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# Viscoelastically prestressed polymeric matrix composites: An overview

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**Abstract**

Elastically prestressed polymeric matrix composites (EPPMCs) exploit the principles of prestressed concrete; i.e. fibres are stretched elastically during matrix curing. On matrix solidification, compressive stresses are created within the matrix, counterbalanced by residual fibre tension. Unidirectional glass fibre EPPMCs have demonstrated 25-50% improvements in impact toughness, strength and stiffness compared with control (unstressed) counterparts. Although these benefits require no increase in section dimensions or weight, the need to apply fibre tension during curing can impose restrictions on processing and product geometry. Also, fibre-matrix interfacial creep may eventually cause the prestress to deteriorate. This paper gives an overview of an alternative approach: viscoelastically prestressed PMCs (VPPMCs). Here, polymeric fibres are subjected to tensile creep, the applied load being removed before the fibres are moulded into the matrix. Following matrix curing, viscoelastic recovery mechanisms cause the previously strained fibres to impart compressive stresses to the matrix. Since fibre stretching and moulding operations are decoupled, VPPMC production offers considerable flexibility. Also, the potential for deterioration through fibre-matrix creep is offset by longer term viscoelastic recovery mechanisms. To date, VPPMCs have been produced from fibre reinforcements such as nylon 6,6, UHMWPE and bamboo. Compared with control counterparts, mechanical property improvements are similar to those of EPPMCs. Of major importance however is longevity: through accelerated ageing, nylon fibre-based VPPMCs show no deterioration in mechanical performance over a duration equivalent to ~25 years at 50ºC ambient. Potential applications include crashworthy and impact-absorbing structures, dental materials, prestressed precast concrete and shape-changing (morphing) structures.

*Keywords:* Polymer-matrix composites (PMCs); Prestress; Mechanical properties; Viscoelasticity.

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## Introduction

Although prestressed concrete is an established structural material, interest in the use of (compressive) prestress, to improve mechanical properties within fibre-reinforced polymeric matrix composites (PMCs) appears to be comparatively recent. Composite mouldings with residual stresses are, in fact, normally considered to be an unfortunate consequence of differential shrinkage from the processing route.[1] Moreover, the intentional application of stress during composite processing is usually confined to improving fibre alignment in filament-wound structures.[2,3] Studies in which prestress is exploited to enhance the mechanical properties of PMCs seem to be relatively uncommon, despite such improvements avoiding any need to increase mass or section thickness within a composite structure.

Elastically prestressed PMCs (EPPMCs) can be produced by using principles comparable to prestressed concrete, in that fibres (e.g. glass) are stretched to maintain an elastic strain during matrix curing. Following curing, the load applied to the fibres is released, so that compressive stresses are created within the solidified matrix, which are balanced by residual fibre tension. Early EPPMC studies focused on laminates,[4-7] to reduce fibre distortion and improve laminate stiffness[4] or to reduce the potentially detrimental effects of thermally induced residual stresses.[5-7] Subsequent investigations with unidirectional glass fibre EPPMCs have demonstrated increases in tensile strength of ~25% and elastic modulus of ~50%,[8] compared with unstressed counterparts. Impact toughness, flexural stiffness and strength have also been found to increase by up to 33%.[9,10] Most recently, with woven glass fibre EPPMCs, fatigue life improvements exceeding 40% have been reported.[11] These improvements can be explained principally by the residual stresses (i) impeding or deflecting propagating cracks and (ii) reducing composite strains resulting from external bending or tensile loads.[8-11]

Investigations within the last few years have included unidirectional EPPMCs based on glass fibre, as potential dental materials, with prestress-induced increases in flexural strength of ~30%;[12] carbon fibre, with impact toughness being increased by ~30%;[13] and natural fibre (flax), with improvements in tensile and flexural properties of up to 36%.[14] There has also been interest in the exploitation of EPPMCs for use as shape-adaptive (morphing) composite structures, either as prestressed laminates[15] or unidirectional fibre prestressed structural elements.[16]

Clearly, there is considerable evidence to demonstrate that elastic prestressing within a PMC offers significant benefits. There are however, two potential drawbacks. First, the need to apply fibre tension during matrix curing may impose restrictions on fibre length, orientation and spatial distribution, ultimately compromising mould geometry.[17] It has also been reported that stretching rig design with appropriate fibre clamping can be technically challenging.[15,18] The second drawback arises from the matrix being a polymeric material: it can be expected that the elastically generated prestress will promote the occurrence of localised matrix creep at fibre-matrix interface regions, which could cause the prestress to deteriorate progressively with time.[17]

This paper provides an overview of research into an alternative approach to EPPMC methodology, which is based on viscoelastically generated prestress. It is fitting to note that one of the first papers on this topic was published in this journal.[19] The principles are covered, followed by mechanical properties, long-term performance, prestress characterisation and processing aspects. Future directions are also discussed. The paper is an extended and updated account of work initially published in conference proceedings.[20]

## Prestress based on viscoelasticity

### *Principles*

Viscoelastically prestressed PMCs (VPPMCs) avoid the need for simultaneous fibre stretching and moulding operations. Instead, high-strength polymeric fibres are stretched over time, so that they undergo (viscoelastic) creep; the creep load is subsequently released before the fibres are moulded into a matrix. Following matrix solidification, the previously strained fibres continue to attempt contraction through viscoelastic recovery. This recovery effect produces compressive stresses in the matrix, and these are counterbalanced by residual tension within the fibres. Thus a prestress state comparable to an EPPMC can be achieved. In contrast with producing EPPMCs however, there is potential for considerable flexibility in VPPMC production, as the fibre stretching and moulding operations are decoupled. Thus relatively simple equipment is required to apply a creep load to fibre tows. Also, on releasing the load, the fibres are unconstrained, so that they can be cut to any length, then positioned in any orientation within any shape of mould that is capable of being filled with a matrix resin.

Another significant advantage offered by VPPMCs is longevity. Although localised matrix creep at the fibre-matrix interface regions can be expected to occur as in EPPMCs, this would be offset by active responses from longer term viscoelastic recovery mechanisms within the polymeric fibres.[17] Nevertheless, a potentially major limitation lies in the fact that viscoelastic activity is temperature-sensitive. Thus prestress within a VPPMC could deteriorate or it may be rendered ineffective by high-temperature curing cycles or long-term exposures to hot ambient conditions. This aspect is addressed later in the paper.

### *Proof of concept*

The basic creep-recovery strain cycle for a polymeric material[21] is shown in Figure 1. The instantaneous strain, $\varepsilon_i$, occurs on application of the creep load, then time-dependent creep strain, $\varepsilon_c(t)$, until the load is released. Following elastic recovery, $\varepsilon_e$, the viscoelastic contribution within the recovery phase, $\varepsilon_r(t)$, is of vital importance to viable VPPMC production, in both magnitude and timescale. Thus any contribution from viscous flow, $\varepsilon_f$ (due to permanent molecular slippage from creep), should be minimal, as this permanent deformation will reduce the contribution from $\varepsilon_r(t)$.

At the inception stage,[22] an experimental study was required to determine the feasibility of VPPMC principles. Nylon 6,6 was selected, as it is a readily available, low-cost, high strength polymeric fibre. Initial work revealed that as-received nylon 6,6 fibre, after being subjected to a 24 h creep load of ~330 MPa, gave a viscoelastic recovery strain that approached zero at 1000 h (6 weeks), i.e. an unacceptably short timescale.[19,23] It was found however, that annealing the fibres prior to creep increased the magnitude and timescale of the viscoelastic recovery strain significantly. Based on published studies,[24,25] the annealing conditions for subsequent nylon 6,6 fibre processing were set to 150°C for 0.5 h.

In addition to magnitude and timescale aspects, evidence that viscoelastic recovery mechanisms would be capable of providing a recovery force within a matrix material was required. To demonstrate the presence of such a force, Figure 2 presents the result of an early experiment.[19] Here, nylon 6,6 monofilament was annealed and then subjected to a 24 h creep stress, before being moulded into a thin, transparent

polyester resin matrix. As Figure 2 shows, a (compressive) stress pattern can be clearly seen under polarised light in the 'test' (VPPMC) sample, compared with the 'control' (unstressed) sample.

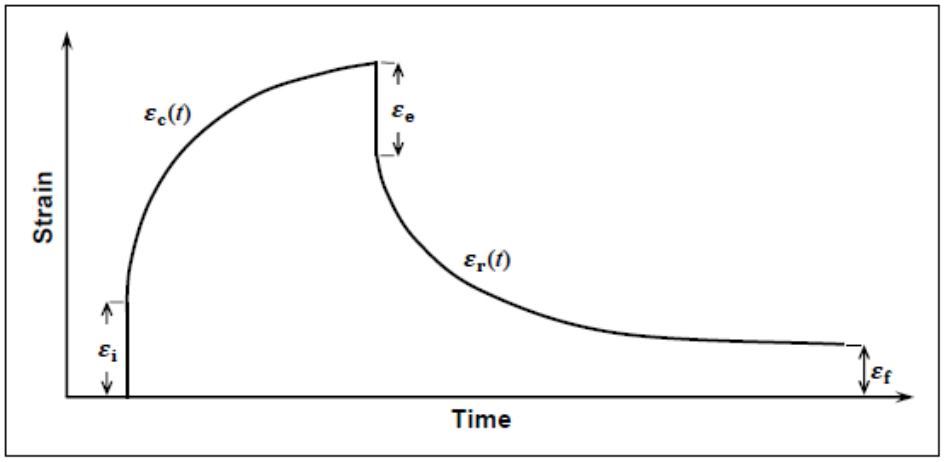


Fig. 1. Schematic tensile creep-recovery strain cycle for a polymeric material.

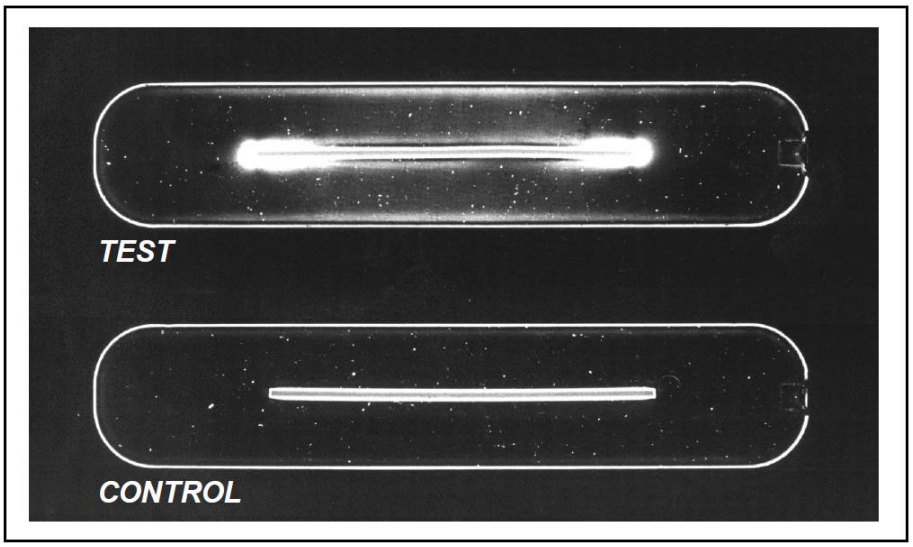


Fig. 2. Nylon 6,6 monofilaments (1.6 mm diameter) in polyester resin samples (150 × 30 × 2 mm) under cross-polarised light. Note the stress pattern from viscoelastic recovery in the 'test' sample, compared with the (unstressed) 'control' sample.[19]

To date, VPPMC studies have focused on composites with unidirectional continuous fibre reinforcement. One of the potential benefits however (as outlined earlier), is that fibres are unconstrained at the moulding stage. Thus VPPMCs could be produced with randomly distributed discontinuous fibres. Nevertheless, as demonstrated by Figure 2, fibre ends will produce stress concentrations, an effect that can be detrimental to mechanical performance.[26,27] For a random fibre VPPMC however, the compressive stresses imparted by fibres neighbouring the vicinity of a fibre end may contribute towards reducing this effect. Moreover, the effect would clearly be reduced by the use of longer discontinuous fibres in VPPMC production.

*Principal mechanical evaluation – impact tests*

Since the earliest studies, the most straightforward method for assessing VPPMC mechanical performance has been to produce batches of unidirectional fibre composite samples for Charpy impact testing. Each batch involved open casting two strips of polyester from the same resin mix: one strip was embedded with a continuous length of 'test' (previously annealed then stretched) nylon 6,6 fibres, the other with 'control' (annealed, not stretched, but otherwise identical) fibres. For both strips, identical aluminium moulds with polished channels were used and the nylon yarns were brushed out into flat ribbons immediately prior to moulding. After sufficient curing, each resulting strip was cut into five lengths (80 × 10 × 3.2 mm) so that a batch consisted of five test and five control samples, ready for impact testing.

Following several studies using Charpy testing, results have consistently shown that the VPPMC test samples absorb typically 25–30% more impact energy than their control (unstressed) counterparts; in some cases, increases of 50% or more have been achieved.[17,19,23,28-31] Figure 3 shows typical test and control samples after impact testing. The test sample shows a region of impact-induced fibre-matrix debonding that is greater than the control sample and this has been consistently observed for all batches studied. Comparable increases in debonded area have been observed with Charpy-tested EPPMC samples relative to unstressed counterparts,[9] and this observation provides evidence of similar prestress effects occurring within VPPMCs.

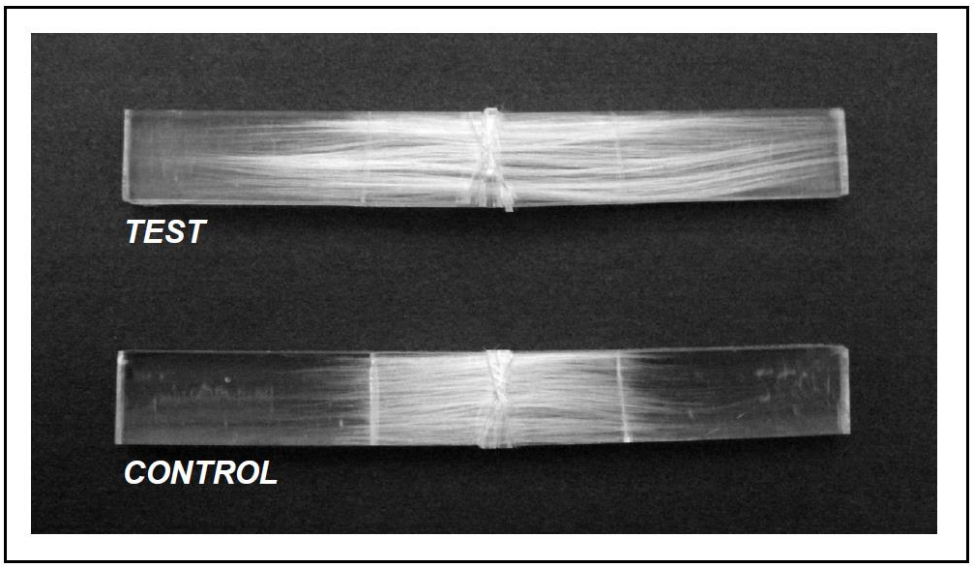


Fig. 3. Typical appearance of test (VPPMC) and control (unstressed) samples after impact testing; note the greater region of fibre-matrix debonding in the test sample.

Results from earlier studies led to the conclusion that prestress-induced increases in impact energy absorption could arise from four mechanisms:[29] (i) matrix compression impedes crack propagation, (ii) matrix compression attenuates dynamic overstress effects, (iii) residual fibre tension creates a more collective response to external loads, and (iv) residual shear stresses at the fibre-matrix interface regions promote (energy absorbing) fibre debonding over transverse fracture. A recent more detailed study however,[30] involving Charpy impact testing over a range of span settings and fibre volume fractions, suggests that (iv) is the principal mechanism. Thus prestress

enhances shear stresses between the fibres and matrix and, during an impact event, these stresses are triggered to promote fibre-matrix debonding, in preference to transverse fracture of the composite sample. Here, the energy absorbed by debonding is notably greater than that required for transverse fracture. This triggering mechanism had also been highlighted in earlier work with glass fibre EPPMCs.[9]

*Other mechanical tests*

The success achieved with Charpy impact testing led to investigations of other basic mechanical characteristics, i.e. the flexural stiffness and tensile properties of VPPMCs. Prior to recent work,[30] all Charpy impact investigations utilised composite samples with a low nylon 6,6 fibre volume fraction, $V_f$, of 2–3%. This had originally resulted from restrictions in the quantity of fibre that could be stretched for VPPMC sample production. Subsequently however, design and construction of improved equipment enabled the fibre stretching capacity to be increased by an order of magnitude.[32]

To study flexural stiffness,[33] samples were produced using the open casting method outlined earlier. In this case however, an epoxy resin matrix and higher $V_f$ values (8–16%) were utilised. Although the epoxy resin had lower viscosity (to facilitate moulding), room temperature gel time at ~15 h was much longer than those of the polyester resins (15–20 min.) previously used and a release film was also required for successful demoulding. Following mould removal, the composite strips were cut to produce two test and two control samples per batch, each sample being 200 × 10 × 3.5 mm. The samples were then subjected to three-point bend tests using a freely suspended load. Here, testing conditions were similar to ASTM D790M recommendations in terms of support pin dimensions and a span/thickness ratio of ~30. The flexural modulus, $E(t)$, was determined from deflections measured at $t$ = 5 s (representing elastic deformation) and 900 s (short-term creep). For both time settings over the range of $V_f$ values studied, $E(t)$ was found to increase by ~50% due to viscoelastically generated prestress.

To evaluate tensile characteristics,[34] composite samples of only 1 mm thickness were required, to meet appropriate test standards. The required accuracy in thickness could not be achieved by open casting; hence a "leaky mould" method was adopted, based on principles from Ladizesky and Ward.[35] This was a closed channel moulding technique, which allowed excess resin to escape from the (open) channel ends. In common with the flexural stiffness study, epoxy resin was used and two test and two control samples per batch were produced, each sample being 200 × 10 × 1 mm. Batches with a wide range of $V_f$ values were evaluated (16–53%), to determine the influence of $V_f$ on tensile properties. As expected, strength and stiffness improved with increasing $V_f$ (e.g. tensile strengths were 130 MPa at 16% and 420 MPa at 53%). It was also found that there were prestress-induced increases in these parameters, but only at intermediate $V_f$ values. The effect is summarised in Figure 4, and this indicates an optimum $V_f$ value (~35–40%) at which the benefits from prestressing are maximised; the increases for strength, modulus and strain-limited toughness exceeding 15, 30 and 40% respectively. This optimum $V_f$ can be attributed to the competing roles between fibres and matrix (the total force exerted by fibres within a VPPMC sample being proportional to $V_f$). At lower $V_f$, less compressive stress will be produced as there are too few fibres; at higher $V_f$, there are too many fibres, which therefore reduces the matrix cross-sectional area available for compression.

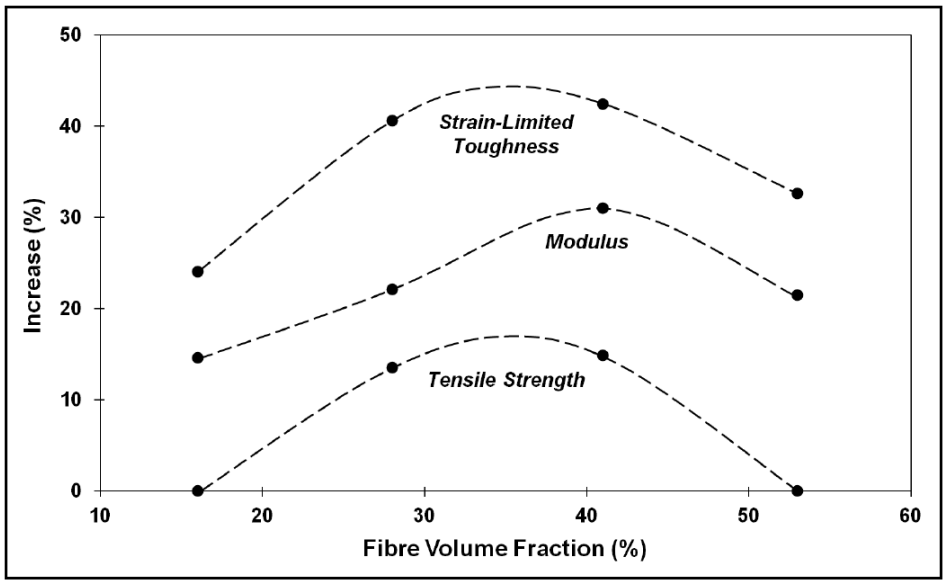


Fig. 4. Effect of prestress on the tensile properties of unidirectional continuous fibre test (VPPMC) samples relative to their control counterparts, as a function of fibre volume fraction. Strain-limited toughness represents energy absorbed/unit volume to a fixed strain (0.25), from area under the stress-strain curve.[34]

## Longevity of VPPMCs

*Long-term viscoelastic activity*

As highlighted earlier, fibres within a VPPMC should be capable of long-term viscoelastic recovery; this is to offset the potential for deterioration in prestress from localised matrix creep, especially at fibre-matrix regions. This capability can be determined by taking recovery strain measurements on fibres after they have been subjected to the creep loading conditions used for VPPMC production. Recovery strain data from previous studies[28,29] are shown in Figure 5 for nylon 6,6 fibre in the form of untwisted continuous yarn. The data show that for non-annealed (i.e. as-received) fibre, recovery strain approaches zero within 1000 h of releasing the creep stress; but fibre annealing (150°C for 0.5 h) prior to creep causes viscoelastic recovery to remain active over a considerably longer timescale, as stated earlier. Here, the white data points represent strain measurements taken in real time, up to 4 years. For longer timescales however, accelerated ageing methods are required, and these were used for obtaining the black data points, up to an equivalent age of 100 years at 20°C. Figure 5 clearly demonstrates good agreement between accelerated ageing and real-time data, and the curve shows the following equation for recovery strain fitted to the black data points:

$$\varepsilon_{\mathrm{rvis}}(t) = \varepsilon_{\mathrm{r}}\left[\exp\left(-\left(\frac{t}{\eta_{\mathrm{r}}}\right)^{\beta_{\mathrm{r}}}\right)\right] + \varepsilon_{\mathrm{f}} \qquad (1)$$

Equation (1) originates from the Weibull or Kohlrausch-Williams-Watts function, in which polymeric deformation can be described by a mechanical model consisting of time-dependent latch elements.[21,36] For viscoelastic recovery, the $\varepsilon_{\mathrm{r}}$ function depends

on the Weibull shape parameter, $\beta$, and characteristic life, $\eta$. As recovery time $t$ approaches $\infty$, there is a residual (permanent) strain, $\varepsilon_f$, resulting from viscous flow effects. These parameters from equation (1) are represented schematically in Figure 1, with values from the curve-fit shown in Figure 5. Since $\varepsilon_f$ is predicted to be very small in Figure 5 ($<10^{-4}$%), virtually all the available recovery is indicated to be viscoelastic, suggesting that viscous flow has an insignificant influence on the viscoelastic prestressing mechanism. By using equation (1) to extrapolate the curve to $8.766 \times 10^6$ h (1000 years), $\varepsilon_{rvis}(t)$ is predicted to be 0.185%, i.e. three orders of magnitude greater than $\varepsilon_f$.[31] Clearly, this suggests that viscoelastic activity, under the conditions considered here, is a long-term phenomenon.

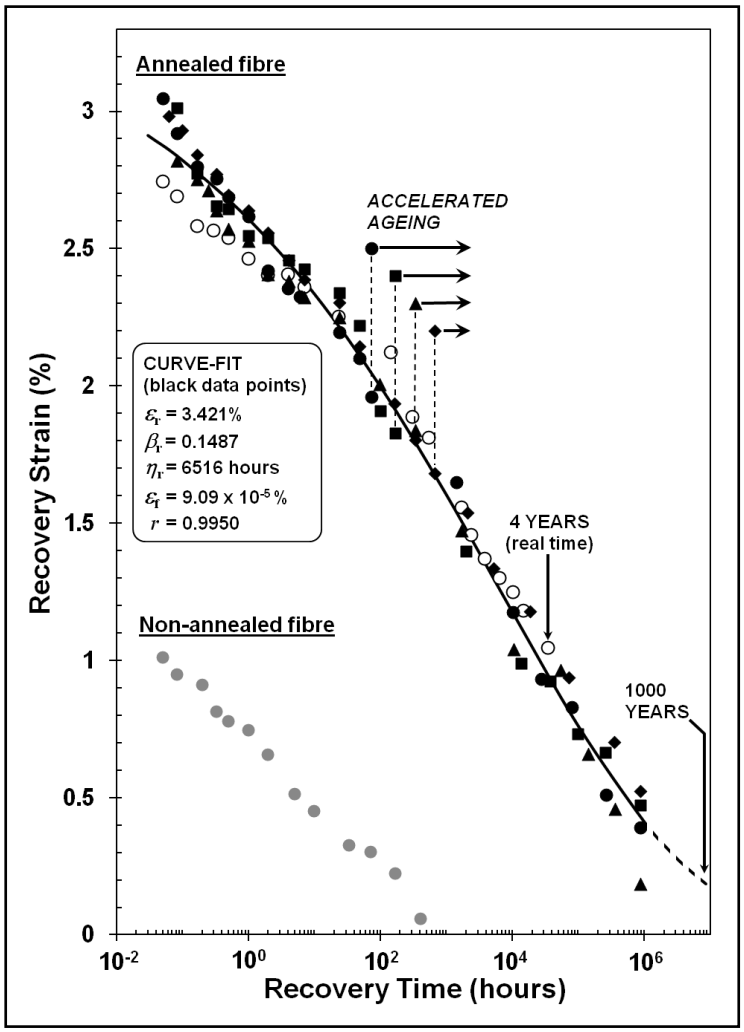


Fig. 5. Recovery strain data at 20°C from nylon 6,6 yarn after being subjected to 24 h creep at 342 MPa. For fibre annealed prior to creep, white data points were measured in real time and black data points are from four samples subjected to periods of accelerated ageing. The curve and parameters are from equation (1), where $r$ is the correlation coefficient.[28,29]

Recovery strain measurements from accelerated ageing, as shown in Figure 5, become impractical beyond the equivalent of 100 years at 20°C. The only alternative therefore, is to subject VPPMC samples (together with control sample counterparts) directly to accelerated ageing. Subsequently, these can be evaluated by Charpy impact testing to determine whether there is any deterioration in performance with age.

*Time-temperature superposition*

When polymeric fibres are subjected to creep, the resulting viscoelastic recovery rate will increase if their temperature is raised; thus time-temperature superposition principles can be considered. For many polymeric materials, these principles enable the implementation of accelerated ageing methods, if the appropriate shift factor, $\alpha_T$, is known. Here, $\alpha_T$ equates an elevated temperature to a shift in time, i.e. ageing. In previous studies,[28,29] $\alpha_T$ was evaluated for 60°C relative to 20°C, so that samples of previously stretched nylon 6,6 yarn could be subjected to periods of increased viscoelastic recovery at 60°C to produce the accelerated ageing data in Figure 5.

As highlighted in the previous section, going beyond 100 years of accelerated ageing becomes impractical for nylon fibre strain measurements. Thus VPPMC samples, with control sample counterparts, were subjected to longer-term exposures at 60°C (up to 2322 h). Following Charpy impact testing at 20°C, no deterioration in impact performance was observed, even at an equivalent age of 1000 years at 20°C.[29] The most recent study[31] has successfully demonstrated that nylon 6,6 VPPMCs can be subjected to accelerated ageing at 70°C. Here, viscoelastic activity would have been 76300 times faster at 70°C, relative to 20°C. Three batches of composite samples (i.e. 15 test and 15 control) were produced and stored at room temperature (19–22°C) for 336 h (2 weeks) before being subjected to a constant temperature of 70°C for 2298 h. The samples were then stored at room temperature for a further 336 h before undergoing Charpy impact testing. The mean (± standard error) impact energy absorption from the VPPMC samples was 47.5 ± 3.3 $kJm^{-2}$ and, with the control samples at 34.1 ± 1.3 $kJm^{-2}$, the increase in impact energy absorbed due to viscoelastically generated prestress was ~40%. Thus although this procedure, at least in the context of time-temperature superposition, resulted in the samples being aged to the equivalent of 20000 years at 20°C there was no observable deterioration in impact performance.

*The VPPMC time-temperature boundary*

Although ageing to an equivalent of 20000 years clearly demonstrates the longevity of these VPPMCs, the result outlined above does not provide a realistic or useful measure of practical life. Increasing the ambient temperature beyond 20°C will reduce VPPMC life (in relation to viscoelastic activity); hence longevity must be quantified by temperature as well as time. This requirement is met by Figure 6. Here, the time-temperature boundary indicates that these VPPMCs should, for example, show no deterioration in impact performance for at least 25 years at a constant ambient temperature of 50°C. Clearly, this suggests that VPPMC technology is viable for most practical applications.

Figure 6 also indicates that VPPMC processing with high temperature matrix curing cycles could be somewhat restricted. Nevertheless, several hours exposure to a moderately raised curing temperature of (for example) 80°C should be feasible, whilst maintaining an acceptable (subsequent) duration of operation at lower ambient temperatures. In this context, it is worth noting that low temperature curing resins are of interest for applications such as aerospace, since they would enable autoclave-free curing and lower cost tooling.[37,38]

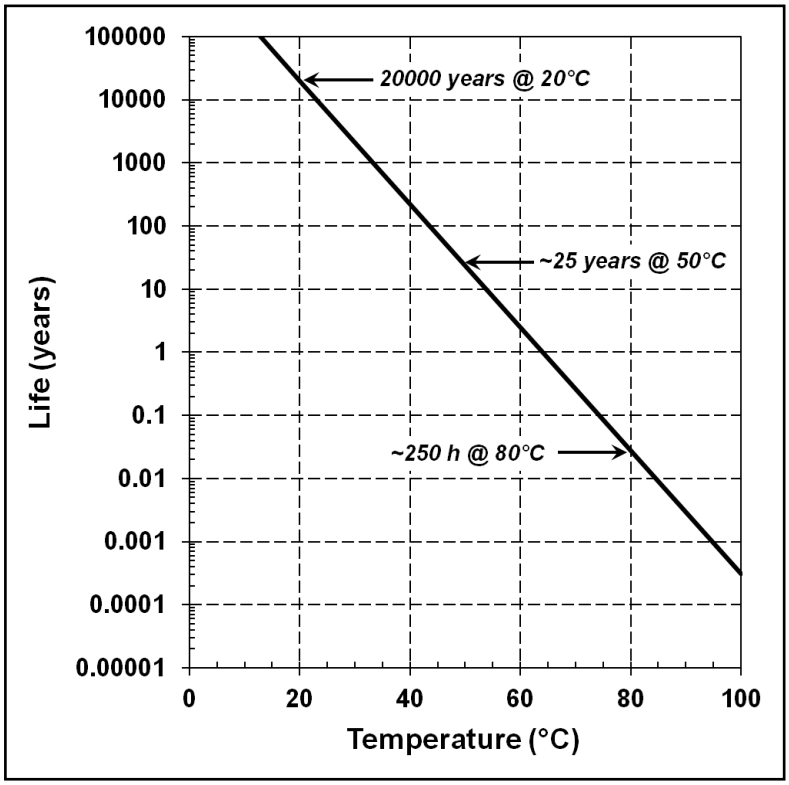


Fig. 6. VPPMC life as a function of ambient temperature, based on a time-temperature equivalent of 20000 years at 20°C.[31]

*EPPMC longevity*

Although EPPMCs are more established than VPPMCs, there appear to have been no studies, historically, relating to the longevity of EPPMCs: only Zhigun[4] referred to samples being stored at room temperature for three months prior to evaluation. Thus the comment in the Introduction section, that fibre-matrix creep effects within an EPPMC could cause the prestress to deteriorate progressively with time, has remained speculative. In a most recent study however, of glass fibre - polyester resin EPPMCs,[39] some age-related testing has been reported. Here, Mostafa et al have observed a decrease of up to 15% in flexural strength within the first three months after moulding. Their subsequent data, up to ~5 months, shows that the rate of decrease may reduce towards zero; nevertheless, longer term behaviour (years) must still remain open to speculation.

The performance of EPPMCs at elevated ambient temperatures is also open to speculation. Although high temperature curing can be used in EPPMC production (whilst prestressing loads are maintained), elevated temperatures in service may exacerbate any fibre-matrix creep effects, thereby reducing the useful life of EPPMCs.

## Characteristics of viscoelastically generated prestress

*Viscoelastic recovery force*

Long-term viscoelastic activity is demonstrated by Figure 5, but there is no information on the force output associated with these fibres when constrained within their VPPMC matrix. The force-time relationship was however obtained from a

separate study.[40] Here, annealed nylon 6,6 yarn was subjected to a 24 h creep stress of 320 MPa and following removal of the creep load, the loose yarn was allowed to contract to a fixed strain (~2%) within a short time $\Delta t$, to become taut. This enabled the resulting viscoelastic recovery force to be monitored. The force was found to increase with time and, using the following modified Weibull equation, was predicted to reach a limiting value of 12 MPa as time $t$ approached $\infty$:

$$\sigma(t) = \sigma_v \left[ \exp\left( -\left( \frac{\Delta t}{\eta} \right)^{\beta} \right) - \exp\left( -\left( \frac{t}{\eta} \right)^{\beta} \right) \right] \qquad (2)$$

Here, the $\sigma_v$ function is the time-dependent viscoelastically generated stress, as determined by the characteristic life ($\eta$) and shape ($\beta$) parameters. Nevertheless, the force output in this work[40] was only monitored over a period of 2700 h. An updated (previously unpublished) plot of this recovery force, over three years, is shown in Figure 7. Here, the longer duration provides a more reliable prediction of the limiting value from equation (2), this being 15.4 MPa (i.e. 4.8% of applied stress) as $t$ approaches $\infty$.

Although these findings provide a direct indication of force output from recovering fibres, the results would not necessarily relate to the behaviour of an actual VPPMC, especially in the longer term. Stress transfer between fibres and matrix within an actual VPPMC occurs through shear at fibre-matrix interfaces and gradual mechanical changes that may occur in a real resin matrix are not accounted for by monitoring force output from fibres being held at a fixed strain. Thus other investigative methods, based directly on VPPMCs, must be considered.

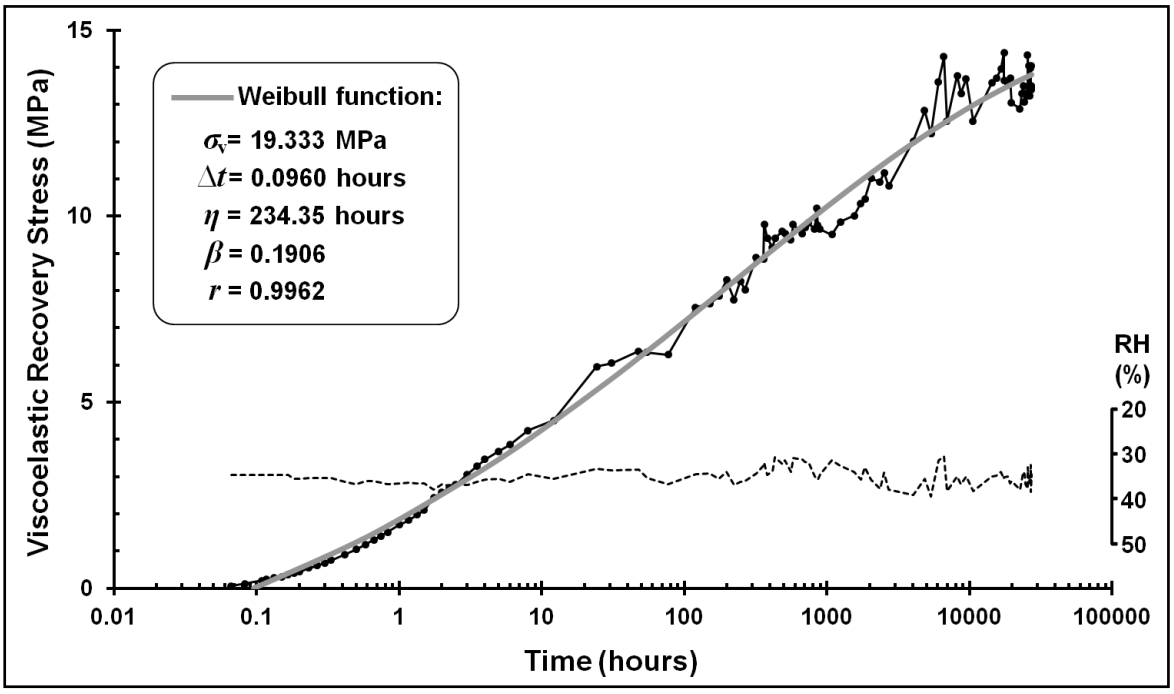


Fig. 7. Viscoelastic recovery stress output (force exerted across fibres) from nylon 6,6 yarn, for readings recorded at 20-20.9 ºC, 31-39% RH. The curve shows equation (2) fitted to the data, with parameters and correlation coefficient, $r$. This is a plot from previous work,[40] updated to 3 years (27000 h).

*Prestress investigations within VPPMCs*

A recent preliminary study[41] of two relatively uncommon methods to investigate fibre-matrix interactions and resulting prestress characteristics were evaluated: (i) the scanning electron microscope mirror effect (SEMME) and (ii) Vickers microhardness measurement.

The SEMME technique involves irradiating an insulating sample in an SEM with a high voltage (10s of kV) over a controlled injection time. This causes negative charges to become trapped and stabilised within the sample, which produce an electric field in the vacuum (sample) chamber of the SEM. Subsequent observation of the sample with a lower energy electron beam (100s of volts), results in the beam electrons being reflected from an equipotential surface produced by the electric field. The arrangement is therefore analogous to the behaviour of a convex mirror in visible light. The resulting mirror image can be observed on the SEM viewing screen as a distorted view of the SEM vacuum chamber, and measurement of the electron beam exit orifice in the mirror image provides information on the quantity of trapped and stabilised charges, compared with charges that have diffused through the sample. Thus it has been used to investigate the dielectric behaviour of fibre-reinforced composites, such as glass fibre/epoxy resin.[42] Here, the fibre/matrix interface regions were observed to play a major role in the trapping or diffusion of charges, where charge diffusion is associated with high interface strength.

Since viscoelastically generated stresses are created at the fibre/matrix interface regions in our composites, SEMME analysis has provided a means to investigate prestress effects within a VPPMC. The work demonstrated that prestressed samples trapped ~30% fewer charges than control samples, implying that the prestressed samples possessed higher interfacial strength. This may be due to the prestress effect reducing the availability of interfacial defects that are capable of trapping charges and the reduction in defects improves fibre-matrix interfacial adhesion.[41,43]

The other method, Vickers microhardness measurement, is an established technique, principally for metal and ceramic materials. It consists of indenting a material with a diamond indenter utilising a specific load for a fixed duration and calculating hardness by measuring the geometrical parameters of the indentation; the larger the indentation, the softer the material. As a result of viscoelastically generated prestress, the microhardness of VPPMC samples was 20% and 33% higher than corresponding control samples at 2.0% and 15% $V_f$ respectively. This can be attributed to compressive stresses within the VPPMC matrix, including the sample surface, and these must impede indentation forces. Since the load applied during microhardness testing must overcome these lateral stresses, a smaller indentation (hence greater microhardness) is produced.[41]

Future investigations with these two techniques are expected to reveal further information on prestress behaviour. These may, for example, provide further insight into the dependence of prestress characteristics on longer term changes in matrix properties.

*Prestress: towards process optimisation and production flexibility*

Traditionally, a 24 h creep stress has been applied to polymeric fibres for VPPMC production. Although this is a convenient duration for research purposes, such a lengthy period would be less practical for VPPMC production in a commercial

environment and recent work[44] has focused on reducing the creep time by increasing the applied creep stress.

By using nylon 6,6 fibres, it was found that the previously adopted viscoelastic creep strain, requiring 330 MPa for 24 h, could be achieved over a shorter duration; i.e. 92 min at 460 MPa and 37 min at 590 MPa. Subject to avoiding fibre damage however, it may be possible to reduce this creep time further, possibly down to several minutes. From the three creep settings investigated, elapsed recovery strain values were similar; moreover, Charpy impact test data from corresponding VPPMC samples showed no significant differences in impact energy absorption, these being ~56% greater than their control counterparts.[44]

As outlined earlier, the decoupling of fibre stretching and moulding operations in VPPMC production facilitates the manufacture of complex composite structures. Viscoelastically generated prestress also offers further production flexibility: previously stretched fibres could be stored, if required, under refrigerated conditions, either as separate yarn or with partially cured resin (i.e. prepreg) for subsequent VPPMC production at other sites. This arises from the time-temperature superposition characteristics represented by Figure 6, in that refrigeration can be expected to retard viscoelastic recovery mechanisms to facilitate long-term storage.

## Future directions

### *Alternatives to nylon fibre VPPMCs*

Although nylon 6,6 fibre VPPMCs have been used as the principal research vehicle, other fibres may have the potential for creating viscoelastic prestress, thereby increasing opportunities for exploitation. For example, eco-friendly VPPMCs based on plant fibres are a possibility. An investigation by other researchers into VPPMCs based on bamboo has demonstrated that flexural toughness increased by 28%.[45] Moreover, it is clear that polymeric fibres with mechanically superior properties to nylon could be utilised, provided they have appropriate viscoelastic properties. Thus recently, our own research has focused on VPPMCs using ultra-high molecular weight polyethylene (UHMWPE) fibres, which are ~4 times stronger and >20 times stiffer than nylon 6,6 fibres. Here, we found increases of 20–40% in flexural modulus[46] and Charpy impact energy absorption.[47]

A further option is to exploit the use of fibre commingling in VPPMCs. For example, nylon 6,6 fibres, used for creating viscoelastically generated prestress, could be commingled with common reinforcing fibres, such as glass or carbon. Other fibres in commercial use may include aramid (Kevlar) fibres which, compared with nylon 6,6, have superior strength and stiffness. An initial study of nylon 6,6–Kevlar fibre hybrid composites by Charpy impact and flexural stiffness testing[48] has demonstrated that (i) hybrid composites (with no prestress) absorb more impact energy than Kevlar fibre-only composites, due to ductility of the nylon fibres; (ii) prestress further increases impact energy absorption in the hybrid case by up to 33% and (iii) prestress increases flexural modulus by 40% in the hybrid composites.

It is evident here, that going beyond basic nylon 6,6 fibre VPPMCs could open up a range of commercial opportunities, where improvements in mechanical properties are required, without the need to increase mass or section sizes. In particular, this would be applicable to requirements for improved impact toughness and flexural stiffness. Thus

potential applications include crashworthy (vehicular) and other structures requiring impact resistance, such as aerospace parts, wind turbine blades and protective apparel.

*Nanofibre-based VPPMCs*

Since the viscoelastic prestress technique has been successfully demonstrated with conventionally sized fibres (i.e. 10–30 μm in diameter), the possibility of applications involving VPPMCs based on nanofibres can be considered. Scaling down VPPMC processing to such small dimensions might be technically challenging, but the ability to produce prestressed nanofibre composites may open up a new range of opportunities. One area of interest could be dental restorative materials (DRMs), such as direct-filling composites (wear-resistant inorganic filler particles in acrylic-based resin). These have been widely accepted as replacements for traditional dental amalgams. Nevertheless, acrylic-based DRMs have lower strengths (80–120 MPa) compared with amalgams (>400 MPa).[49] Although there are many variables and some of the published evidence can appear to be contradictory, acrylic-based DRMs tend to have a shorter life (5–10 years) than amalgams (>15 years).[49,50] Fracture in acrylic-based DRMs is the main cause of failure within the first 5 years.[51] Short life has been attributed to masticatory stresses being transmitted to filler particles projecting from the occlusal (biting) surface; the submerged regions of these particles provide stress concentrations which enable small cracks to propagate into the (softer) matrix.[49]

Clearly, matrix crack propagation could be impeded by compressive prestress produced from fibre reinforcement. Glass fibre-reinforced acrylic-based DRMs are available[52] and there has been some interest in the feasibility of glass fibre EPPMCs as DRMs.[12] Polymeric nanofibre reinforcement also offers possibilities, e.g. DRMs using nylon electrospun nanofibres.[49] Thus VPPMCs based on nanofibres such as nylon or UHMWPE could hold promise for such a small-scale application in a biological environment. Here, after the fibre stretching operation, VPPMC technology would allow these fibres to be chopped and randomly distributed throughout the DRM matrix, which could then be stored as refrigerated prepreg prior to in-situ curing at the dental clinic.

*Viscoelastically prestressed ceramic matrix composites (VPCMCs)*

Fibre-reinforced concrete (FRC) has been developing since the early 1960s.[53] FRC contains randomly oriented fibres to impede cracking and polymer fibres are routinely employed.[53-55] Polypropylene fibres are the most commonly used, though nylon fibres show a rising acceptance.[54] For example, nylon fibre-based FRC has been found to sustain higher flexural stress levels.[55] Therefore, viscoelastic prestressing principles may offer further opportunities for increasing crack resistance within FRC materials. The polymeric fibres could be processed (i.e. annealed, subjected to creep, then chopped to size) and if required, stored under refrigerated conditions (to retard viscoelastic recovery), prior to being mixed on site. In addition to on-site casting, this technology could provide significant benefits to precast plant production, as it would enable prestressed, precast concrete components to be produced with complex shapes.

*Shape-changing (morphing) structures based on VPPMC technology*

As outlined in the Introduction section, there has been interest in the exploitation of EPPMCs for use as shape-adaptive (morphing) composite structures. These offer opportunities for improved aerodynamic performance and functionality without the need for increased mass and complex construction. Thus for example, morphing aerofoils can facilitate camber and twist changes without the need for conventional actuation mechanisms.[16] The simplest morphing structures are those which are bistable; i.e. they can 'snap through' between one of two states. Recently, a bistable structure has been developed, based on VPPMC technology. This consists of VPPMC strips bonded to the sides of a thin, flexible resin-impregnated fibre-glass sheet.[56,57] Each strip has an inherent deflection, from bending forces caused by non-uniform fibre spatial distributions. This enables pairs of strips to be orientated to give opposing cylindrical configurations within the sheet, thereby enabling the sheet to snap-through between two states. Figure 8 shows a VPPMC-based bistable sample in both of these states.

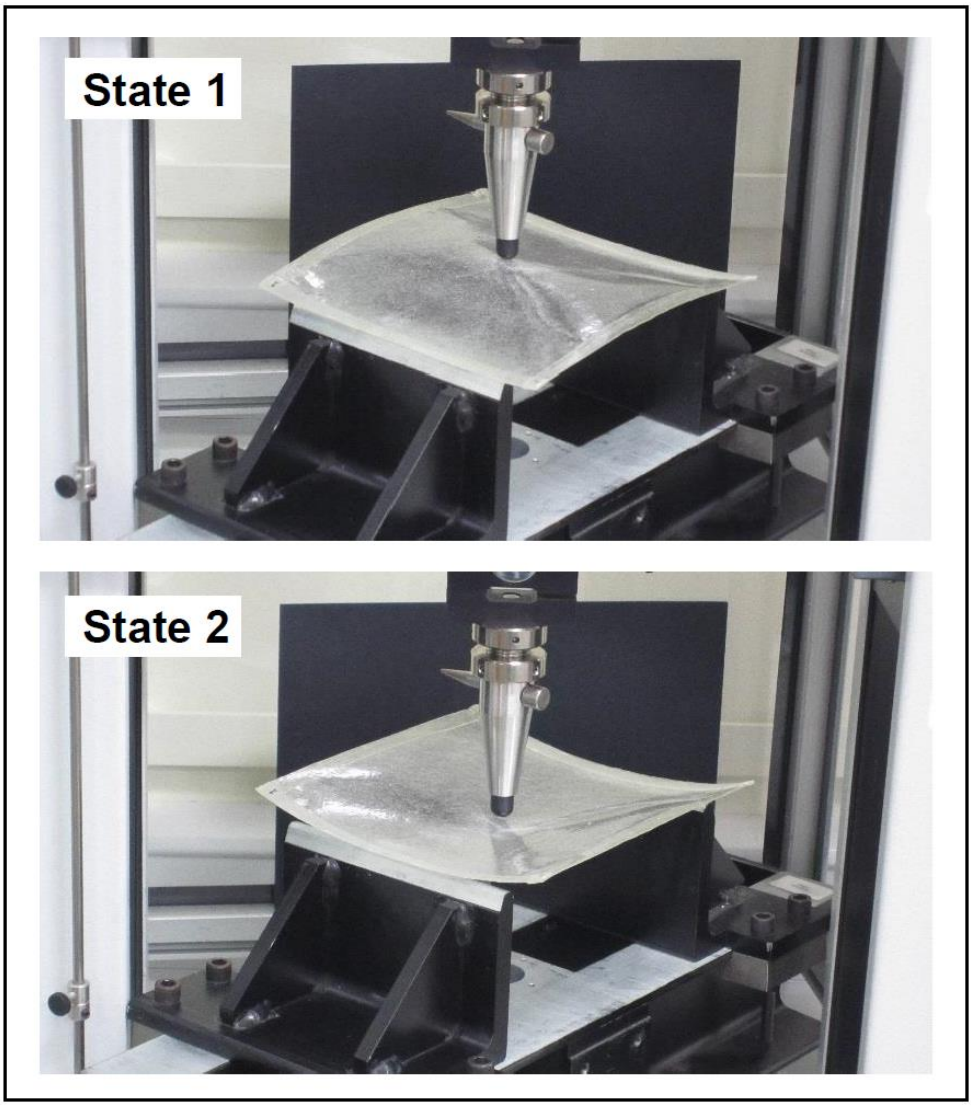


Fig. 8. Set-up used to evaluate the snap-through characteristics of a VPPMC-based bistable composite sample, showing the two states.[56,57]

## Conclusions

An overview has been presented of research into an alternative approach to create prestress in polymeric matrix composites. In contrast with conventional methods, which rely on elastically generated prestress to improve the mechanical properties of a fibre-reinforced composite, the approach exploits viscoelastic recovery mechanisms from polymeric fibres within the composite matrix. Mechanical properties of the resulting viscoelastically prestressed composites can be improved by up to 50% compared with control (unstressed) counterparts. Most importantly however, is that this method offers the benefits of increased flexibility in manufacture and, for polymeric matrices, the probability of greater longevity in service, compared with the elastic prestressing route. With appropriate interest and support from industry, opportunities could exist for a wide range of commercial developments, from the small-scale (e.g. dental restorative materials) to large scale structures (e.g. wind turbine blades).

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