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NANOPOROUS CARBON FIBRES BY PYROLYSIS OF NOMEX POLYARAMID FIBRES
TG and DTA studies

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The development of porosity upon pyrolysis of Nomex® [poly (*m*-phenylene isophthalamide)] fibres has been investigated up to a temperature of 1173 K through physical adsorption of N_2 (77 K) and CO_2 (273 K). The carbonisation temperatures were chosen on the basis of thermal analysis studies (TG and DTA). The results of porous texture characterisation were compared with characteristic features in the TG and DTA curves. A temperature of 1073 K was chosen as appropriate for pyrolysis regarding activated carbon fibres preparation.

Keywords: *aramid fibres, DTA, nanoporous carbons, TG*

Introduction

Polyaramid fibres such as Nomex® [poly(*m*-phenylene isophthalamide)] constitute suitable precursors for activated carbon fibres (ACFs) with a narrow pore size distribution in the subnanopore range [1–9]. However, the properties of an activated carbon or an activated carbon fibre are conditioned not only by the nature of the precursor used but also by the activating agent and the conditions of the pyrolysis and activation processes [10–14]. In this sense, the knowledge of the phenomena involved in the thermal degradation of the raw material can contribute to the right choice of the pyrolysis conditions [11, 12, 15].

Thermal analysis has being widely used to study the degradation of natural and synthetic polymers [16–19]. The aim of this paper is to show the usefulness of thermal analysis techniques (TG and DTA) for selecting adequate pyrolysis conditions regarding the preparation of Nomex-based nanoporous carbon adsorbents. To this end, samples carbonised at different temperatures in the 823–1173 K range were characterised by CO_2 adsorption at 273 K and, whenever possible, by N_2 adsorption at 77 K.

Experimental

The starting material employed was commercial poly(*m*-phenylene isophthalamide) fibre, known as Nomex®, manufactured by DuPont. For the present study, a variety named crystalline Nomex tow, 2.2 dtf (decitex per filament) was used.

A Stanton-Redcroft STA-1500 thermobalance provided with a Plus-V software was used for simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) measurements. As-received fibres (without drying) were used in all the thermal treatments. Samples (~10 mg) were placed in Pt crucibles 5 mm in diameter and 5 mm in height. An argon (99.9990% pure by volume) constant flow of 50 $cm^3 min^{-1}$ was used. Temperatures were measured with Pt/Rh thermocouples placed at the bottom of the Pt crucibles, in contact with them. α-Alumina was the reference material for DTA measurements. Samples pyrolysed to various carefully controlled extents were prepared in the same thermobalance under the same conditions, by heating at 10 K min^{-1} to different selected temperatures and effectively stopping the process by rapid cooling to room temperature.

Elemental analyses of the starting material and the heat-treated samples were carried out in a LECO CHNS-932 microanalysis apparatus with a LECO VTF-900 accessory for oxygen.

Adsorption isotherms of N_2 (77 K) and CO_2 (273 K) were assessed in a Micromeritics ASAP 2010 and a Quantachrome NOVA 1200 volumetric adsorption analyser, respectively. Samples were outgassed overnight under vacuum at 523 K prior to every adsorption experiment. BET surface areas, S_{BET}, were obtained by the standard BET method. Micropore volumes were deduced from the application of the Dubinin–Radushkevich (DR) equation to CO_2 adsorption data, using 1.182 g cm^{-3} (solid phase) as the density for adsorbed CO_2 (273 K) [20].

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Results

Thermal analysis studies: choice of the pyrolysis temperatures

Figure 1 shows TG (together with its derivative *vs.* time, DTG) and DTA curves obtained during Nomex pyrolysis under argon with a heating rate of 10 K min^{-1}. A detailed explanation of the processes undergone by the material based on a combination of thermal analysis with other techniques is given elsewhere [21–23]. However, the TG and DTA results are summarised here for the sake of the choice of different pyrolysis temperatures.

The release of adsorbed moisture promotes the first mass loss observed in the TG curve from room temperature to 378 K and is accompanied by an endothermal effect in the DTA curve with minimum at 333 K. No further changes occur until 543 K, where a small mass loss of approximately 1 mass% is recorded in the TG curve and highlighted in the corresponding DTG curve; a coincident endothermal DTA peak with minimum centred at 590 K is also appreciated. The major mass loss starts at approximately 673 K. Two steps are observed in the TG curve in the temperature ranges 673–753 and 753–873 K. As regards the DTA curve, there is a well-defined endothermal peak with minimum at 700 K in the middle of the first mass loss step, whereas peaks are not well-defined in the temperature range corresponding to the second TG step, suggesting that endothermal and exothermal effects are superimposed. From 873 K on, the TG curve shows a small but continuous mass loss accompanied by an exothermal effect in the DTA curve, with maximum around 1073 K. In the last stretch of the TG curve (from 1123 K onwards) a slight change in slope – highlighted in the DTG curve – towards a higher mass loss rate is observed, along with a tendency to endothermicity in the corresponding temperature range (1123–1300 K) in the DTA.

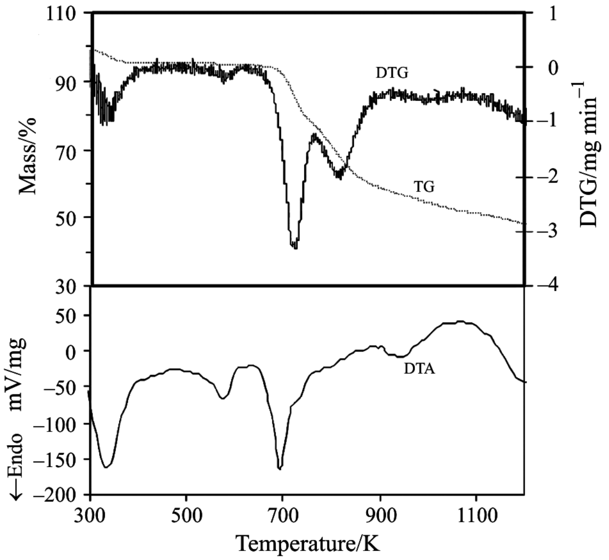

Fig. 1 TG, DTG and DTA curves of Nomex pyrolysis

According to these results, several temperatures were chosen as representative of the different stages of the carbon fibre transformation: 823 and 873 K were chosen as indicative of the middle and end, respectively, of the second main degradation step of the polymer; 1023 and 1073 K, as representative of the first post-degradation stage (that with the lowest mass loss rate) and 1123 and 1173 K, of the second one (with a higher rate).

The yields in a dry basis for some of the chars prepared are shown in Table 1 together with their elemental analyses. The analysed elements (C, H, O, N) sum 100 mass% within the experimental error for the starting material, which indicates that inorganic impurities are not present in a detectable amount. As expected in any carbonisation process, the solid residue gradually increases its content of C with heat-treatment temperature, while its atomic percentage of hydrogen decreases. The other heteroatoms – nitrogen and oxygen – are retained to a great extent throughout the process. This is the reason why the established limit to consider a fibre as a carbon fibre (at least 92 mass%) [24] is not reached even at the highest temperature tested.

Table 1 Chemical analyses of Nomex, fresh and heat-treated to various temperatures

Temperature/K	Yield/mass%	C/mass%	H/mass%	O/mass%	N/mass%
293	–	71.2	3.9	15.6	9.7
473	100	69.7	4.7	16.2	9.5
823	63	76.5	4.1	6.3	10.2
973	58	78.6	3.6	6.0	9.5
923	51	79.8	3.5	5.8	9.0
1023	50	80.4	2.2	7.4	7.0
1173	47	83.6	1.4	8.0	6.7

Physical adsorption of N_2 (77 K) and CO_2 (273 K)

Nitrogen barely adsorbs on the materials under study, leading to S_{BET} close to 0. In fact, the actual value for both the untreated material and that heat-treated to 1173 K is 0.3 m^2 g^{-1}, which corresponds to the geometrical surface of the fibres. On the other hand, all the fibres adsorb CO_2 in significant amounts, as shown in Fig. 2. The lowest adsorption capacity is found for the untreated sample, which shows a linear adsorption isotherm characteristic of a non porous material. Conversely, the rest of the samples show isotherms which are indicative of a highly developed microporosity: a pronounced initial raise in the low relative pressure range is followed by a stretch with a less pronounced slope. This type of porous texture leading to a negligible N_2 adsorption but a significant amount of adsorbed CO_2 is typical of ultramicroporous carbonised materials exhibiting activated diffusion for N_2 at 77 K [25].

The total CO_2 adsorption capacity at the maximal relative pressure measured (0.03) increases with the treatment temperature until 1073 K and the trend reverses at higher pyrolysis temperatures. The same occurs for the DR micropore volumes, which are shown in Table 2: there is a high initial rise of micropore volume from 823 to 1073 K as narrow micropores are developed owing to volatile loss; at higher temperatures, the CO_2 adsorption volumes remain similar but slightly diminish, probably due to closure of some of the pores previously created by sintering of the material.

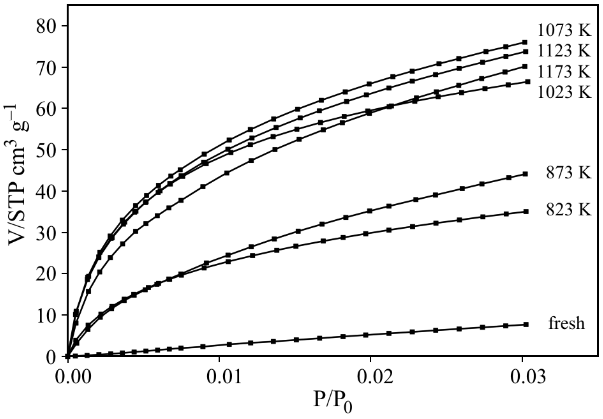

Fig. 2 Quantity of adsorbed CO_2 at different temperature

Table 2 DR micropore volumes

Temperature/K	V/cm^3 g^{-1}
823	0.11
873	0.15
1023	0.19
1073	0.22
1123	0.21
1173	0.20

Discussion

Progressive development of microporosity occurs in carbonised Nomex with increasing pyrolysis temperature, particularly at 873–1073 K. This coincides with the end of the main mass loss step for Nomex and beginning of a small, continuous mass loss.

These results allow choosing an appropriate temperature for the pyrolysis process which precedes physical activation. First of all, one must depart from a carbon-rich material. This requirement is met at temperatures above the end of the main degradation step of the polymer at 873 K (Fig. 1 and Table 1). Besides, for a better effectiveness of the activation process, it is interesting to use a carbon fibre with an already developed microporous texture. The development of the porous network of the carbon fibre takes place through a further mass loss at temperatures higher than that of degradation. The maximum micropore volume is obtained for a temperature of 1073 K (Table 2). However, the higher mass loss rate found at higher temperatures is coincident with a decrease in micropore volume. Therefore, 1073 K turns out to be a convenient temperature for Nomex pyrolysis as regards ACF preparation.

Conclusions

Thermal analysis has been successfully applied as a tool to establish the appropriate temperature for Nomex pyrolysis regarding activated carbon fibres preparation. Indeed, from the results obtained, it was concluded that 1073 K is a suitable temperature to that end.

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