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THERMAL MEASUREMENTS ON POLY[2,2'-(*m*-PHENYLENE)-5,5'-BIBENZIMIDAZOLE] FIBERS

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Abstract

Fibers drawn form poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) were studied by DSC and DMA. PBI is a high temperature polymer T_g is between 387 and 450°C depending on the measurement technique used. The as-spun fiber is free of orientation. The oriented fiber exhibits considerable dependence on whether the DSC measurements were carried out in free-to-shrink or fixed-length modes. The β-relaxation is at 290°C, and was associated with loss of water. The γ-transition at 20°C was not identified, while the δ-transition at –90°C seems to correspond to rotation of the *m*-phenylene ring.

Keywords: DMA, DSC, fibers, polybenzimidazole, secondary transitions

Introduction

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (polybenzimidazole, PBI) is one of the most thermally stable polymers. It is copolymer of tetra-aminobiphenyl-(3,3'-diaminobenzidine) and diphenyl isophthalate. PBI has good dimensional stability at high temperatures, and excellent resistance to chemical [1–3]. The equilibrium moisture content of PBI is relatively high (ca 15%). Its limiting oxygen index (LOI) is 41%, therefore it will not burn in air. In addition, PBI emits little smoke at extremely high temperatures. Thus, this fiber is an excellent material choice for firefighters' protective apparel, race car drivers and armed forces flight suits. In addition, it is used for fireblocking layers and wall fabrics of aircrafts, and as an asbestos substitute.

A 25% solution of PBI in dimethylacetamide is used to produce PBI fibers by the method of dry-spinning [4]. Later the fiber is drawn, and a two-stage sulfonation process is employed to reduce its flame shrinkage [5].

Experimental

The DSC measurements were carried out using a TA Instrument 2100/910 DSC at heating rates of 20°C min^{-1}. The glass transition temperature was taken as the temper-

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ature of the mid-point of the heat capacity increase. The DSC measurements were made in free-to-shrink and fixed-length modes.

The DMA measurements were performed on a Rheometrics RSA2 Solid Analyzer at 1 Hz test frequency using a 3°C temperature step method in autotension mode.

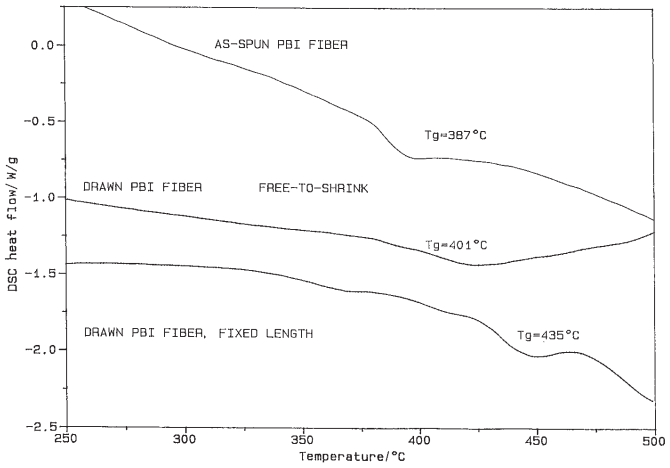

Fig. 1 The DSC curves of as-spun and drawn PBI fibers recorded in free-to-shrink and fixed-length modes

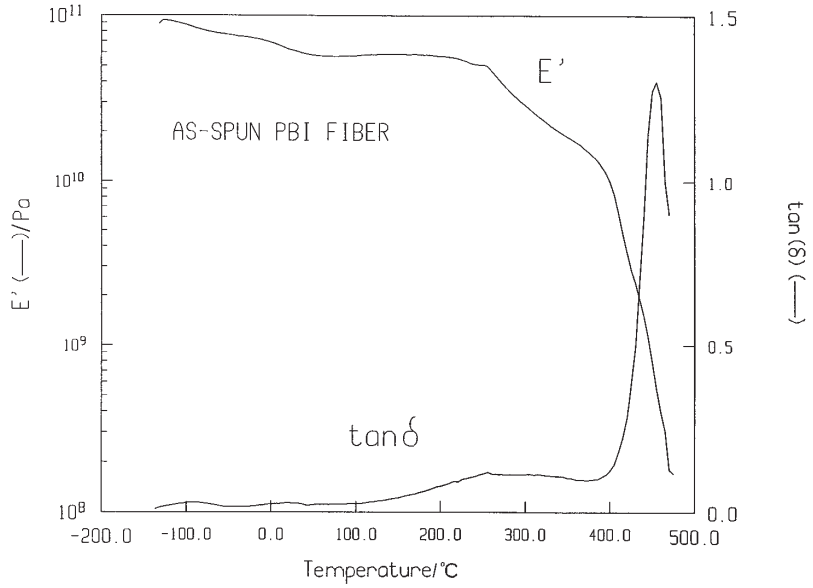

Fig. 2 The temperature dependence of the tensile storage modulus and tanδ for as-spun PBI fiber

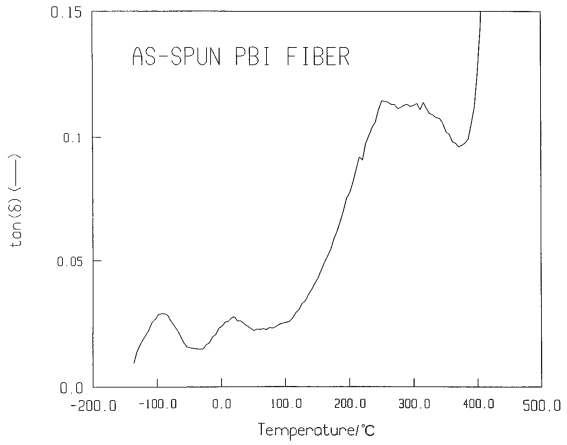

Fig. 3 The same tanδ *vs*. temperature curve for the as-spun PBI fiber as in Fig. 2, but at higher sensitivity

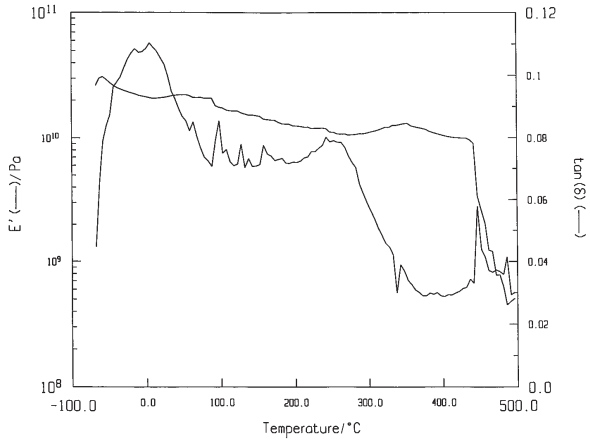

Fig. 4 The temperature dependence of the tensile storage modulus and tanδ for drawn PBI fiber

Results and discussion

PBI is an amorphous polymer, it has the highest glass transition temperature among the commercial polymers: it is between 400 and 450°C depending on the method of measurement used.

The DSC trace of PBI fibers in the glass transition region is shown in Fig. 1. An extremely broad water evaporation peak is recorded below 250°C (not shown in Fig. 1). T_g of the as-spun PBI fiber is 387°C. T_g of the as-spun fiber does not depend on whether the measurement is made in free-to-shrink or fixed length states, indicating the absence of orientation. On the other hand, T_g of the drawn fiber has a consider-

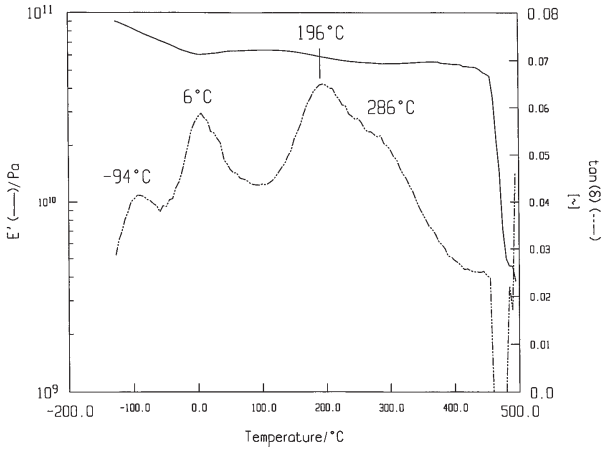

Fig. 5 Similar DMA curves as shown in Fig. 4, but for another piece of drawn PBI fiber

able dependence on the mode of the measurement. When fine fiber pieces are crimped in a standard aluminum DSC-pan (free-to-shrink) measurement), T_g of the drawn fiber is 401°C. If the fiber is wound around a steel plate before crimping in a DSC-pan, the glass transition temperature is considerably higher (435°C), as expected [6] (Fig. 1).

The DMA-trace of the as-spun PBI yarn is shown in Fig. 2, the magnified portion of the tanδ *vs*. temperature curve is shown in Fig. 3. The temperature of the primary relaxation is ca 465°C for the as-spun fiber, and three sub-T_g relaxations have been recorded at –90, 20 and 290°C. The primary (α-) relaxation is the glass transition, the lowest temperature relaxation (δ) is likely to correspond to the onset of rotation of the *m*-phenylene ring. It is more difficult to assign the remaining two dispersion [β at 290°C (this is an extremely broad relaxation ranging from 100 to ca 370°C) and γ at 20°C].

The lower temperature one of these may correspond to the rotation of the two benzimidazole-rings in the repeating unit of the polymer, while the β-transition may be the consequence of water or solvent loss. This is partially supported by the considerably lower intensity of the β-relaxation in the drawn fiber (Fig. 4), although it has to be mentioned that the β-relaxation sometimes is split into two sub-relaxations (Fig. 5). Also, the primary (α-) relaxation is often not seen for the drawn fiber: degradation should be responsible for this phenomenon.

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