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Tensile fatigue behaviour of PBO fibres

P. Davies · A. R. Bunsell · E. Chailleux

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Abstract Poly(*p*-phenylene benzobisoxazole) (PBO) fibres are finding increasing applications on account of their exceptional stiffness and strength. This article presents results from tests on single PBO filaments, to characterize their intrinsic behaviour under quasi-static and cyclic tensile loading. Scanning electron microscopy is used to show the fibrillation mechanism leading to failure. Results are compared to data for polyester, aramid and high modulus polyethylene fibres. PBO fibres show shorter fatigue lifetimes than the other fibres when maximum stress is expressed as a percentage of quasi-static break load, but the absolute stress values applied are much higher for an equivalent lifetime.

Introduction

Polybenzazole polymers were developed by the US Air Force in the 1980s [1], and poly(*p*-phenylene benzobisoxazole) (PBO) fibres were first presented by Krause et al. [2]. Several authors have discussed their morphology, and Kitagawa et al. [3] proposed a model for the structure of the currently commercialized PBO fibres. The mechanical properties of these fibres are exceptional, Young et al. [4] and Orndoff [5] have presented quasi-static mechanical properties, and structure–property relationships were described by Kitagawa et al. [6]. The fibre suppliers also provide mechanical property data under tensile creep loading [7]. There are many high performance polymer fibres commercially available, including a range of aramids and high modulus polyethylenes (HMPE) (Table 1), but manufacturers' data indicate that PBO shows some of the highest properties. Two grades are available, under the trade name *Zylon*™ [7].

Two weaknesses of the PBO fibre have been detected. First, it is very sensitive to light [8], so PBO fibre ropes are always protected by outer covers. Second, moisture can also affect properties [9, 10]. Although these fibres have been commercially available for over 10 years, and are now widely used in high performance ropes, particularly for racing yacht rigging, there are very few data available on their fatigue properties. This article provides results from quasi-static and cyclic tensile tests on high modulus grade PBO fibres in order to evaluate their fatigue behaviour and compare it to that of other commercially available fibres.

Materials and experimental methods

The high modulus grade of PBO was used in this study. A new bobbin of zero twist fibres was supplied by Toyobo (Japan) for tests. Both quasi-static and cyclic fibre tests were performed on single fibres on the test machine developed by Bunsell et al. [11] (Fig. 1).

Samples were bonded between two cardboard frames using a neoprene adhesive, fibre diameter was measured with a laser interferometer on each fibre, the sample was then placed in the machine grips and the cardboard window was cut. Thirty samples were tested for each condition, on

P. Davies (✉)
IFREMER, Centre de Brest, Materials & Structures Laboratory, Plouzané 29280, France
e-mail: peter.davies@ifremer.fr

A. R. Bunsell
Centre des Matériaux, Ecole de Mines de Paris, Evry 91003, France

E. Chailleux
Laboratoire Centrale des Ponts et Chaussées, Bouguenais 44341, France

Table 1 Comparison of typical commercial fibre property ranges (suppliers data)

Fibre	Density	Stiffness (GPa)	Strength (MPa)
PBO (Zylon HM)	1.56	280	5800
Polyester (High Tenacity)	1.38	15	1300
Aramid (Kevlar 29)	1.44	70	2920
HMPE (Dyneema SK75)	0.97	110	3500

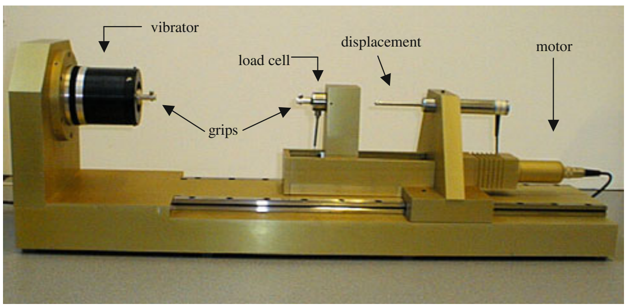

Fig. 1 Fibre test machine

50 mm long specimens. Fibres appear smooth (Fig. 2a) and are approximately circular (Fig. 2b). A circular cross section was assumed for stress calculations and strain values were corrected to account for machine rigidity.

Fracture morphologies of the fibres were observed with a *Gemini 982 Zeiss* scanning electron microscope (SEM) fitted with a field effect gun which allows studies to be performed at low accelerating voltages. For this study a voltage of 2 kV was used. The fibres were however coated with gold–palladium, to avoid any possible problem of charging. The complementary ends of broken fibres were examined.

Results

Quasi-static tests

Tensile test results are summarized in Table 2, examples of stress–strain plots and a histogram showing all the break stresses are shown in Fig. 3.

Modulus values are very close to expected values. Mean measured tensile strengths are lower than the datasheet value, but scatter is quite high and as seen in Fig. 3 some values close to 6000 MPa were measured. The datasheet values were determined on yarns with optimum twist for strength, which increases strength by about 10% compared to untwisted yarn but reduces modulus by a similar amount [7]. Tensile failure involves splitting and fibrillation (Fig. 4a), a mechanism seen in many highly oriented fibres [12]. After failure a compression stress wave results in compression bands (Fig. 4b).

Cyclic tests

PBO fibres were cycled at 50 Hz between 0 and 70% of the mean measured tensile breaking load (5030 MPa). Results were obtained from 30 valid tests (failure away from the grips). A smaller number of tests were performed at a second stress level, 60% of static break strength. Figure 5 shows a plot of failure probability versus cycles to failure for PBO at the two maximum stress levels.

Table 2 Suppliers' data and measured properties, PBO HM

Sample	Stiffness (GPa)	Strength (MPa)	Diameter (μm)
Supplier data [7]	280	5800	–
Measured values	290 ± 15	5030 ± 750	11.2 ± 0.6

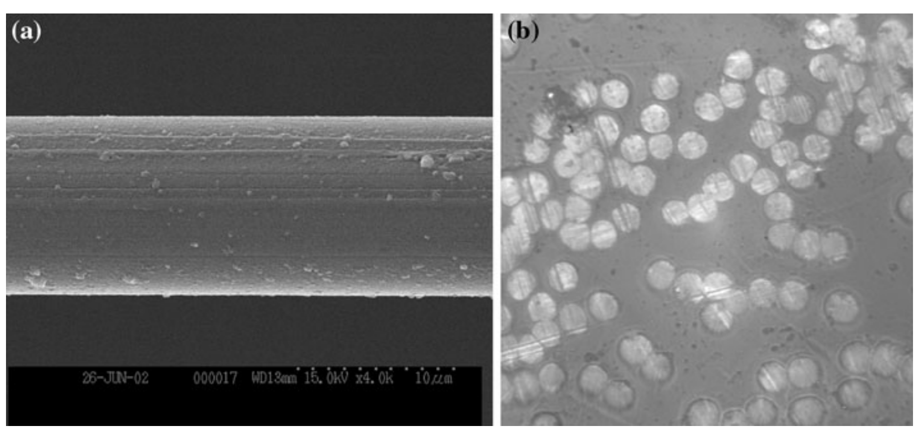

Fig. 2 PBO fibres before test. **a** SEM photo of fibre, **b** polished sections of fibres potted in resin

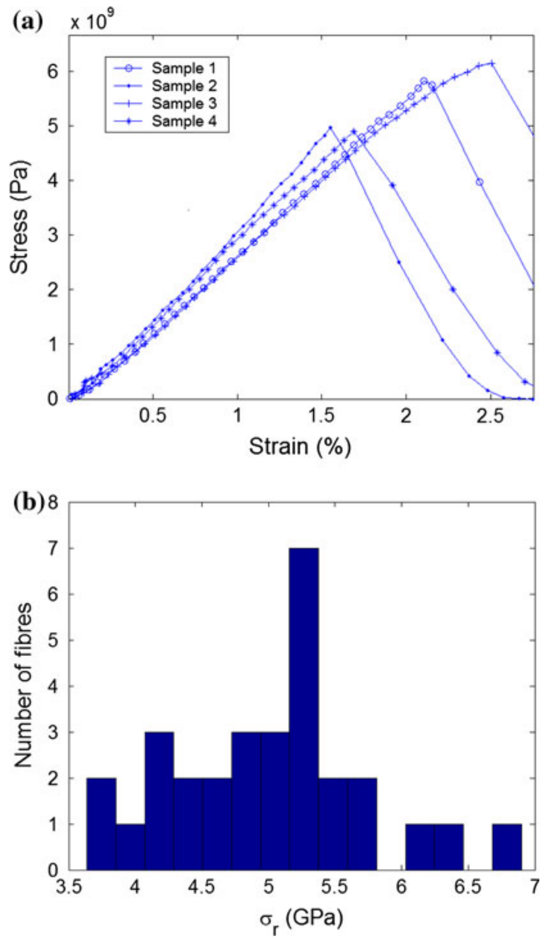

Fig. 3 PBO fibre quasi-static tensile tests. **a** Examples of stress–strain plots. **b** Histogram showing break loads from 30 tests

Examination of the fracture surfaces of fibres in the SEM once again revealed extensive fibrillation. Fibres which had survived for longer times tend to peel from deeper within the fibre than those which failed more quickly (Fig. 6) and the fibrillation length appears to increase with cycling time. This suggests that crack propagation contributes to the failure process.

Discussion

It is interesting to examine these results with respect to those for other fibres. Data have been measured using the same test set-up in previous studies on polyester [13], aramid (Kevlar29) [14] and HMPE (Dyneema SK75) (unpublished data, Ecole des Mines de Paris, 2002) fibres. Figure 7 shows a comparison with these fibres at the same cycling range of 0–70% break load. Polyester fibres are generally considered to be fatigue resistant, and in large ropes their fatigue performance has been shown to be better than that of steel cables used for mooring offshore platforms [15]. This comparison shows that the fatigue lifetimes of PBO are shorter than those of the other fibres when compared on this basis. Recent studies by Raman spectroscopy have improved our understanding of the mechanisms involved in fatigue behaviour of polymer fibres [16]. Thermoplastic fibres such as PA 66 and PET fail by similar fatigue processes, involving distinct stages of crack growth leading to distinctive fracture morphologies. It appears that the ordering of the amorphous polymer chains in such fibres provides an essential contribution to fatigue crack resistance, and the highly crystalline PBO fibres do not benefit from this. In addition the particular microstructure of PBO fibres, with very little space between chains to accommodate transverse compression, makes them quite sensitive to kinking and compression failure [17].

An alternative presentation of the results can be made in terms of the absolute value of maximum stress. Figure 8 and Table 3 show this comparison. Here it is apparent that for the same lifetime the PBO fibres can support much higher maximum stresses than any of the other fibres.

Examples of the cyclic failure modes of the polyester and HMPE fibres in this load range are shown in Fig. 9. An aramid fracture from a quasi-static test is also shown, for this fibre it was not possible to distinguish between static and cyclic test fracture surfaces [14]. The polyester fibre fatigue mechanism has been described in detail recently [18], fatigue fracture surfaces are quite different to those found after tensile or creep tests which do not show the long peeled tongue. The high performance fibres HMPE and aramid show similar fractures to the PBO in static and cyclic tests, with extensive fibrillation.

At high loads there is a tendency for creep failure to replace the fatigue mechanism. This can be examined by comparing the lifetimes under constant load (creep) and cyclic load (fatigue) conditions. Polyester, HMPE and aramid fibres all show significantly shorter lifetimes under fatigue loading, indicating that a distinct failure mechanism is deteriorating the fibres under cyclic loads [14, 18] (unpublished data, Ecole des Mines de Paris, 2002), even though this is not detectable on broken sample fracture surfaces. PBO fibres show very little creep even at high loads [7] so fatigue is likely to be the main concern in design.

Only one type of loading condition, involving complete unloading during each cycle, has been described here, as this is usually the most severe case (without deliberately adding compression). Maintaining a non-zero minimum load can prevent the developing of fatigue mechanism, and this has been described elsewhere [14, 18–20].

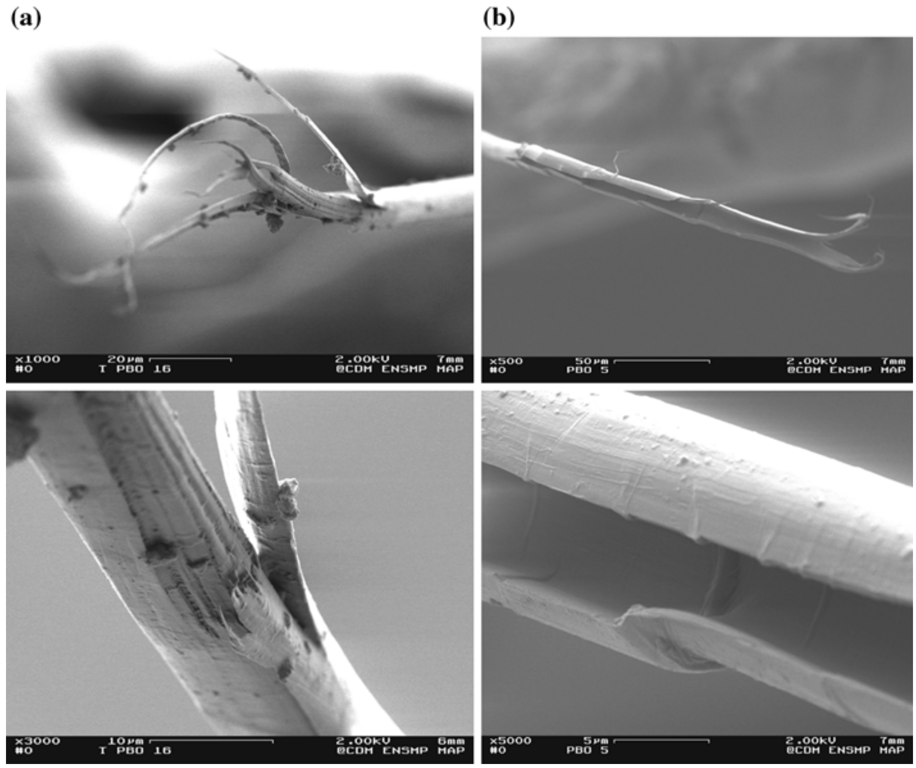

Fig. 4 PBO tensile fracture surfaces, quasi-static test. **a** Longitudinal splitting, **b** compression bands

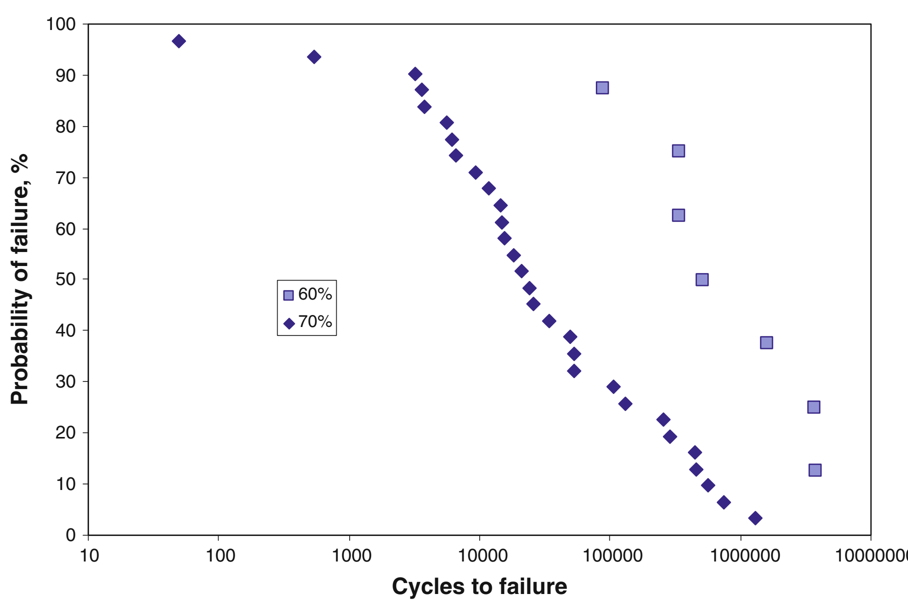

Fig. 5 Failure probability versus cycles to failure, PBO with 0–70 and 0–60% cycling

Conclusions

Tests on single PBO filaments have shown the exceptional static and cyclic properties of these fibres. A single PBO fibre can support much higher cyclic stresses than other fibres. Failure occurs by fibrillation under both static and cyclic loads, in a similar way to that observed in other high performance fibres.

These results show the intrinsic material fatigue performance of PBO fibres. In applications such as ropes, assemblies of large numbers of fibres are used, and the fatigue behaviour may be dominated by construction effects (crossover points in braids, cover/core interactions, terminations). The remarkable potential of the fibres may not then be fully realized, and work is underway to explore the translation of fibre performance to ropes.

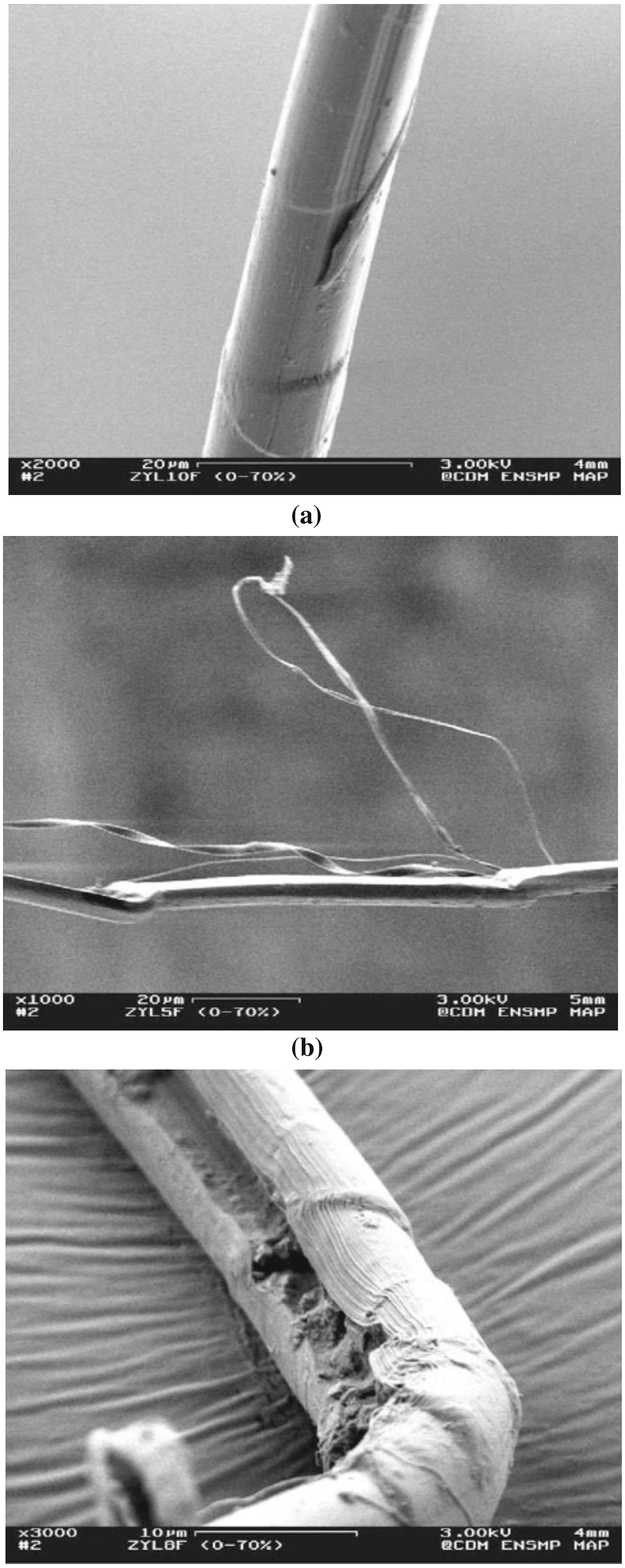

Fig. 6 PBO fracture surfaces, cyclic tests. **a** 9,000 cycles, **b** 33,000 cycles, **c** 132,000 cycles

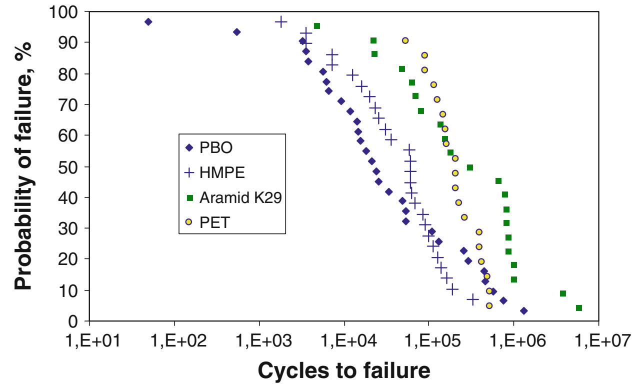

Fig. 7 Comparison between fibres, 0–70% cyclic load

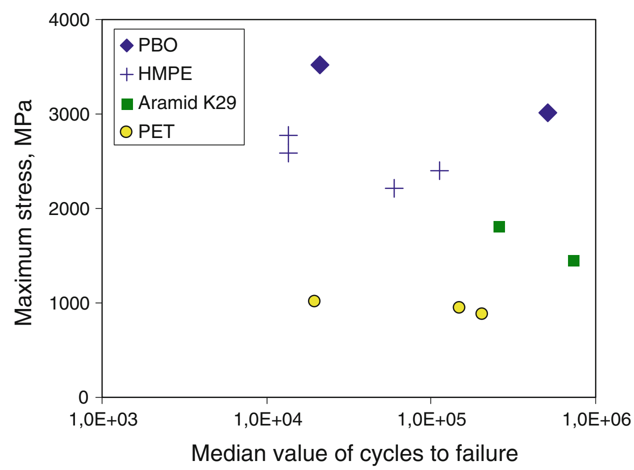

Fig. 8 Comparison of PBO cyclic behaviour with polyester, aramid and HMPE in terms of applied stress

Table 3 Test details and median cycles to failure

Material	Break stress (MPa)	Maximum applied stress level (%)	Median cycles to fail	Number of valid tests
PBO HM	5030	60	514800	7
		70	21060	30
PET	1260	70	206550	19
		75	149400	19
		80	19800	19
HMPE SK75	3700	60	118800	23
		65	117000	12
		70	59400	27
		75	13500	28
Aramid K29 [14]	2600	56	730000	25
		70	260000	21

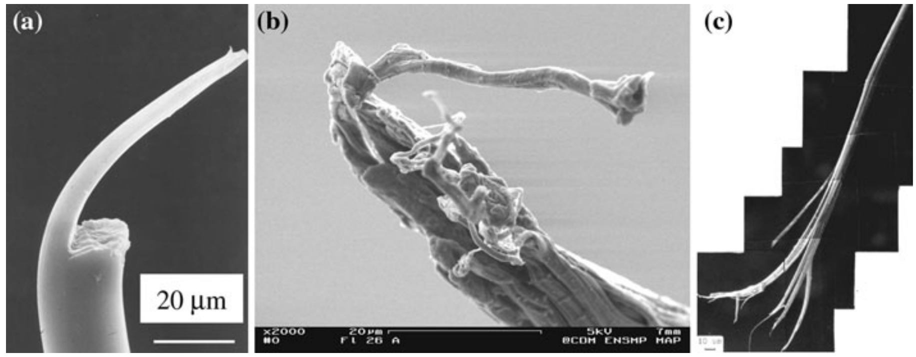

Fig. 9 Failure modes, **a** polyester (cyclic), **b** HMPE (cyclic) and **c** aramid (static)

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