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Mechanical stability of rigid rod polymer fibres under the influence of compression and temperature

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This work presents a mathematical model for the compressive strength of a rigid rod polymer fibre based on an approach describing the fibre fibril as an end-loaded column on an elastic base. Also, it is suggested that the model of elastic stability of the coated fibre includes the influence of thermal stresses. A good agreement with experimental data is received. From this model one can propose that if an interfibrilar matrix material is incorporated in the fibre, at a small volume fraction of about a few per cent, this material may have a pronounced influence on the fibre's compressive strength.

1. Introduction

Fibres drawn from rigid rod polymers have extraordinary tensile properties, but their transverse and compressive behaviours are deficient. These fibres are inclined to buckle because of their relatively low transverse mechanical properties, caused by the presence of microvoids and their skin–core structure [1, 2]. Compressive failure is initiated by buckling at or just beneath the fibre surface [3]. Many efforts have been made to improve the compressive properties of rigid rod polymer fibres, such as, the introduction of chemical crosslinking transverse to the fibre axis [4], coating the fibre surface with a thin layer of a high modulus material [3, 5], infiltration of a high modulus filling material (e.g. glass [6]) into the surface or bulk of the fibre. A preferred method for improving the fibre's compressive strength is absent as yet, but it is possible to consider that the main idea of most methods is to change the instability mechanism from buckling to bending and failure of an orthotropic body.

2. Theoretical considerations

A common approach in the description of a rigid rod polymer fibre is as a microcomposite, in which the inner structure of the fibre is described as a collection of laterally interacting extended units (either chains or microfibrils). It may be possible that the interaction is mediated by an interfibrilar material. The axial compressive strength of these fibres is limited by elastic microbuckling instabilities and not by bending and material failure. The best estimate of the compressive strength, σ_{cr}, is given by [7, 8]

$$\sigma_{cr} = G \tag{1}$$

where G is the longitudinal shear modulus of the anisotropic fibre. Experiments show that the predictions of Equation 1 are overestimated [9]. For rigid polymer fibres DeTeresa *et al.* [9] suggested an empirical correction to Equation 1 so that

$$\sigma_{cr} = 0.3\,G \tag{1a}$$

The authors propose to describe the behavior of a fibril in a fibre under compressive loading as an end-loaded column on an elastic base. The elastic base represents the field around the fibril under consideration, which can be either the effective field of the surrounding fibrils or the interfibrilar material if it exists. This approach implies the following boundary conditions: pinned column ends; Hookean elastic behaviour; colinearity of the load and the fibril axis; no crushing or yielding of the column ends; good contact (no slip) between the fibril and the elastic base. Given all of these conditions, the buckling load, P_{cr}, is [10]

$$P_{cr} = 2(IE_m E_f)^{1/2} \tag{2}$$

where E_f is the tensile elastic modulus of the fibril, taken to be equivalent to the fibre modulus [9]; E_m is Young's modulus of the elastic base; I is the moment of inertia of the fibril cross-section. From Equation 2, the compressive strength is given by

$$\sigma_{cr} = (E_f E_m/\pi)^{1/2} \tag{3}$$

The transversal Young's modulus of the fibre, E_T, can be given by [11]

$$\frac{1}{E_T} = \frac{\nu_f}{E_f} + \frac{1-\nu_f}{E_m} \tag{4}$$

where ν_f is the volume fraction of fibrils in the fibre, so that E_m is given by

$$E_m = \frac{E_T E_f(1-\nu_f)}{E_f - \nu_f E_T} \tag{5}$$

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Equations 1 and 3 show that increasing G and E_m increases the ultimate compressive strength of the fibre.

Of the methods presented in an attempt to improve the compressive strength of rigid polymer fibres, now consider the following: coating the fibre surface with a thin layer of a high modulus material and infiltration of a high modulus filling material into the surface or whole volume of the fibre. These methods may produce a pronounced skin–core structure in the fibre. Coating shells or fibre skin–core structures may possess a great difference in the thermal expansion coefficients. It requires one to take into account the influence of the residual thermal stresses on the compressive stability of the fibres.

A model is suggested based on the stability model of cylindrical shells [10]. This model applies both to the case of a fibre coated with a high modulus material as well as to the case of an uncoated fibre with a pronounced skin–core structure. This approach implies the following assumptions and boundary conditions: a thin shell; the axial stress is uniformly distributed in fibre cross-section; the fibre ends are pinned; there are no temperature gradients; good contact (no slip) between the core and shell. The initial differential equation is [10]

$$\frac{D}{h}\nabla^2\nabla^2\nabla^2\nabla^2 w + \frac{E_{sh}}{R^2}\frac{\partial^4 w}{\partial x^4} + \sigma_x\nabla^2\nabla^2\frac{\partial^2 w}{\partial x^2} + \sigma_y\nabla^2\nabla^2\frac{\partial^2 w}{\partial y^2} + \frac{E_f^{\perp}}{h}\nabla^2\nabla^2 w = 0 \quad (6)$$

where w is the bending displacement; x, y are the co-ordinate axes along the fibre and radial directions, respectively; σ_x, σ_y the components of the compressive stress; ∇^2 the Laplace operator; D the flexural rigidity of the fibre; E_{sh} the skin (shell) elastic modulus; h the thickness of the skin (shell); R the fibre (core) radius; $E_f^{\perp}$ the fibre (core) transversal elastic modulus. In this model $E_f^{\perp} = E_T$.

$$\sigma_y = \frac{E_f^{\perp}\Delta\beta\Delta T R^2}{h\delta} \quad (7)$$

where

$$\delta = 1 + \frac{E_f^{\perp}R^2}{E_{sh}h}(1 - \mu^2) \quad (8)$$

where $\Delta\beta$ is the difference between coefficients of linear thermal expansion of fibre (core) and shell (skin); ΔT the difference between the temperature in which the fibre was formed (or coated) and the temperature at which the fibre is used; μ the Poisson's coefficient.

A particular solution of Equation 6, which agrees with the boundary conditions, is

$$w = f\sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{ny}{R}\right) \quad (9)$$

where f is the amplitude of bend; m, n the number of half-waves along the fibre and tangential directions, respectively; L the length of the investigated fibre sample.

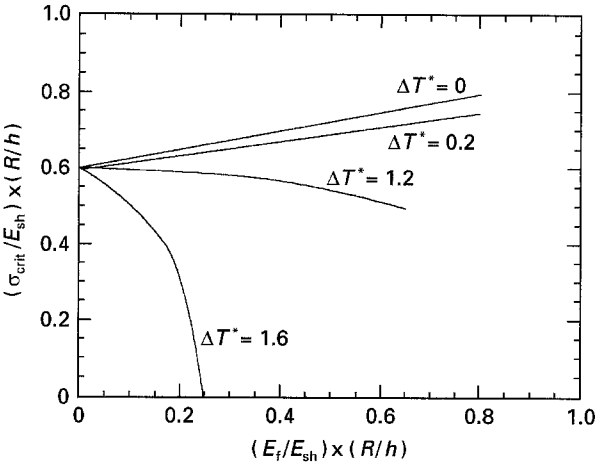

Figure 1 The critical stress for fibre buckling, as calculated numerically by Equations 6–12.

Inserting Equation 9 into Equation 6 yields

$$\sigma_x^* = \frac{1}{12(1-\mu^2)}\frac{(1+\theta^2)^2}{\theta^2}\eta + \frac{\theta^2}{1+\theta^2}\frac{1}{\eta} - \frac{\omega\Delta T^*}{\delta\theta^2} + \frac{\omega}{\eta\theta^2} \quad (10)$$

where

$$\sigma_x^* = \frac{\sigma_x R}{E_{sh}h}; \quad \theta = \frac{m\pi R}{nL}; \quad \eta = n^2\frac{h}{R};$$
$$\Delta T^* = \Delta\beta\Delta T\frac{R}{h}; \quad \omega = \frac{E_f^{\perp}R}{E_{sh}h} \quad (11)$$

The critical stress which produces buckling of the fibre, σ_{crit}, can be obtained from the condition

$$\frac{\partial\sigma_x^*}{\partial\eta} = \frac{\partial\sigma_x^*}{\partial\theta} = 0. \quad (12)$$

The critical stress for fibre buckling, as calculated numerically by Equations 6–12, is presented in Fig. 1. It is easy to see that, under high temperatures, fibres with minimal $\Delta\beta$ and $E_f^{\perp}/E_{sh}$ are more stable against buckling.

3. Comparison with experiments

The theoretical predictions were compared with experimental data for Kevlar fibres, as shown in Table I. In order for the compressive strength of the fibre to equal its tensile strength (3.2 GPa for Kevlar 49 [2]), it is necessary to achieve a shear modulus of interfibrilar material at values of 3.2 GPa by Equation (1) or 1 GPa by Equation (1a). On the other hand, with Equations 3–5, equality of fibre compressive and tensile strengths may be achieved at $E_T = 11.8$ GPa (using the data described in the second footnote to Table I). Interestingly, if the volume fraction of the interfibrilar material could be increased slightly by some method so that $v_f = 0.95$, equality of the compressive and tensile strengths would be achieved, by Equation 3 at $E_T = 5$ GPa. These values, in the range of 1–5 GPa, correspond to the properties of common unorientated bulk polymers.

TABLE I Comparison of the predicted and measured axial compressive strength of Kevlar fibres

Measured compressive strength (MPa) [9]	Prediction by Equation 1[a] (MPa)	Prediction by Equation 3[b] (MPa)
≈ 345	1500	780

[a] The value of G was taken from reference [9].
[b] Using the values of: $E_f = 124$ GPa [1]; $E_T = 0.77$ GPa [12]; $v_f = 0.98$ estimated from the ratio of the theoretical and experimental densities of Kevlar fibres [2].

Now consider the experimental data for ceramic coated fibres from poly(p-phenylene benzobisoxazole) of McGarry and Moalli [3, 5]. Comparison of the calculated results from the mathematical model presented by Equations 6–12 and the experimental data [5] is shown in Fig. 2. In the calculations it was considered that $\mu = 0.1 \div 0.3$ [11] and $\Delta T \approx 0$. Experimental data were presented for two batches of fibres, yielding different values of the compressive strength as a function of coating thickness. A good approximation of the experimental data was achieved by the model using the following parameters: $E_f^{\perp} = 0.7$ and $E_{sh} = 6.5$ GPa for one batch and $E_f^{\perp} = 0.3$ and $E_{sh} = 2.7$ GPa for the other. The values of the transverse moduli of the fibres are in good agreement with theoretical notions on orientated rigid polymer fibres [12, 13]. The values of the elastic moduli of the ceramic layers (2.7, 6.5 GPa) seem somewhat low in comparison with known moduli of *in situ* ceramics. This deviation can be explained by a smaller degree of densification achieved in the deposition process of the ceramic layer [14].

Inspection of Table I and Fig. 2 reveals a deviation between the approximated values of the calculated transverse moduli of the two fibre batches and between these values and the reported data for aramid fibres [12]. The model was constructed with several simplifications and assumptions. Several effects were not taken into considerations: the anisotropy of mechanical properties within the fibre; the structural inhomogenity, which may lead to initiation of local instabilities at compressive loads less than the predicted value; the presence of voids in the fibre [1]; the distribution of molecular orientation, which may allow failure to initiate in the most poorly aligned regions. The proclaimed boundary conditions of the model also are idealized, and estimation of the fibril volume fraction is very approximate. However, one can confirm that the predicted and measured fibre compressive strengths are not extremely different.

The model presented by Equations 6–12 can be used to predict the critical temperature difference for thermal buckling of coated fibre. For example, for ceramic coated Kevlar fibre, $\Delta\beta \approx 6 \times 10^{-5}\,K^{-1}$. Using the following values: $R/h = 3$, $E_f^{\perp} = 0.5$ GPa, $E_{sh} = 5$ GPa, it is obtained that thermal buckling will ensue when $\Delta T > 400\,^{\circ}C$. However, even the simplest calculation of the tensile strength of the ceramic layer, σ_c, due to the mismatch of the thermal expansion

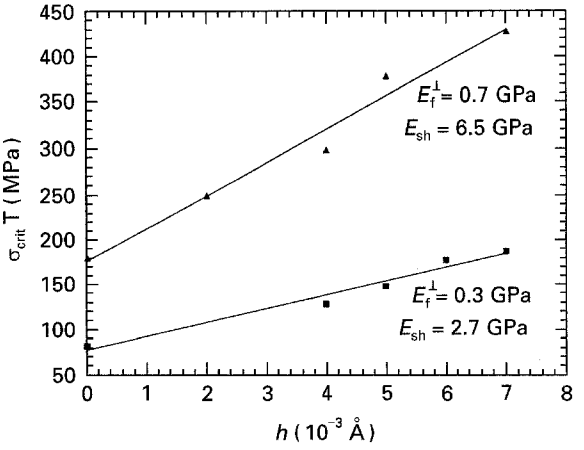

Figure 2 Comparison of the calculated results from the mathematical model presented by Equations 6–12 and the experimental data [5].

coefficients yields

$$\sigma_c = E_{sh}\Delta\beta\,\Delta T \quad (13)$$

Taking into consideration an ultimate value of σ_c for the ceramic layer, ~ 0.5 GPa, failure of the ceramic coating must already occur at $\Delta T \sim 170\,^{\circ}C$. This estimation is in accord with experimental results [14], in which at $\Delta T > 150\,^{\circ}C$ thermal cracking of the fibre coating was observed. The helical shape of the cracks, suggests the mismatch of thermal expansion coefficients of the polymer fibre and ceramic coating to be the reason for failure of the coating. From this one can infer that thermal buckling should only be more relevant in the case of a small difference between the thermal expansion coefficients of fibre and coating.

4. Conclusions

The present model can now be used to discuss some of the methods presented for enhancement of fibre compressive strength: coating the fibre and formation of an interfibrilar matrix. From the model one can propose that if an interfibrilar matrix material can be incorporated into the fibre, at a small volume fraction of about a few per cent, it may have a pronounced influence on the fibre compressive strength. The interfibrilar matrix may be formed by infiltration of a matrix-forming material during the spinning process [15]. The matrix material may be either polymeric, such as an epoxy resin, or an inorganic glass-forming material. Alternatively, preliminary investigations suggest that swelling of fibres in a solvent under special conditions allows formation of an unorientated interfibrilar matrix of the same polymer of which the fibre is made [16]. The interfibrilar matrix, chemically identical to the fibrils, may have advantages with respect to adhesion, matching of thermal expansion and ability to undergo further thermal treatments. The present analysis indicates that if such a matrix is formed, optimal properties may be obtained with a minimal volume fraction of matrix. As for coating of the fibre, if the shell elastic modulus is close to that of the unorientated bulk polymer (~ 5 GPa), increase of the fibre's compressive

strength will require the thickness of the shell to be equal to the fibre radius.

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