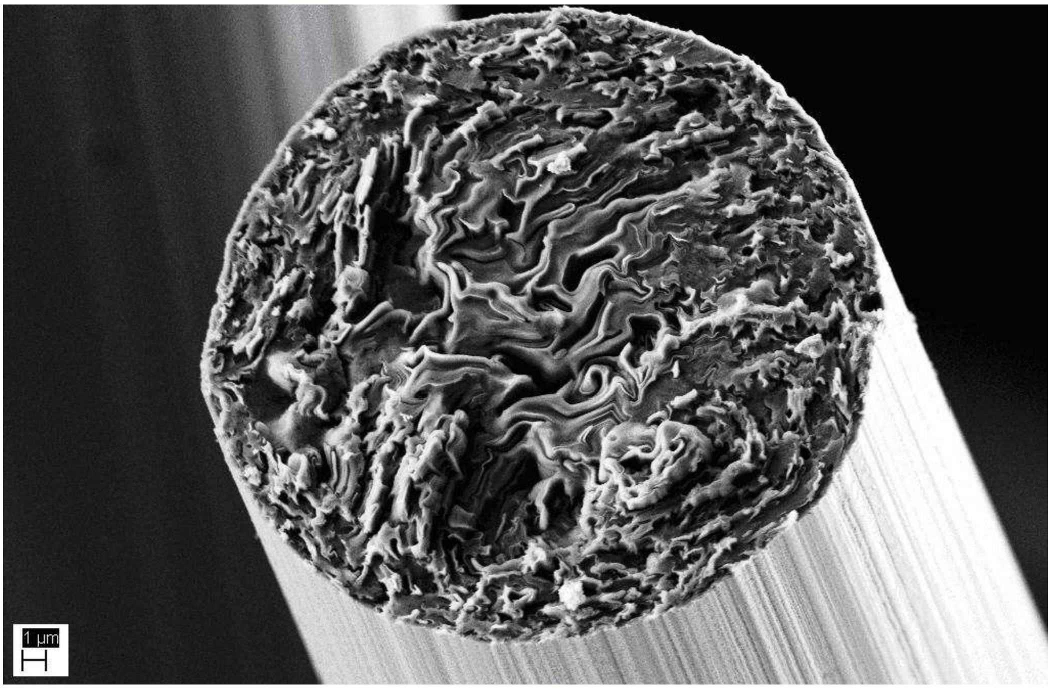

Figure 8. Scanning electron microscopy photo of a random structure sample.

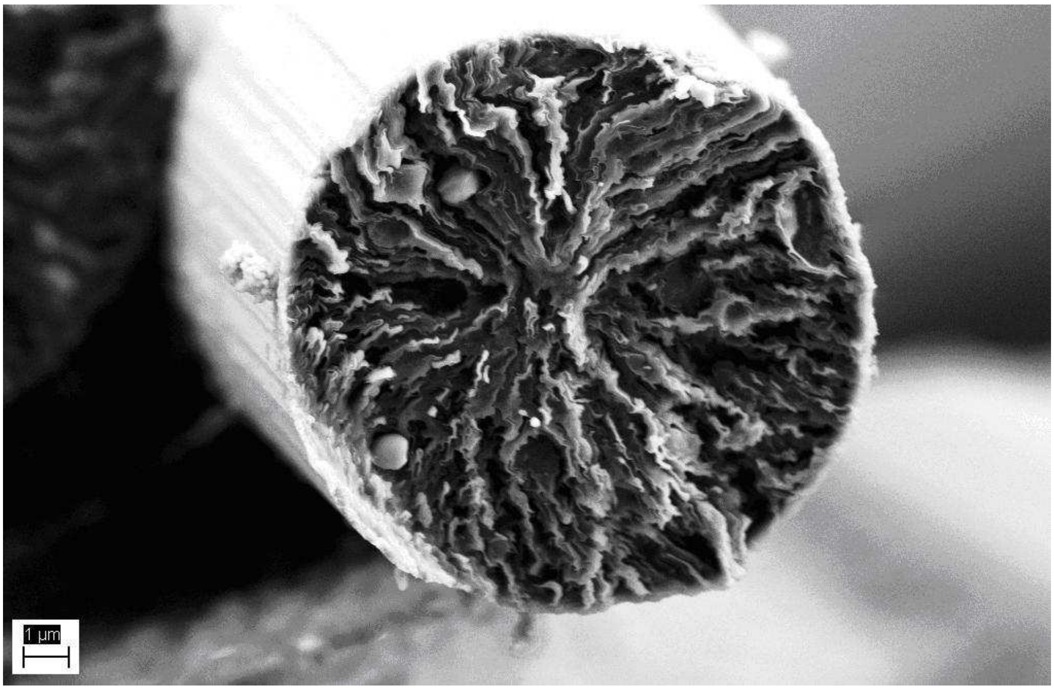

Figure 9. Scanning electron microscopy photo of a radial distorted structure sample.

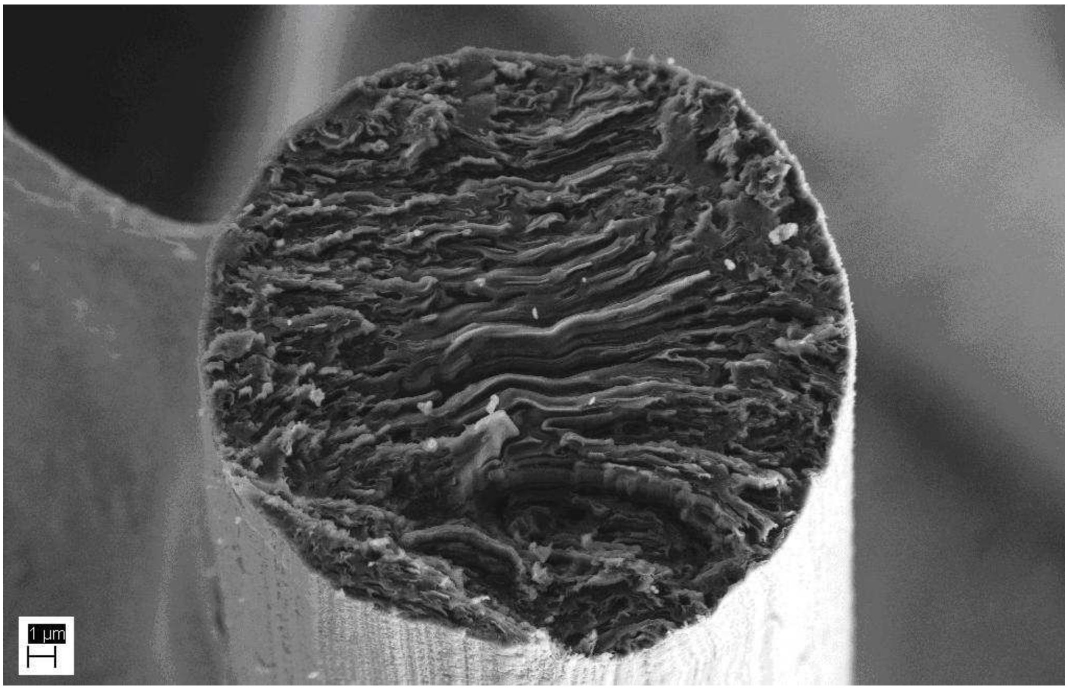

Figure 10. Scanning electron microscopy photo of a flat-layer structure sample.

4 DISCUSSION

The optical microscopy photos (FiguresFigure **2** toFigure **7**) obtained with polarized light confirmed that this technique is a powerful tool to determine the structure of carbon fibers.

It is possible to visualize, in the aforementioned figures, the purple area, which corresponds to the isotropic resin used for mounting the carbon fibers, and the colored areas, which corresponds to anisotropic regions, representing the carbon fibers themselves.(7-9)

The dark ring formed around each carbon fiber is due to the resin shrinkage during the curing process. However, its presence does not interfere in the determination of carbon fiber structures.

The photos obtained by scanning electron microscopy (FiguresFigure **8** toFigure **10**) confirm the type of structure visualized by optical microscopy and show well defined carbon filaments structures.

A good agreement between the obtained structures and the structures listed in the literature was achieved by both microscopy techniques.

The use of filters in the melt spinning process and another very important variable, the capillary geometry (Table 2), were successfully tested and evaluated.

The melt-spun technique using capillary diameters of 0.1 mm and 0.2 mm were not successful without filters and for the former the only successful configuration was achieved with the capillary length of 1 mm and a 40 µm filter.

The melt-spun technique using capillary diameters of 0.3 mm and 0.4 mm were successful with or without filters.

Exception for some configurations using filters, which showed radial type structures (radial distorted and flat layer structures), all the others exhibited random structure.

Edie(6) reported that the random structures could be obtained by using a tensile stress during the winding process, which is the stress configuration used in the present work.

The fact that the majority of configurations exhibited random structures is in accordance with Fathollahi,(12) who reported that a convergent flux, which is not the geometry used in this work, is more efficient though in producing radial structures.

Matsumoto(11) reported that the radial-type structures are formed when high shear rates are used. The higher shear rates were obtained, in this work, when the filters were used, specially the 40 microns filter.

When 0.3 mm and 0.4 mm capillary diameters were used with filters, only random structures were obtained.

A better texture definition, represented by a finer mosaic, was obtained for lower capillary diameters/smaller mesh filter configurations. The texture definition could be determined by the comparison between the obtained microstructures and the reference ones from the literature.(5-6) Matsumoto(5) stated that the use of filters caused finer anisotropic domains.

5 CONCLUSION

It is possible to identify the microtextures of the carbon filaments using polarized light microscopy and scanning electron microscopy and to relate them with those presented in the literature.

Most of the analyzed configurations produced random microtextures while the use of filters allowed the production of filaments with the radial microtexture.

While the filters were essential to successful produce filaments using low capillary diameters, they showed no influence when the larger ones were used.

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