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Characterisation of thermal relaxations of polyaniline fibers by dynamic mechanical thermal analysis

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Abstract

Molecular motions and thermal transitions in polyaniline fibers ($\varnothing = 50$ μm), cast from emeraldine base powder dissolved in N,N'-dimethylpropylene urea (DMPU), have been investigated by dynamic mechanical thermal analysis (DMTA). For this purpose, a special picopendulum has been used, and a double sweep DMTA study has been performed. From these preliminary experiments, different relaxations observed have been discussed and compared to what is found in the literature.
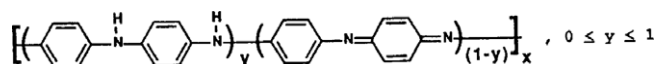© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Due to its unique electrochemical behaviour and thermal and environmental stability [1], polyaniline (PANi) is a very important intrinsic conductive polymer (ICP). In particular, PANi is a good candidate for actuators (artificial muscles). In this purpose, finding optimal processing conditions in which conductivity, mechanical and physical properties are kept in good level is a very important thing. So, it is necessary (and interesting) to make some investigations on the variation of physical properties and thermal stability of polyaniline under various thermal conditions. In fact, the most important parameter in the polymer characterisation is its glass transition, because the processing temperature of the material [2,3] and its end-use temperature depends on this parameter [4].

The base (undoped) form of polyaniline could be represented by the following formula [1]:

$$\left[\left(\!\!\underset{H}{\underset{|}{\bigodot}}\!\!-\!\!N\!\!-\!\!\underset{H}{\underset{|}{\bigodot}}\!\!-\!\!N\!\!-\!\!\right)_y\!\!\left(\bigodot\!\!-\!\!N\!=\!\!\bigodot\!\!=\!\!N\!\!-\!\!\right)_{(1-y)}\right]_x, \quad 0 \leq y \leq 1$$

where y equals 0.5 for polyaniline in the "emeraldine base" oxidation state (PANi-EB). When this PANi-EB is immersed in an acid solution, it results in emeraldine salt, the most interesting and conducting form of polyaniline.

The polyaniline in its emeraldine base form (PANi-EB) is very often processed by dissolution in N-methylpyrrolidone (NMP), a high boiling point (202 °C) organic solvent, resulting in cast films: PANi-EB(NMP). The resulting polymers usually contain an important amount of solvent and residual water from the polymerization reaction. Indeed, an important amount of NMP remains in the material because of its high boiling point and the formation of hydrogen bonding between the carbonyl group of the solvent and the NH group of PANi [3,5–7].

The effect of residual solvent (NMP) on the thermal properties of polyaniline films has been largely investigated. It proved that NMP has a strong plasticizer effect, so glass temperature of PANi-EB(NMP) is strongly dependent on the content of residual solvent [1–7]. Indeed, several dynamic mechanical analysis show that the main relaxation temperature, associated to the glass transition shifts to higher temperatures with decreasing weight fraction of solvent in the polymer [1,5]. Moreover, a few studies show the effect of residual water and the combined effect of residual NMP/water in PANi-EB films [7–10].

Milton and Monkman [2,3] have tried to have further molecular information by submitting the polymer to two successive temperature sweeps in the range of -130–300 °C

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(1 Hz). So the thermal transitions that they have observed during the rescanning (second sweep) are not affected by NMP and are only attributed to the polymeric material, because the material which have been previously heated to 300 °C is crosslinked and solvent free [2,3].

If a lot of papers have been made on thermal stability, thermal reactions, glass transition temperature and dynamic mechanical properties of polyaniline in the form of film, studies are much more rare on polyaniline in the form of fiber. So, this paper deals with the study, using DMTA, of the different thermal relaxations of a fiber of PANi-EB processed in an other organic solvent DMPU (boiling point: 146 °C): PANi-EB(DMPU). Nevertheless, this solvent has a carbonyl function as the NMP.

2. Experimental

2.1. Preparation of PANi-EB(DMPU) fiber

The fiber is produced by the team of Prof. De Rossi from the Faculty of Engineering of the University of Pisa, Italy [11]. The method they have adopted to produce polyaniline fibers is similar to the one reported by Tzou and Gregory [12] and based on extrusion through a spinnerette. Undoped polyaniline in powder form, with granulometry of $60-75$ μm is dissolved ($20-25\%$ by weight) in N,N'-dimethylpropylene urea (DMPU). Then the fiber is obtained by a system of extrusion. After that, it is immersed in a coagulation water bath and rolled up on a cylinder at a speed of $4-6$ m/s. Finally the fiber resides in a second water bath for 30 min. The fiber is then drawn at $160-180$ °C with draw ratios ranging from 1 to 3 (Figs. 1 and 2).

2.2. Thermal characterisation

The DMTA tests have been done using a very special spectrometer (picopendulum) developed in the GEMPPM (INSA) laboratory. DMTA is performed in torsion mode. The device consists of a forced oscillation pendulum working in the temperature range of $-120-325$ °C, and a large frequency range of $10^{-5}-10^2$ Hz.
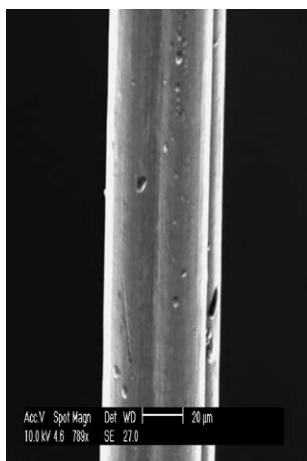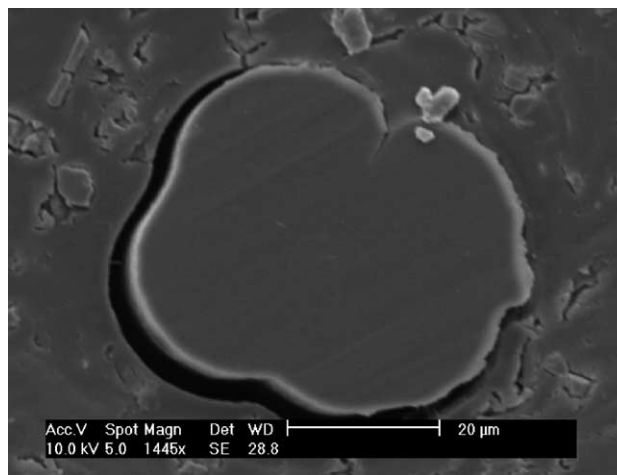

Fig. 1. SEM micrograph of PANi fiber.

Fig. 2. SEM micrograph of the cross-section of the fiber ($\varnothing=50$ μm).

The possibilities of this mechanical miniaturised high resolution spectrometer are very extended. Indeed:

– the weak mechanical inertia of the mobile equipment affords a dynamic of measurements that can be extended on $6-7$ decades in frequency.
– The automatic scale change on the measures of the couple and angle deformation as well as the precision of conversions A/D and D/A allow to study a change in the modulus in a yield of 1 to 10,000.
– The measure without contact of the deformation angle allows a high resolution on the measure of the internal friction (tan) in a order of 10^{-4}.
– The low frequency excitation allows the study of the secondary relaxations phenomena.

The device provides the real (G') and the imaginary (G'') parts of the Coulomb modulus and internal friction (tan $\delta = G''/G'$) as a function of temperature.

3. Results and discussion

The tests are performed on as received undoped PANi-EB(DMPU) fiber, in the temperature range of $-110-300$ °C at a heating rate of 0.5 °C/min, and at fixed frequency of 0.1 Hz. The dimensions of the samples are: a diameter of 50 μm, and a length of 1.5 mm.

The tan δ spectrum versus temperature obtained during the first DMTA scan (Fig. 3) exhibits different relaxations: there is a peak centred at -85 °C, followed by an other maximum at 30 °C. Then the tan δ curve is dominated by an extremely broad relaxation showing peaks in the range of temperature from 31 to 170 °C. Moreover, when the temperature rises beyond this zone, G' increases from 170 up to 210 °C. The last peak in the tan δ curve is centred at 270 °C.

3.1. Relaxation at -85 °C

The first relaxation is centred at -85 °C (Fig. 3). Chen and Lee have also detected a similar transition here after called β (1