

## **THE USE OF DSC TO ASSESS THE STABILIZATION OF THERMOPLASTIC EUCALYPTUS TAR PITCH FIBERS**

*M. J. Prauchner*<sup>1\*</sup>, *V. M. D. Pasa*<sup>2</sup>, *C. Otani*<sup>3</sup> and *S. Otani*<sup>3</sup>

<sup>1</sup>Instituto de Química, Universidade de Brasília, C.P. 4478, Brasília, CEP: 70910 970, Brazil

<sup>2</sup>Departamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, CEP: 31270 901, Brazil

<sup>3</sup>Instituto de Tecnologia Aeronáutica, Centro Técnico Aeroespacial, São José dos Campos, CEP: 12228 901, Brazil

(Received 23 April, 2003; in revised form 16 February, 2004)

### **Abstract**

During the production of pitch-based carbon fibers, oxidative thermal stabilization is an important intermediary step, because it permits the thermoplastic as-spun fibers to be rendered thermosetting. In the present work, DSC analyses are employed to assess the stabilization of eucalyptus tar pitch fibers. This is possible due to the pronounced differences noticed between DSC profiles of green and oxidized fibers, which reflect the changes that the fiber structure undergoes during stabilization.

**Keywords:** biopitch, carbon fiber, DSC, pitch, stabilization

### **Introduction**

#### *Pitch-based carbon fibers*

Fossil pitches (petroleum pitches and coal tar pitches) have been largely employed as carbon fiber precursors. They are thermoplastic materials formed by complex mixtures of macromolecules and can be converted into carbon fibers through a four-step process: pitch pre-treatment and spinning, and posterior fiber stabilization and carbonization. In this process, stabilization is a key step, because it renders thermoplastic as-spun pitch fibers, also called green fibers, infusible in order to prevent the fibers from melting and/or deforming during carbonization. In the production of high performance carbon fibers (HPCF), stabilization plays an additional role: it permits the fiber molecules to retain the preferred orientation acquired in spinning during the posterior carbonization, which is important for the properties of the final material [1].

In the production of general purpose carbon fibers (GPCF) from isotropic pitches, stabilization is usually carried out by thermal treatments under air atmosphere at temperatures below the fiber softening point (SP). In turn, in order to produce HPCF

\* Author for correspondence: E-mail: marcosjp@unb.br

from anisotropic pitches, the treatment has to be carried out below glass transition temperature ( $T_g$ ). Stabilization treatment introduces oxygenated functional groups and cross-links among the molecules, thereby raising  $T_g$  and SP, and making it possible to use progressively higher temperatures until the complete fiber stabilization [2, 3].

#### *Eucalyptus tar pitches*

In Brazil, a different type of pitch is generated as a byproduct of the charcoal-making industry: eucalyptus tar pitches. They have isotropic character and a macromolecular structure constituted basically by phenol, guaiacyl, and syringyl units common to lignin. Furthermore, they have large molar mass distributions, and differently from fossil pitches, low aromaticities (60–70%) and high O/C ratios (0.20–0.27%) [4].

Efforts have been made to develop applications for eucalyptus tar pitches, which is important to stimulate tar recovering in the industry's chimneys and to aggregate revenue to the charcoal-making industry. Araújo *et al.* [5, 6] have partially replaced poly(ethylene glycol) for eucalyptus tar pitches in the production of polyurethane elastomers. In turn, our research group has investigated these pitches as alternative precursors of GPCF. Although the process employed still needs to be optimized to make large-scale production possible, isotropic carbon fibers with diameter of 27  $\mu\text{m}$  and apparent density of 1.84  $\text{g cm}^{-3}$  have been obtained [7].

#### *DSC as a tool to assess the stabilization of pitch-based fibers*

The degree of stabilization of fossil pitch-based fibers is usually assessed by indirect methods such as measurements of mass gain and oxygen uptake [2]. In turn, Hayashi *et al.* [8] used differential scanning calorimetry (DSC) under inert atmosphere ( $\text{N}_2$ ) with this purpose, because they realized that the DSC profiles of stabilized fibers were far different from those of as-spun fibers. The specific heat ( $C_p$ ) of thermoplastic as-spun fibers increases with increasing temperature above glass transition until the complete fusion of the material. This occurs because  $C_p$  is closely related to the mobility of pitch molecules [9]. In fact, enhancement in molecule mobility requires endothermic disruption of non-covalent interactions, which in turn demands higher and higher energies. On the other hand, molecular movement in stabilized fibers is not possible so that  $C_p$  is approximately constant through a large temperature range until pyrolytic exothermic reactions take place.

In the present work, DSC was used to evaluate the changes undergone by eucalyptus tar pitch filaments during oxidative thermal treatments carried out in order to reach their stabilization.

## **Experimental**

Fibers were prepared using a pitch feedstock obtained by pre-treatment of a precursor eucalyptus tar pitch (raw pitch) at 250°C for 6 h. Pre-treatment was carried out to increase pitch SP, and therefore, to make filament stabilization possible. A more detailed

discussion of this subject [7], as well as details about production, chemical characterization and pre-treatment of the precursor pitch [4, 10], and the spinning procedure [7] are given elsewhere. Heat treatments aiming fiber stabilization were carried out under air atmosphere at different final temperatures, in the range 180–240°C, with a heating rate of 2.4°C h<sup>-1</sup>. Such a low heating rate was necessary due to the low SP of as-spun fibers, 134°C, being important to point out that pitches with higher SP did not have a good spinnability because elevated spinning temperatures damage the process stability since they lead to bubble formation and pitch degradation [7, 11].

DSC analyses were carried out in a Shimadzu DSC-50 Calorimeter. To obtain first scan curves, finely chopped fibers (about 8 mg) were placed into an uncovered aluminum pan, cooled down to -60°C, and then heated at a rate of 5.0°C min<sup>-1</sup> under helium dynamic atmosphere (50 mL min<sup>-1</sup>). Cooling to -60°C was carried out in order to achieve a well equilibrated signal when temperature neared pitch  $T_g$ . To obtain second scans, the samples were firstly heated from room temperature up to 100°C (20.0°C min<sup>-1</sup>; 10 min) prior to cooling. The heat flow of each sample was obtained by applying a baseline correction of the DSC signal in J s<sup>-1</sup> and then the obtained values were divided by the sample mass and heating rate.

## Results and discussions

Table 1 presents some physical-chemical characteristics of the pitch spun to generate as-spun fibers (pitch feedstock). In turn, Table 2 presents the elemental composition of as-spun fibers and of those submitted to oxidative thermal treatments up to 180, 200, 220 and 240 (180HT, 200HT, 220HT and 240 HT, respectively).

**Table 1** Characterization of the feedstock pitch (pre-treated at 250°C for 6 h)

$T_g^a/^\circ\text{C}$	$SP^b/^\circ\text{C}$	$AF^c/\%$	Ashes <sup>d</sup> /%	Coke yield <sup>e</sup> /%
32	134	37	1.2	46

<sup>a</sup> ASTM D 3418-82

<sup>b</sup> ASTM D2398-73 ('ring and ball' method)

<sup>c</sup> acetone insoluble content according to DIN 53700 norm

<sup>d</sup> ISO DIS 8006

<sup>e</sup> by TG (650°C; 10°C min<sup>-1</sup>; N<sub>2</sub>)

**Table 2** Elemental analyses of green and oxidized fibers

Sample fibers	C/%	H/%	N/%	O <sup>a</sup> /%	H/C	O/C
as-spun	72.5	5.9	0.3	20.1	0.98	0.21
180HT	63.3	3.7	0.2	31.6	0.70	0.37
200HT	59.3	3.2	0.3	35.9	0.65	0.45
220HT	57.1	2.9	0.1	38.0	0.61	0.50
240HT	56.5	2.8	0.2	38.2	0.59	0.51

<sup>a</sup> by difference and taking into account the ash content

The data show that the treatments lead to the increase in fiber oxygen content, which confirms the insertion of oxygenated functional groups and cross-links in the material structure. The higher the final treatment temperature, the higher the oxygen incorporation.

#### *DSC analyses of as-spun fibers*

The first DSC scan of the as-spun fibers showed an endothermic peak overlapping the glass transition (Fig. 1). Although an endothermic peak is characteristic of melting in polymeric crystalline structures, it is also observed for amorphous polymeric materials with  $T_g$  near room temperature [12, 13]. It occurs because even in the glassy state, some molecular motions of short reach are possible, especially if the polymer is maintained at temperatures moderately lower than  $T_g$  [14]. Therefore, if sufficient time is given, these motions lead to lower energy states. Some authors explain it as being a partial ordering of the structure, similar to crystallization [15], while others attribute this behavior to the relaxation of a non-equilibrium conformational state toward the equilibrium state, known as physical aging or enthalpy relaxation [16–18]. After the first scan, the material thermal history was erased. On a new scan after cooling, only the glass transition appeared.

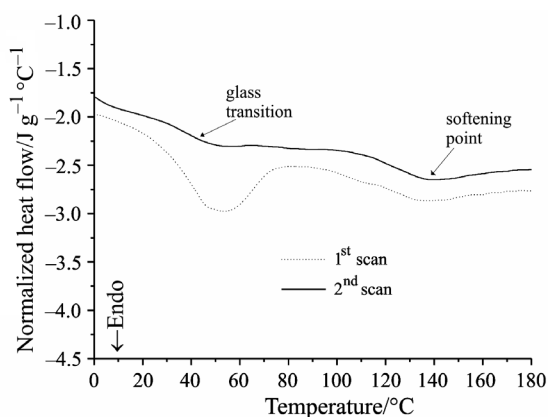


Fig. 1 1<sup>st</sup> and 2<sup>nd</sup> DSC scans of the as-spun fibers

In Fig. 1 we can also observe that the specific heat ( $C_p$ ) of as-spun fibers increases with increasing temperature above glass transition, specially nearing the SP of the precursor pitch (134°C). Once the temperature neared SP, the increase ceases.

#### *DSC analyses of oxidized fibers*

DSC curves of 180HT and 240HT samples are presented in Figs 2 and 3. These curves illustrate the general behavior presented by all oxidized fibers well, and allow pointing out important features. Concerning the first scan (Fig. 2), it can be observed that 180HT and 240HT fibers presented even more pronounced endothermic peaks.

In addition, contrary to what occurs for as-spun fibers, the second DSC scans of oxidized fibers presented a residual endothermic peak (Fig. 3).

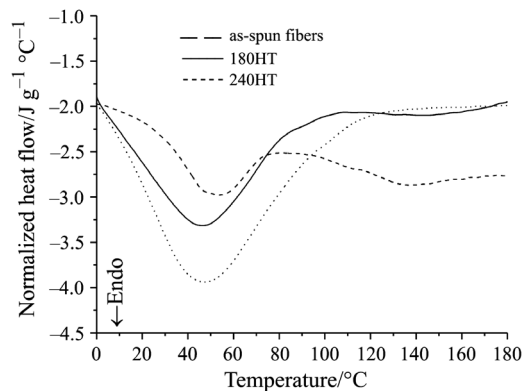


Fig. 2 1<sup>st</sup> DSC scans of the as-spun fiber and oxidized at 180 and 240°C

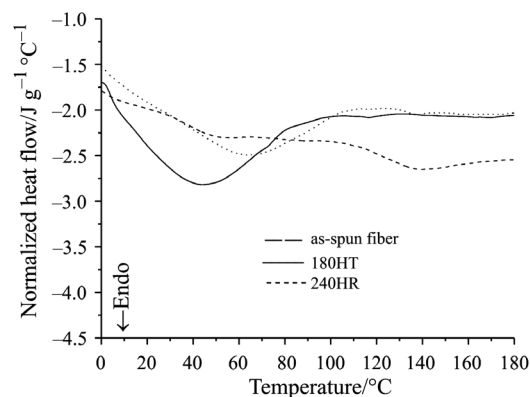


Fig. 3 2<sup>nd</sup> DSC scans of the as-spun fiber and oxidized at 180 and 240°C

However, the more interesting features are that the oxidized fibers did not present the gradual  $C_p$  increase verified for as-spun fibers. Conversely,  $C_p$  was approximately constant from the endothermic peak to the point when exothermic reactions of fiber pyrolysis took place, showing that the oxidative thermal treatments were successful in stabilizing the fibers. This result could be proved because, after carrying out scans up to 400°C, it was possible to verify visually that 180HT and 240HT fibers neither melted nor stuck together within the pan.

Taking into account that 180HT and 240HT fibers were stabilized, it sounds surprising to a certain extent that endothermic peaks were present in the first DSC scan. This means that although motions with medium and long reach are not possible in oxidized fibers due to molecule cross-links, the structure changes to a less energetic state if maintained under resting. Since any crystallization sounds improbable in

cross-linked structures, it seems that the endotherms result from enthalpy relaxation, as proposed by Málek and Pustková [16, 17] and by Hutchinson [18]. The larger area of the endotherms of oxidized fibers, if compared to as-spun-fibers, can be attributed to the higher energies necessary to promote the molecules from lower energy states in cross-linked structures, due to their elevated molecular stiffness.

In turn, the presence of residual endothermic peaks in the second DSC scans of the oxidized fibers demonstrates that after first scan they partially recovered the less energetic structure in a rapid way, as if they present a kind of elastic behavior. Such behavior can be understood based on the highly cross-linked three-dimensional structure of the filaments after stabilization.

## Conclusions

The present work showed that DSC is a useful tool to assess the thermal oxidative stabilization of eucalyptus tar pitch fibers. Pronounced differences could be noticed between DSC profiles of green and oxidized fibers. Firstly, oxidized fibers give rise to larger endothermic peaks in the first DSC scan. Next, a residual peak appears in the second scan. Finally, while the specific heat ( $C_p$ ) of green fibers increases with increasing temperature above glass transition up to about sample SP, for oxidized fibers  $C_p$  is approximately constant through a large temperature range, until exothermic reactions of fiber pyrolysis take place.

## References

- 1 J. B. Donnet and R.C. Bansal, Carbon Fibers, Marcel Dekker, New York 1990.
- 2 T. Matsumoto and I. Mochida, Carbon, 30 (1992) 1041.
- 3 T. Matsumoto and I. Mochida, Carbon, 31 (1993) 143.
- 4 M. J. Prauchner, V. M. D. Pasa, C. Otani and S. Otani, Energy Fuels, 15 (2001) 449.
- 5 R. C. S. Araújo and V. M. D. Pasa, J. Therm. Anal. Cal., 67 (2002) 313.
- 6 R. C. S. Araújo and V. M. D. Pasa, J. Appl. Polym. Sci., 88 (2003) 759.
- 7 M. J. Prauchner, V. M. D. Pasa, C. Otani and S. Otani, Carbon, accepted to be published.
- 8 J.-I. Hayashi, M. Nakashima, K. Kusakabe, S. Morooka and S. Mitsuda, Carbon, 33 (1995) 1567.
- 9 M. Alula, D. Cagniant and J. C. Lauer, Fuel, 69 (1990) 177.
- 10 M. J. Prauchner, V. M. D. Pasa, C. Otani, S. Otani and S. M. C. de Menezes, J. Appl. Polym. Sci., 91 (2004) 1604.
- 11 M. J. Prauchner, V. M. D. Pasa, C. Otani and S. Otani, J. Appl. Polym. Sci., 84 (2002) 900.
- 12 R. Mörck, A. Reimann and K. P. Kringsstad, In Lignin – Properties and Materials, W. G. Gassler and S. Sarkanen, Eds., ACS, Washington 1989, p. 390.
- 13 P. M. Khandare, J. W. Zondlo and A. S. Pavlovic, Carbon, 34 (1996) 663.
- 14 I. Voigt-Martin and J. Wendorff, In Encycl. Polym. Sci. Eng.; 2<sup>nd</sup> Ed., Wiley, New York 1985, Vol. 1, p. 789.
- 15 B. Rand and P. M. Shepherd, Fuel, 59 (1980) 814.
- 16 J. Málek and P. Pustková, J. Therm. Anal. Cal., 60 (2000) 975.
- 17 J. Málek and P. Pustková, J. Therm. Anal. Cal., 72 (2003) 289.
- 18 J. M. Hutchinson, J. Therm. Anal. Cal., 72 (2003) 619.