EVALUATION OF DIFFERENT CONDITIONS IN THE MELT-SPINNING PROCESS OF PETROLEUM PITCHES

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Introduction

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 mesophase pitch based carbon fibers prepared by melt spinning, which is a key step in the producing process [1], are used in high strength structural materials [2].

Tensile strength is a very important mechanical property for carbon fibers in all applications. It is governed mainly by the local defects and the structure of fibers [3]. The control of structure and the interaction between the structure and properties has been extensively studied since 1960s [4].

The production of a high quality 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 [5].

Experimental

In order to produce an anisotropic petroleum pitch, an aromatic heavy oil (sediments-free decanted oil) obtained from the fluid catalytic cracking of Brazilian crude bottoms was used as feedstock. This pitch was thus obtained by a sequence of thermal treatments of this decanted oil [6] and its final properties are: Elemental analysis – C(%) = 94.6, H(%) = 4.2, N(%) < 0.3, S(%) = 0.6 (dif.) and O(%) = 0.3 and Chemical/physico-chemical analysis – Melting Point (^{0}C) = 334.2, Anisotropy (%) = 84.7, Toluene Insoluble (%) = 67.8, Quinoline Insoluble (%) = 56.2, Density (g/cm3) = 1.364 and Coke value (%) = 92.5.

To produce the carbon filaments, around 20 g of pitch were melt-spun through a 6-hole spinnerette. The values of the capillary diameters ranged from 0.1 to 0.4 mm and 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.

A LEICA optical microscope was used in this work, and a polarizer was used to distinguish between the anisotropic and isotropic portions by color.

The carbon filaments obtained were also evaluated by scanning electron microscopy (SEM). A Carl Zeiss FEG (field emission gun) microscope was utilized and the photos were obtained by the secondary electrons detector.

The tensile properties of the carbon fibers were determined using a single filament tensile test, according to the ASTM C1557 Standard [7]. For this work, a DMA Q800 – TA Instruments was utilized with a force rate of 0.150 N/min. The gauge length utilized was 6 mm.

Results and Discussion

Table 1 shows the obtained structures for each studied configuration.

Table 1. Carbon fiber structures analyzed by optical and scanning electron microscopy

Capillary Length and Diameter (mm)	Structures		
	no filter	filter (100 μm)	filter (40 μm)
1/0.1	NFO	NFO	random / radial
1/0.2	NFO	random / radial	random / radial
1/0.3	random	random / radial	random / layers
1/0.4	random	random / radial	random / radial / onion
2/0.1	NFO	NFO	NFO
2/0.2	NFO	random / radial / layers	random / radial
2/0.3	random	random	random / onion
2/0.4	random	random	random / radial
3/0.1	NFO	NFO	NFO
3/0.2	NFO	random / radial	random / radial
3/0.3	random	random / onion	random / radial
3/0.4	random	random	random / radial
4/0.1	NFO	NFO	NFO
4/0.2	NFO	random / radial	random / radial
4/0.3	random	random	random / layers
4/0.4	random	random	random

NFO: no filaments obtained

Fig. 1 exemplifies the different types of carbon filaments structures observed by optical microscopy and the strucutres obtained by SEM are exemplified by fig. 2.

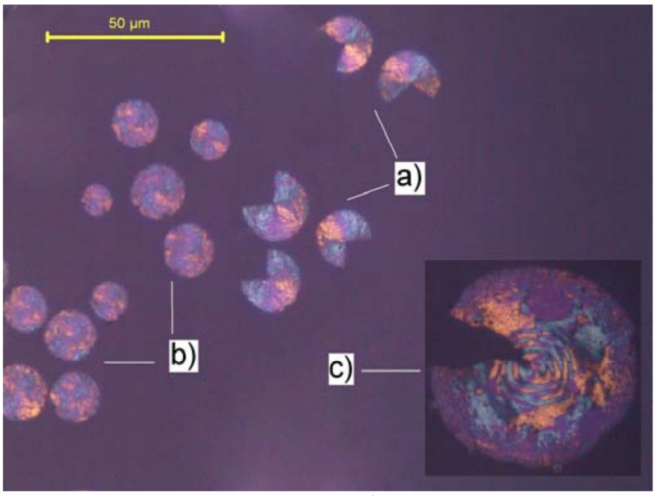

Fig. 1 Optical microscopy photo of a) radial, b) random and c) onion-like structure samples, 500 x.

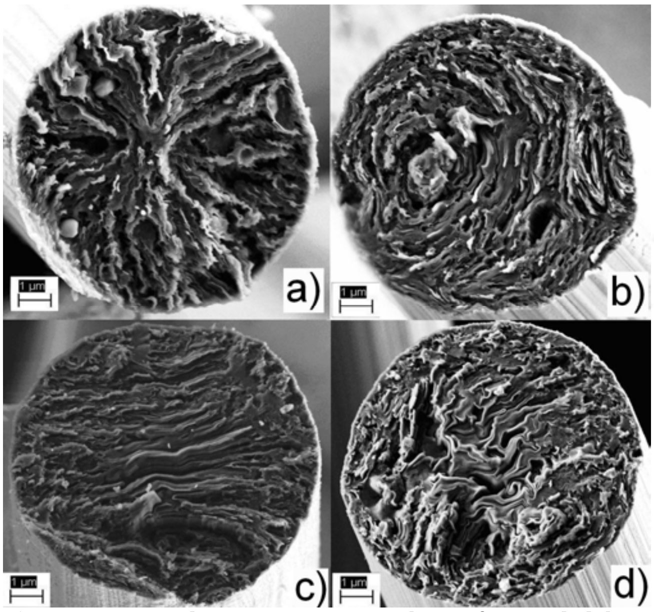

Fig. 2 Scanning electron microscopy photo of a a) radial, b) onion-like, c) layers and d) random structure sample.

The photos obtained by scanning electron microscopy (Fig.2) confirm the type of structure visualized by optical microscopy (Fig.1) and show well defined carbon filaments structures. A good agreement between the obtained structures and the structures listed in the literature was achieved.

The melt-spun technique using capillary diameters of 0.1 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 and 0.4 mm were successful with or without filters.

Except for some configurations using filters, which showed radial type structures (radial, flat layer and onion like structures), all the others exhibited random structures.

Matsumoto [8] reported that the radial-type structures are formed when high shear rates are applied. The higher shear rates were obtained, in this work, when the filters were used, specially the 40 microns filter.

When 0.3 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. Matsumoto [3] stated that the use of filters caused finer anisotropic domains.

The produced carbon filaments were evaluated by mechanical testing. The results obtained were as good as 1.08 ± 0.35 GPa, for tensile strength values, and 0.53 ± 0.15 %, for elongation values. Radial structured carbon filaments showed radial fractures and lower mechanical properties

Conclusions

The techniques used in the present work such as polarized light microscopy and scanning electron microscopy, were able to identify the micro structures of the carbon filaments and to correlate them with those presented in the literature.

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

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

The mechanical properties of the carbon filaments were dependent on the structure obtained and the tensile strength values were close to commercial values (commercial carbon fiber as CYTEC P25 – tensile strength = 1.38 GPa and elongation = 0.9).

Acknowledgment. The authors thank Petrobras for the financial support and Centro Tecnológico do Exército (CTEx) for laboratory facilities.

References

[1] Zha Q-F, Shi J-L, Ji Y, Liu L, Qian S-A. The effect of composition and process variables on the spinnability of mesophase pitch. Carbon 1992: 30(5):739-745.
[2] Watanabe F, Korai Y, Mochida I, Nishimura Y. Structure of melt-blown mesophase pitch-based carbon fiber. Carbon 2000:38:741-747.
[3] Matsumoto M, Iwashita T, Arai Y, Tomioka T. Effect of spinning conditions on structures of pitch-based carbon fiber. Carbon 1993: 31(5):715-720.
[4] Edie DD. The effect of processing on the structure and properties of carbon fibers. Carbon 1998;36 (4):345-362.
[5] Depine de Castro L. Anisotropy and mesophase formation towards carbon fibre production from coal tar and petroleum pitches – A review. Journal Braz. Chem. Soc. 2006: 17 (6):1096-1108.
[6] Fabio Franceschi P, Depine de Castro L. Produção de piches de petróleo anisotrópicos. Internal Report 2008: 26: 136-144.
[7] ASTM C 1557. Standard Test Method for Tensile Strength and Young's Modulus of Fibers 2003.
[8] Matsumoto T. Mesophase pitch and its carbon fibers. Pure & Applied Chem. 1985:57 (11):1553-1562.