Mechanical behaviour of rigid-rod polymer fibres: 2. Improvement of compressive strength

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Under axial compression, both poly(*p*-phenylene benzobisoxazole) and Kevlar® fibres fail by buckling of fibrils located just beneath the outer surface where lateral constraint is minimal. As the fibrils cascade buckle through the bulk of the fibre, a kink band is formed. A thin, well-adhered high-modulus ceramic coating on the surface increases the axial compressive strength by restraining the fibrils against buckling and kink band initiation. Compressive strength improvement is a function of coating thickness. The coating also reduces the radial thermal expansion coefficient in accord with finite-element predictions.

(Keywords: mechanical behaviour; rigid-rod polymer; compressibility)

INTRODUCTION

Almost since their inception, fibres based on rigid-rod polymers have provoked much excitement: their tensile properties, combined with their low specific gravity, promise extraordinary benefits for structural composites, especially in mobile applications[1]. The performance of many aircraft, missiles, land vehicles and boats could be measurably improved by using structural materials with higher specific properties. Unfortunately this has not proved to be the case in practice; the low compressive strengths of the fibres have severely constrained their utility, since relatively few structural components or systems function exclusively under tension.

The need to correct this deficiency, to increase the axial compressive strength, has been apparent for some time, and many efforts to do so have been made[2]. Principally these have been chemical in nature, seeking to provide primary bonding transversely across the fibre. The motivating idea was, and still is, that if the axially aligned polymer chains could be crosslinked in some way, their resistance to compressive failure would be increased. (Implicit is the assumption that the failure mechanism is by buckling of the chain and, indeed, there have been attempts to model the fibre behaviour quantitatively on this basis[3].) The crosslinks would laterally stabilize the chain and thereby increase its buckling load: the compressive strength of the fibre would improve. These attempts have not been very successful. Despite the apparent achievement of crosslinking, modest changes in fibre compressive strength have been reported, often at the expense of tensile strength. This suggests that the failure mechanism is in fact not as assumed, which is consistent with the observations we report here.

FAILURE OBSERVATIONS

Figure 1 is a scanning electron micrograph of the skin of a poly(*p*-phenylene benzobisoxazole) (PBO) fibre that has been peeled off the core and then bent parallel to the fibre axis such that the surface shown, which is the outer surface of the fibre, underwent compression. An enlarged view, *Figure 2*, shows rows of buckled skin arrayed in a remarkably regular pattern of ripples*. We believe that

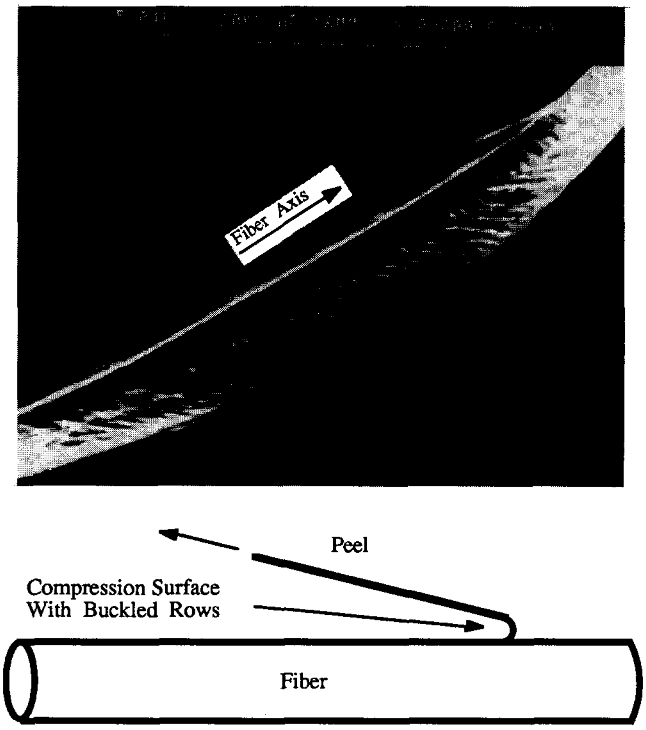

Figure 1 Arrays of buckled rows in the skin of a PBO fibre that has been pelled off the core of the fibre and then bent to produce compressive deformation on the peeled surface shown. Orientation is shown schematically

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* We term this the R4 effect since it was first observed by an undergraduate student member of the research team: Rodrigo R. Rubiano's ripples

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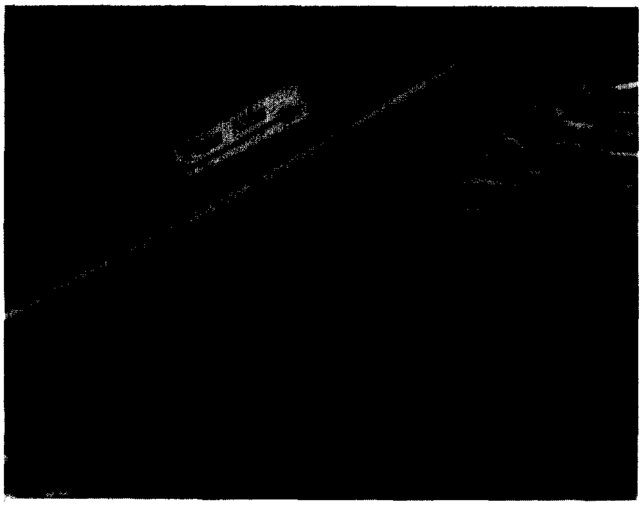

Figure 2 Same as *Figure 1*, higher magnification

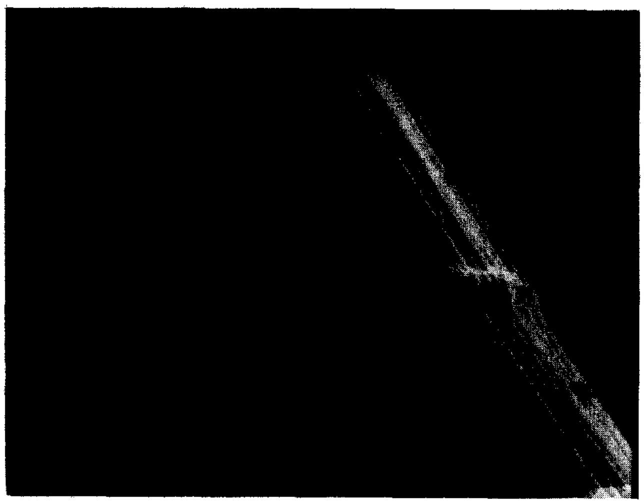

Figure 3 Kink band in PBO fibre, initiating on surface, from tensile recoil loading of fibre

this reveals the controlling failure micromechanism in PBO: skin buckling, initiating a kink band on the surface as shown in *Figure 3*. The latter appears to be the typical mode of fibre compressive failure in that kink bands start on the surface and progress across the cross-section of the fibre in the fashion shown in *Figure 4*.

The R4 effect is particularly striking and easy to observe in peels taken from PBO fibres, once the recognition of it is established. In Kevlar® fibres a similar phenomenon appears to take place, as can be seen in *Figure 5*. Here the surface of the Kevlar 49 fibre has been removed and then a sheath of fibrils just below the surface has been peeled from the core and bent in a manner similar to that used in *Figures 1* and *2*. The buckling of the fibrils in the sheath is easily seen. *Figure 6* explains the orientation of the image shown in *Figure 7*: a thicker peel from the Kevlar 49 fibre surface, where the right edge is the skin surface and to the left is the fibril structure just beneath the skin. *Figure 8* is a composite micrograph of the same bent Kevlar 49 peel, at another location, where the skin of the fibre again is located at the right edge of the image. It may explain why the ripples in Kevlar are less evident than in PBO: the fibril buckling seems to be more prevalent just beneath the Kevlar skin, whereas in PBO apparently the skin itself buckles first.

In an effort to model the compressive strength of these fibres on the basis of fibril buckling, use is made of such micrographs. For PBO, the buckled fibril length is taken as the averaged length of the buckled skin arrays shown in *Figures 1* and *2*. This assumes that, if the skin buckles first, the fibrils just beneath it will follow, and exhibit the same buckling length. For Kevlar 49, the fibril buckling

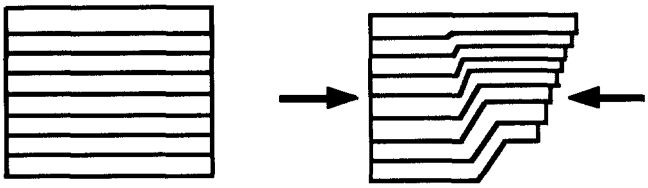

Figure 4 Schematic illustration of kink band formation from fibril buckling. See also ref. 5

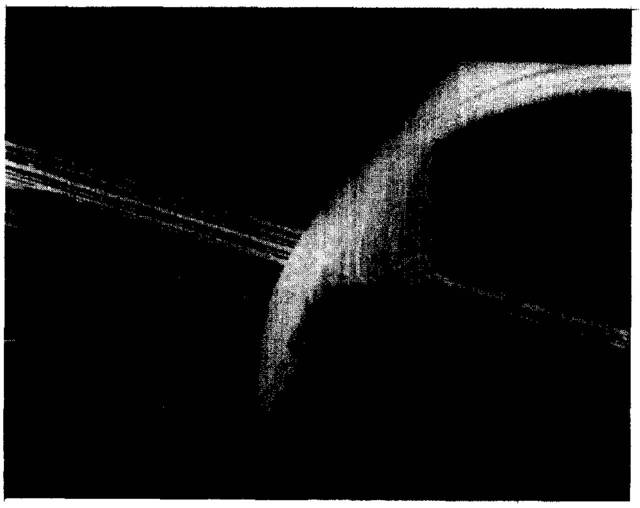

Figure 5 Sheath of fibrils beneath skin peeled from Kevlar 49 fibre, bent as shown. Buckling of fibrils in high-curvature region is evident

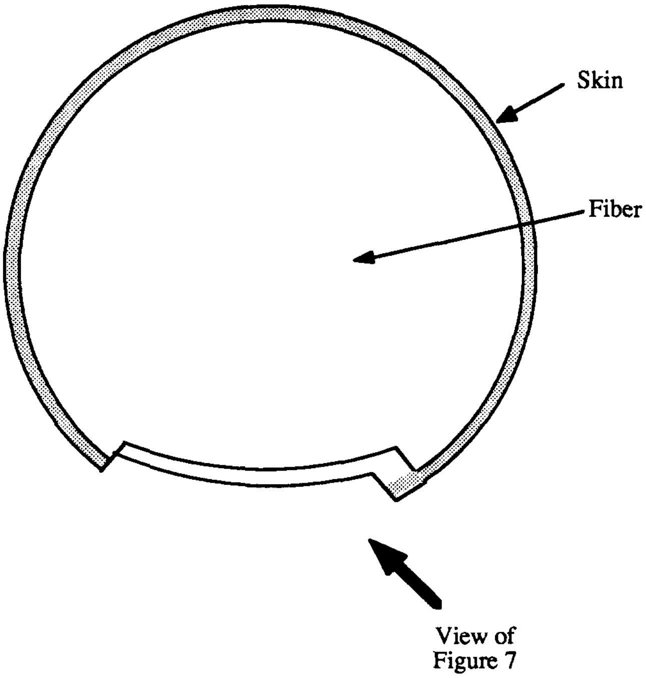

Figure 6 Orientation of view of *Figure 7*

Figure 7 Thicker peel from Kevlar 49 fibre surface. The buckled skin surface is located at the right edge of the peel and the fibril structure inside of it is evident on the left. View is from exterior towards the fibre centre

length is found from measurements on micrographs such as *Figure 8*. For both, the fibril diameters are obtained by measurements from other micrographs of transversely split fibres presented in part 1 of this paper. (Note that the buckled entities in *Figure 8* are probably bundles of fibrils or sheets of fibrils rather than individual fibrils, which are much smaller in diameter.) From such measurements as described, the average results are as follows:

	Buckled length (nm)	Diameter (nm)
Kevlar 49	1510 ± 220	160 ± 20
PBO	1400 ± 200	220 ± 30

MODEL ANALYSIS

Our analysis of the fibril as an end-loaded column to calculate the force to produce buckling cannot be precise, for a number of reasons. The classical Euler treatment assumes pinned column ends, Hookean elastic behaviour, elastic buckling of the column (no end crushing or yielding), no interactions between adjacent columns (fibrils) and perfect colinearity of the load and the column axis (no eccentricity). Given all of these conditions, the buckling load P is:

$$P = \pi^2 EI/L^2 \qquad (1)$$

where E is the modulus of elasticity, I the moment of inertia of the cross-section and L the length of the buckled column. Applying this to the above data, assuming that the observed fibrils are the failing elements and that they are densely packed into the fibre cross-section, results in the following fibre compressive strengths:

	Predicted [MPa (ksi)]	Measured [MPa (ksi)]	Modulus[a] [GPa (Msi)]
Kevlar 49	620(90) ± 205(30)	345(50) ± 35(5)	89.6(13)
PBO-1	620(90) ± 276(40)	207(30) ± 35(5)	41.4(6)

[a] The value of each compressive modulus was determined from single-fibre, three-point bending tests described in part 1 of this paper. Compressive strengths were measured by the tensile recoil technique, at room temperature

In view of all the uncertainties implicit in applying the Euler analysis to such a complicated physical system, the predicted and measured fibre compressive strengths are not ridiculously different. There is uncertainty regarding the interactions between fibrils; probably they do not behave elastically; their end conditions are not pinned; because of non-linear behaviour the applicable modulus value is not obvious; eccentricity of loading probably is prevalent; and the packing of the fibrils in the fibre may not be dense. Despite all of this, the predictions appear more reasonable than unreasonable.

Another test of the fibril buckling idea has been explored. If compressive failure is initiated by buckling at or just beneath the fibre surface, a stiff coating applied to the surface should stabilize the fibrils and produce an increase in the fibre compressive strength. Using physical deposition methods, high-modulus ceramic coatings have been put down on individual fibres, primarily PBO, with the results presented in *Figure 9*. A compressively failed

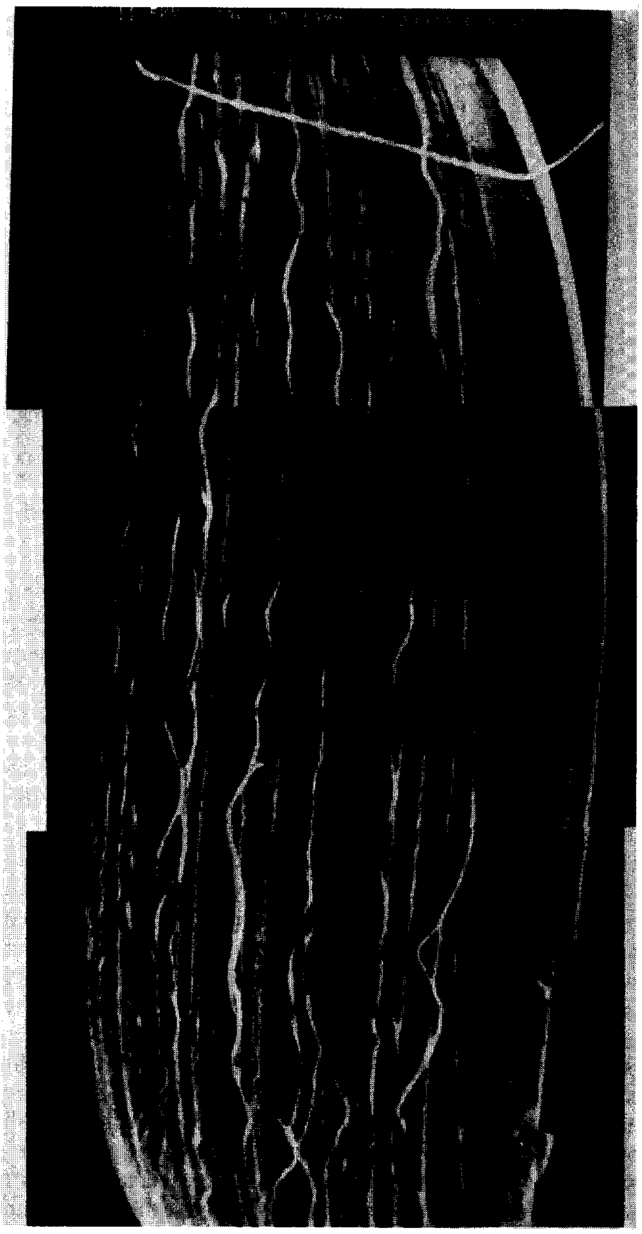

Figure 8 Composite micrograph of peel from Kevlar 49 fibre surface. Outer skin of fibre is right edge of the image. Extensive buckling of fibril bundles beneath the skin is evident. View as shown in *Figure 6*

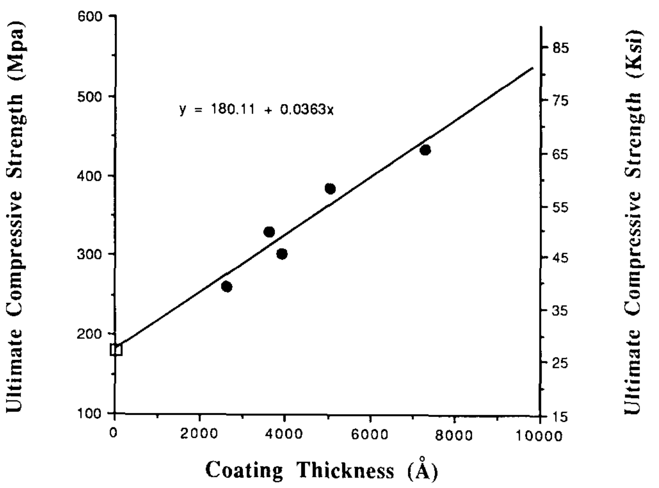

Figure 9 PBO fibre. Ultimate compressive strength *versus* ceramic coating thickness. Tensile recoil tests

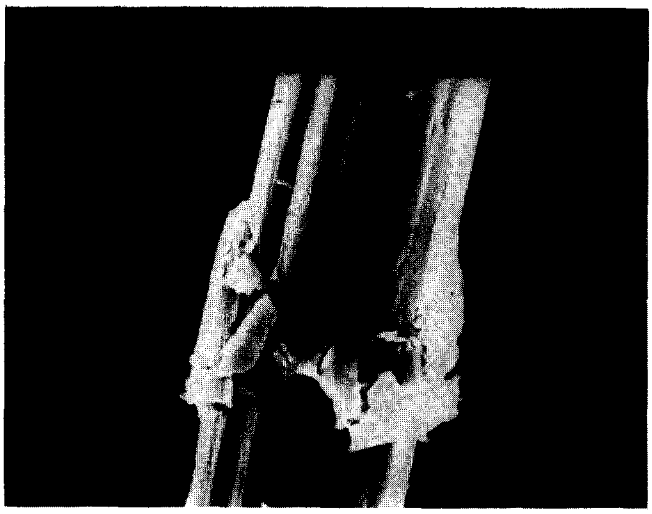

Figure 10 Kink band, in coated PBO fibre, produced in tensile recoil test. Good adhesion of coating is evident

fibre is shown in *Figure 10*, where the kink bands that formed in the fibre beneath the coating can be discerned. The good adhesion between the coating and the fibre is further confirmed by the micrograph in *Figure 11*: heating the fibre to 430°C *in vacuo* produced substantial radial expansion, which multiply cracked the coating but it did not spall off*. (A poorly adhered coating in this test shows only one or two major cracks along the fibre axis direction and spalling can be expected.)

The increase in fibre compressive strength with coating thickness shown in *Figure 9* is consistent with the idea of stiffening the kink-initiating fibrils against buckling. Unfortunately we do not know how to analyse or model this situation: predicting the axial load capacity of a laterally supported column requires such detailed knowledge of the constraint and end conditions that any analysis degenerates to an exercise in seeing how starting assumptions affect the results. However, the data from another set of experiments are useful here. We have had difficulty in consistently getting good adhesion of a ceramic coating to Kevlar 49 fibres despite washing the fibres in a variety of liquids and other attempts to clean the surfaces. Perhaps the various processing aids and other constituents known to be present in the fibres form weak boundary layers at the coating–fibre interface[4]. With poor adhesion, no increase in the compressive strength of the fibres was evident. When, fortuitously, good adhesion was achieved, the compressive strength increased in direct proportion to the coating thickness, in the same way as it did for the PBO fibres. This sensitivity of the strengthening effect to good adhesion lends credence to the idea that stiffening the surface against buckling is one way to increase the strength of the fibres. Poor adhesion would not provide such stiffening; good adhesion does.

There is another way to explain the coated fibre data: modelling it as a composite fibre. In such, both the fibre and the coating are assumed to strain equally when loaded in compression and the first to reach its ultimate strength causes simultaneous failure in the other. At that point the load borne by the coated fibre is the sum of the loads in the fibre and in the coating: a rule of mixtures. If reasonable values of modulus and compressive strength are assigned to each component, and each is assumed to exhibit Hookean elasticity, the strength *versus* coating thickness relationships so predicted are not very close to those which have been measured experimentally. (Though the model does not explicitly assume good adhesion, or require it, the comparison of its predictions to the measured results does do so.) Even though such a model does not correlate well to the measured data, it is recognized that this may be the correct explanation of the coated fibre data. Perhaps even other models may be applicable also.

CONCLUSIONS

At this point in the research we believe the correct explanation of the coating effect is in its stiffening of the surface against compressive buckling. This belief derives from several factors. There is abundant evidence that the compressive failure mechanism in the fibre is by fibril buckling, which is why crosslinking between the polymer chains has been ineffective. Such buckling can be easily

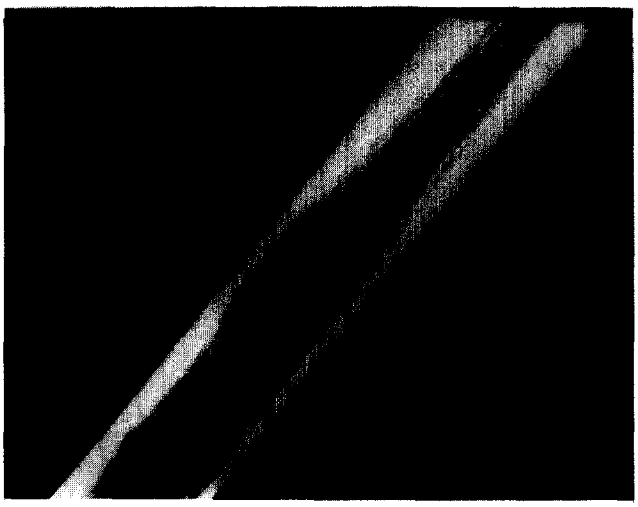

Figure 11 Coated PBO fibre cycled to 430°C *in vacuo*. Differential radial thermal expansion cracked coating. Good adhesion prevents spalling. Despite cracking, radial coefficient of thermal expansion of coated fibre remained below that of uncoated fibre

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* Even after the cracking as shown, the radial coefficient of thermal expansion of the coated fibre remains substantially less than that of an uncoated one. This is consistent with an analysis of the coated fibre that assumes ideal adhesion of the coating

seen, and indeed was first reported some time ago[5]. It initiates kink bands at or near the surface, and putting a stiffening coating on the surface delays it. The coating functions even though tensile preloading, as encountered in the tensile recoil test, may crack it extensively: the reinforcement action of it is very localized, consistent with the dimensions of the fibrils. Good adhesion is essential to its function, since it is attached to only one 'side' of the buckling fibril rather than entirely surrounding it. In fact, however, a definitive explanation remains to be achieved. In the near future we plan to use several different types of ceramic for the coating to see if this will better clarify its role.

The more important finding of this work is the observed mechanism of compressive failure: fibril buckling at or very near the surface of the fibre. Modelling it produces results consistent with experimental measurements. Physical evidence via scanning electron microscopy is persuasive. The stabilizing effect of the coating has been demonstrated. The real test of the idea will come when shorter, larger-diameter fibril buckling elements are caused to exist in the fibre independent of composition changes. Higher-compressive-strength fibres should result.

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