

COMBINING THERMAL ANALYSIS WITH OTHER TECHNIQUES TO MONITOR THE DECOMPOSITION OF POLY(*m*-PHENYLENE ISOPHTHALAMIDE)

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Abstract

The pyrolysis behaviour of Nomex, poly(*m*-phenylene isophthalamide) fibres under argon has been investigated up to a temperature of 1173 K with different methods to get direct information on the progressive changes taking place in the solid material and its carbon fibre residues. The main stages of the pyrolytic degradation of the fibres were determined by thermal analysis (TG and DTA) and their chemical and morphological evolution through the different steps was subsequently followed by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) measurements, respectively, on samples treated to various temperatures.

Keywords: AFM, aramid fibres, DTA, Nomex, TG, thermal decomposition

Introduction

The thermal degradation of certain advanced polymers presents interest mainly in connection with applications, such as the manufacturing of fire-resistant materials, that take advantage of their excellent mechanical properties and thermal stability at moderate temperatures [1–9]. One of such polymers is the poly(*m*-phenylene isophthalamide) fibre, known as Nomex, which is increasingly employed for the mentioned and several other uses in modern technology [10–14].

In this context, thermal analysis techniques can provide valuable information in studies concerning the thermal transformation of Nomex during pyrolysis, since they allow the identification of different stages in the process. However, the information provided by these techniques alone is far from yielding a complete picture of the degradation mechanisms and processes taking place in the solid residue of the polymer during pyrolysis. It is the reason why, in the present work, thermal analysis (TG/DTA) was used in combination with Fourier transform infrared spectroscopy (FTIR) and both atomic force and scanning tunneling microscopy (AFM/STM) studies at different steps of the degradation process. FTIR showed direct evidence of the changes taking place in the chemistry of Nomex, whereas AFM/STM visualization

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revealed the nanometer-scale morphological changes accompanying the degradation of the material. FTIR has been employed in the past to characterize the transformations of other polymers during pyrolysis [5–8, 15–21]. By contrast, the use of AFM/STM to follow the different steps of the thermal decomposition of a polymer is uncommon (very few related examples can be found in literature [22–25]), although both types of microscopy demonstrated previously their ability for very high resolution imaging of a large variety of materials [26–29]. As exemplified in the present work, the combination of the thermal analysis techniques with both FTIR and AFM/STM provided a rather complete and consistent step-by-step description of the pyrolysis of Nomex up to a temperature of 1173 K, when the polymeric fibres were completely transformed into carbon fibres.

Experimental

The starting material was commercial polymer Nomex[®] T450 2.2 dtex. This product is manufactured by DuPont and its chemical composition is poly(*m*-phenylene isophthalamide). Simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) experiments were carried out in a Stanton-Redcroft STA-1500 thermogravimetric analyzer. As received fibres (~10 mg), without drying, were used in all thermal treatments. An argon (99.99990% pure by volume) constant flow of 50 cm³ min⁻¹ at atmospheric pressure was used. The reference material for DTA measurements was α -alumina. Several heating rates (3, 10, 15 and 30 K min⁻¹) were tried in the temperature range from 298 to 1173 K. Samples pyrolyzed to various carefully controlled extents were prepared in the same thermobalance by heating at 10 K min⁻¹ to different selected temperatures (633, 706, 823, and 1173 K) followed by rapid cooling to room temperature.

Fourier transform infrared (FTIR) transmission/absorption spectra were collected with a Nicolet Magna IR560 spectrometer. The pellets used contained sample concentrations of 2 to 5·10⁻¹ mass% in KBr. All the spectra shown have been normalized to 1 mg cm⁻². Atomic force microscopy studies of the samples heat-treated to selected temperatures were carried out in air at room temperature with a Nanoscope Multimode IIIa from Digital Instruments. The tapping mode of operation [30, 31] was chosen over the more conventional contact mode due to its better resolution of nanometre-sized features [32]. To improve their visual presentation, the images shown here have been flattened and then smoothed by a low-pass filter, taking special care to ensure that no artefacts or distortions were introduced by this procedure. For STM, mechanically prepared Pt/Ir (80/20) tips were used. All the STM images were collected in the constant current mode.

Results

Figure 1 shows TG and DTA curves obtained for Nomex by using different heating rates in its pyrolysis. In spite of what is found in the case of other carbon fibre precu-

sors, such as rayon [33], the yield increases with increasing heating rates. TG curves simply shift in parallel to higher temperatures without changes in their pattern. As can be seen in Fig. 1, at low heating rates the phenomena involved appear less superimposed in the temperature range 600–800 K while at high heating rates DTA signals are more intense resulting in a better appreciation of weak thermal effects, such as that taking place around 550–580 K. Therefore, an experimentally convenient intermediate heating rate of 10 K min^{-1} (TG and DTA curves not shown) was chosen for subsequent studies. The temperatures reported correspond to a heating rate of 10 K min^{-1} . The first mass loss, taking place from room temperature to 378 K and being accompanied by an endothermic effect in the DTA curve, is obviously due to moisture release. The sample undergoes some transformation at 543 K accompanied by a barely noticeable mass loss of 1% mass but an easily perceptible endothermic DTA minimum centred at 590 K. The major degradation process starts at approximately 673 K through two steps reflected in the TG curve in the temperature ranges 673–753 and 753–873 K. The first step is accompanied by an endothermic DTA effect with minimum centred at 700 K while endothermic and exothermic effects superimpose in the second step temperature range. From 873 K to the maximum tempera-

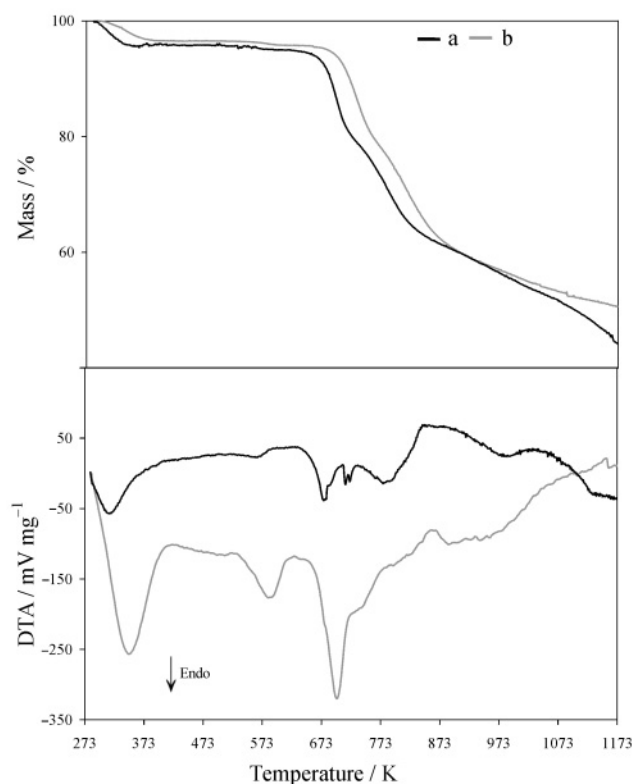


Fig. 1 TG and DTA curves obtained for heating rates of a – 3 and b – 15 K min^{-1} in the temperature range from 298 to 1173 K

ture reached, 1173 K, the TG curve shows a slight but continuous mass loss. The samples prepared for FTIR and AFM studies were chosen as representative of the different stages of pyrolysis on the basis of the thermal analysis results.

FTIR spectra of fresh Nomex and several of its heat-treated residues are shown in Fig. 2. The number and position of the absorption bands remain invariable through thermal treatments up to 823 K (Figs 2a–d), except for a slight shift ($\sim 10\text{ cm}^{-1}$) to higher wavenumbers of the amide N–H stretching absorption band already noticeable at 633 K (Fig. 2b) and the appearance of an aryl nitrile band (2230 cm^{-1}) at 823 K. At increasing temperatures, there is a drop in the intensity of the bands ascribed to amide bonds (amide I, amide II, amide III and amide V bands centred at 1660, 1536, 1240 and 720 cm^{-1} , respectively) vs. that of those corresponding to aromatic rings (C–H stretching and C=C stretching centred at 3065 and 1608 cm^{-1}). Finally, FTIR spectrum of the sample heated to 1173 K (Fig. 3e) shows the typical absence of absorption bands of many carbonaceous materials.

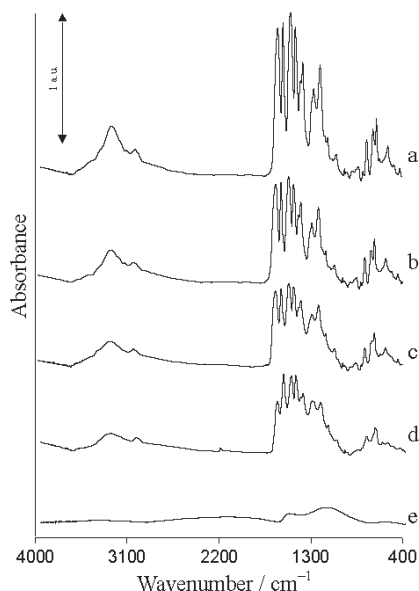


Fig. 2 FTIR spectra of a – fresh Nomex and its solid decomposition products at b – 633 c – 706, d – 823 and e – 1173 K

AFM images showing the surface morphology of fibres heat-treated to selected temperatures can be seen in Fig. 3. The images shown were chosen to be representative of the set recorded for each sample. In the particular case of the sample treated to the highest temperature (1173 K), a STM image is also shown. The rest of the samples were not conductive enough for STM imaging to be viable. From this series of images, it can be concluded that the fibre changes gradually from highly anisotropic (Fig. 3a), being constituted by long fibrils approximately parallel to the fibre axis, to isotropic (Fig 3d and e). The images of the fibre treated to the two highest tempera-

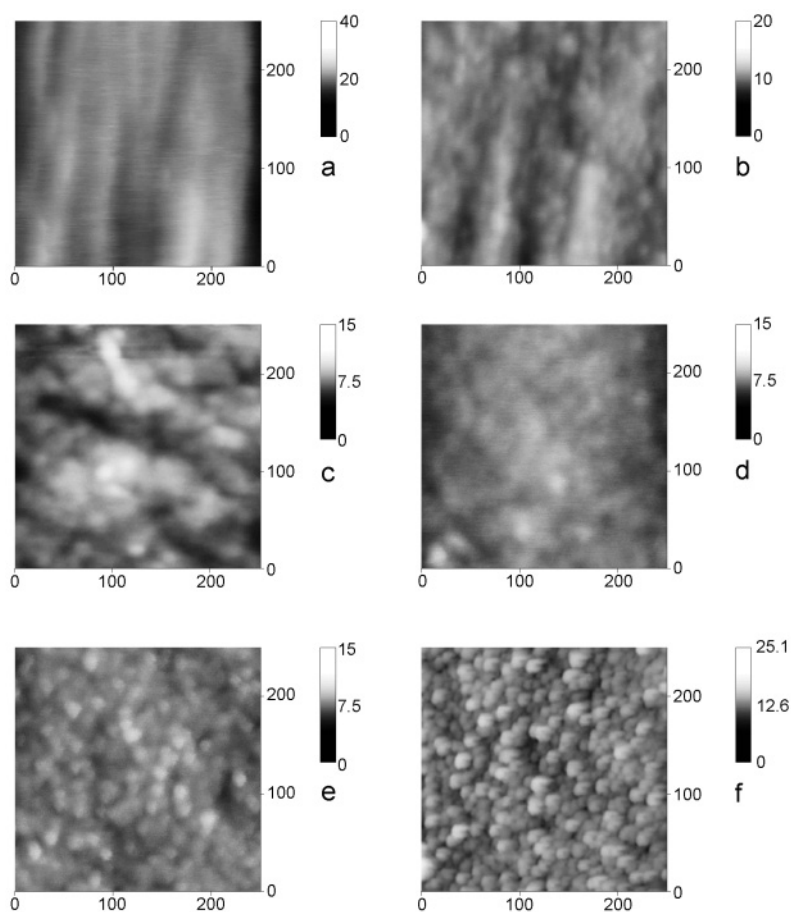


Fig. 3 AFM images of the surface morphological evolution of a – fresh Nomex and its solid decomposition products at b – 633, c – 706 and d – 823 K. Finally, e – AFM and f – STM images of Nomex heat-treated to e – 1173 K. Lateral size: 250 nm

tures (823 and 1173 K) are quite similar: a highly isotropic surface comprised of rounded nanometre-sized domains. The images acquired by STM for the 1173 K sample (Fig. 3f) agreed totally with those obtained by AFM (Fig. 3e).

Discussion

The chemical and morphological changes observed by FTIR and AFM, respectively, were found to be consistent with each other and with TG/DTA results:

a) The rupture of hydrogen bonds between polyaramide chains revealed by the shifting of the N–H amide band observed between the FTIR spectra of fresh Nomex and that heat treated to 633 K ($\sim 10\text{ cm}^{-1}$) was also evidenced by an increasing disorganization

and a noticeable reduction of anisotropy in the AFM images on the nanometre scale. The breaking of the hydrogen bonds in Nomex was already suggested by the endothermal effect recorded in its DTA curve (Fig. 1), and also by the small mass loss (~1%) recorded in the TG curve (Fig. 1) due to release of water present in the crystalline lattice, which was most probably forming hydrogen bonds with the amide groups.

b) The main degradation process begins with the disruption of the amide bonds. This is reflected in the drop of intensity of the amide absorption bands relative to those corresponding to aromatic rings in the FTIR spectra indicated. Concerning the AFM results, the breaking of the polyaramide chains into smaller units and the subsequent disorder this effect brings about is reflected in a further reduction of anisotropy in the sample surface morphology (Fig. 3). The occurrence of both polycondensation reactions, which are exothermal processes, and rupture of the amide bonds (endothermal) simultaneously, would explain the superposition of the two types of effects in the DTA curve in the temperature range between 480 and 600 K.

c) The early (823 K) signs of polycondensation reactions appearing in the FTIR spectra and the dehydrogenation which follows at higher temperatures were coherent with the similarity between AFM images at 823 K and higher temperatures, this resemblance strongly suggesting the formation of polyaromatic compounds at the former temperature.

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The authors wish to thank their colleagues, Javier Fernández and Celina Blanco (DuPont Asturias) for providing the Nomex sample. Financial support from CICYT (Project 1FD1997-1915) is gratefully acknowledged. We also acknowledge a predoctoral fellowship from the Spanish Ministry of Education awarded to S. V.-R.

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