

Prestressed Polymeric Matrix Composites: Longevity Aspects

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Elastically prestressed polymeric matrix composites (EPPMCs) are produced by stretching fibers (e.g., glass) within the composite during matrix curing. The resulting prestress can enhance mechanical performance, without increasing section dimensions or weight. Viscoelastically prestressed polymeric matrix composites (VPPMCs) can provide similar benefits, these being produced by subjecting polymeric fibers (e.g., nylon 6,6) to a creep load, which is released prior to molding. Although VPPMCs offer simplified processing and flexibility in product geometry, long-term viscoelastic activity within the prestressing fibers is sensitive to time-temperature limitations. In this study, nylon 6,6 fiber-polyester resin samples were subjected to accelerated ageing. Using time-temperature superposition, the samples were maintained at 70°C for 2,298 h, representing a 20-fold ageing increase over previous work. Subsequent Charpy impact testing (at 20°C) demonstrated that the VPPMC samples absorbed ~40% more energy than corresponding control (unstressed) counterparts; i.e., no deterioration in impact performance was observed, over a duration equivalent to ~25 years at 50°C. In contrast, the longevity of EPPMCs remains unknown, but it is suggested that progressive localized matrix creep at the fiber-matrix interface regions may cause a deterioration in elastically generated prestress with time and/or elevated ambient temperatures. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

Elastically prestressed polymeric matrix composites (EPPMCs) are comparable to prestressed concrete, in that fibers within the composite are stretched to maintain an elastic strain during matrix curing. Compressive stresses are produced within the matrix on solidification, counterbalanced by residual fiber tension. While early EPPMC studies were focused on laminates [1, 2], later investigations with unidirectional glass fiber EPPMCs have indicated increases in tensile strength and elastic modulus of ~25% and ~50% respectively [3], compared with unstressed counterparts. Moreover, impact resistance and

flexural properties (stiffness and strength) have been found to increase by up to 33% [4, 5]. These improvements are explained by the residual stresses (i) impeding or deflecting propagating cracks and (ii) reducing strains within the composites from external tensile or bending loads [3–5]. More recent investigations include unidirectional glass fiber EPPMCs as potential dental materials, the prestress increasing flexural strength by ~30% [6] and unidirectional carbon fiber EPPMCs, with increases of ~30% in impact toughness [7]. In addition to opportunities for EPPMCs to improve mechanical properties (without the need to increase section dimensions or weight), there has been interest in their use as bistable (morphing) composites, either as prestressed laminates [8] or as unidirectional fiber prestressed structural elements [9].

Despite the benefits elastic prestressing may offer, the need to apply fiber tension while the matrix cures may cause fiber length, orientation, and spatial distribution to be restricted, which compromises mold geometry [10]. Moreover, stretching rig design with appropriate fiber clamping can be technically challenging [8, 11]. A potential major limitation to the use of EPPMCs however, arises from the matrix being polymeric: localized creep at the fiber-matrix interface regions may be expected, in response to the elastically generated prestress, so that there could be a progressive deterioration in this prestress with time [10].

Viscoelastically prestressed PMCs (VPPMCs) avoid the need for simultaneous fiber stretching and molding operations. Instead, polymeric fibers are subjected to tensile (viscoelastic) creep and the creep load is released before the fibers are molded into a matrix. On solidification, the previously strained fibers continue to attempt viscoelastic recovery; this produces compressive stresses in the matrix, which are counterbalanced by residual tension within the fibers, similar to an EPPMC. Since fiber stretching and molding operations are decoupled, a key benefit is the flexibility that VPPMC production can offer: relatively simple equipment is required for applying a creep load to fiber tow and following load release, the fibers can be chopped to any length and placed in any orientation within any shape of mold that can be filled with a matrix resin.

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Using nylon 6,6 fibers, VPPMC samples absorb typically 25–30% more impact energy from Charpy impact tests than their control (unstressed) counterparts, with some samples reaching increases of 50% [10, 12–16]. Other mechanical tests have shown that these VPPMCs possess improved properties over their control equivalents, i.e., increases in tensile strength, modulus, and energy absorption exceeding 15, 30, and 40%, respectively [17] and ~50% higher flexural modulus [18]. As well as nylon fiber-based VPPMCs, other researchers have successfully demonstrated VPPMCs based on bamboo, which increased flexural toughness by 28% [19]. Our most recent published research has focused on VPPMCs using ultra-high molecular weight polyethylene (UHMWPE) fibers; we have found increases of 20–40% in flexural modulus [20] and Charpy impact energy absorption [21]. Therefore, various reinforcements may hold promise; however, nylon fiber-based VPPMCs are, to date, the most established.

In addition to production flexibility, a key advantage of VPPMCs is that any potential for deterioration through localized matrix creep would be offset by an active response from longer term viscoelastic recovery mechanisms within the polymeric fibers [10]. Nevertheless, there is potentially a major limitation with VPPMCs, in that viscoelastic activity is temperature-sensitive. Thus high-temperature curing cycles or lengthy exposures to hot ambient conditions could damage or at least accelerate the viscoelastic recovery mechanisms, which may render the prestress ineffective. Therefore, despite the benefits that VPPMC principles may offer, time-temperature limitations could impede the development of VPPMC technology into practical composite structures. This article addresses further investigations (by Charpy impact testing) using time-temperature superposition techniques.

BACKGROUND AND DEVELOPMENT OF AGEING PARAMETERS

Long-Term Viscoelastic Activity

To offset the potential for deterioration in prestress from matrix creep (especially at the fiber-matrix interface), the fibers within a VPPMC should be capable of long-term viscoelastic recovery. For polymeric fibers, this capability can be determined from recovery strain measurements resulting from creep loading conditions used for VPPMC production. Figure 1 shows recovery strain data, measured at 20°C, for nylon 6,6 fiber as untwisted continuous yarn [14, 15]. Full details are available in Refs. 14 and 15 but the main points are summarized here. Recovery strain becomes insignificant for non-annealed (i.e., as-received) yarn within 1,000 h of releasing the creep stress; however, annealing the yarn prior to creep (150°C for 0.5 h) causes viscoelastic recovery to remain active over a much longer timescale. The gray data points

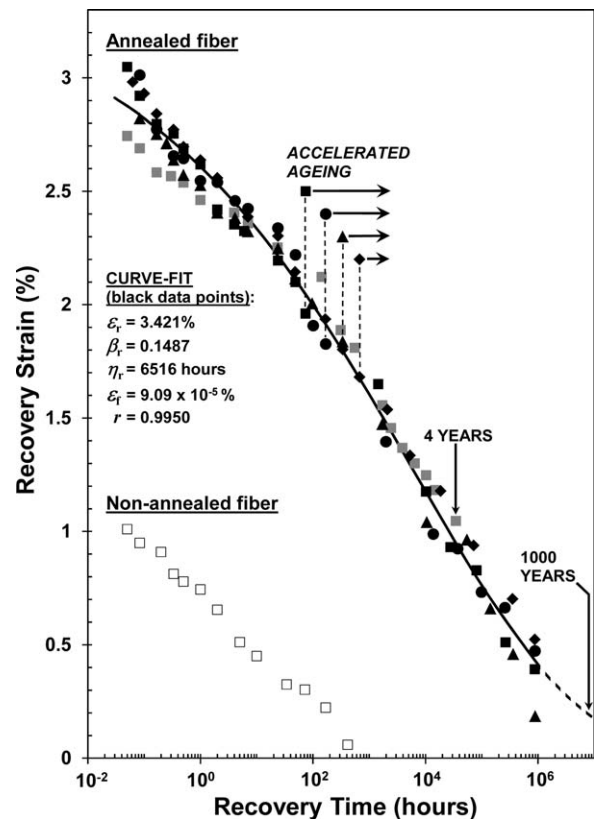


FIG. 1. Recovery strain data at 20°C from nylon 6,6 yarn following 24 h creep at 342 MPa. For yarn annealed prior to creep, gray data points were measured in real time up to 3.5×10^4 h (4 years); black data points are from four samples, each subjected to periods of accelerated ageing initiated at different recovery times (as shown), up to 9×10^5 h (100 years). The curve shows Eq. 1 fitted to the black data, with listed parameters and r , the correlation coefficient; after Refs. 14 and 15.

in Fig. 1 represent strain measurements taken in real time, up to 4 years. To go beyond a few years, accelerated ageing techniques are required and these were used to obtain the black data points, up to the equivalent of 100 years at 20°C. It is clear from Fig. 1 that the data from real-time and accelerated ageing show good agreement and the curve, fitted to the black data points, represents the following equation for recovery strain as a function of time, t :

$$\varepsilon_{vis}(t) = \varepsilon_r \left[\exp \left(- \left(\frac{t}{\eta_r} \right)^{\beta_r} \right) \right] + \varepsilon_f \quad (1)$$

Equation 1 is based on the Weibull or Kohlrausch-Williams-Watts (KWW) function, in which polymeric deformation can be represented by a model consisting of time-dependent mechanical latch elements [22, 23]. The permanent strain from viscous flow, ε_f , is a residual strain as recovery time t approaches ∞ . For viscoelastic strain recovery, the ε_r function depends on the Weibull shape parameter, β_r , and characteristic life, η_r , and the resulting parameter values are shown in Fig. 1. Since ε_f is predicted to be close to zero ($<10^{-4}\%$), virtually all

available recovery is viscoelastic, indicating that viscous flow would have an insignificant effect on the viscoelastic prestressing mechanism. By extrapolating to 8.766×10^6 h (1,000 years), Eq. 1 predicts $\varepsilon_{\text{vis}}(t)$ to be 0.185%, i.e., three orders of magnitude greater than ε_f . Thus viscoelastic activity, under these conditions, is a long-term phenomenon.

Although Fig. 1 demonstrates long-term viscoelastic activity, it provides no information on the associated force output from such fibers constrained within the VPPMC matrix. In a separate study, the force-time relationship was determined by monitoring force output from viscoelastically recovering nylon 6,6 yarn [24]. Here, annealed yarn was subjected to a 24 h creep stress of 320 MPa and, following stress removal, the loose yarn was allowed to contract to a fixed strain, from which the recovery force could then be monitored. The main finding from Ref. 24 was that the viscoelastic recovery force increased with time (to 2,700 h), and was predicted to reach a limiting value of 12 MPa (i.e., 3.8% of applied stress) as t approached ∞ . Subsequent monitoring to 25,000 h has shown force output to progress in accordance with this trend [15].

Although recovery strain measurements (Fig. 1) can be made from samples subjected to accelerated ageing, strain measurements beyond the equivalent of 100 years at 20°C become impractical; thus Eq. 1 must be relied upon to predict values over longer timescales. Moreover, if accelerated ageing techniques could be applied to viscoelastic recovery force measurements, the results may further verify earlier findings, that force grows to a limiting value with time [24] but they would not necessarily relate to the long-term behavior of a VPPMC, since matrix behavior is not accounted for. Therefore, the only alternative is to subject VPPMC samples (and control counterparts) directly to accelerated ageing; these can then be evaluated, by Charpy impact testing, for evidence of any deterioration in performance with age.

Time-Temperature Superposition

If a polymeric fiber is subjected to creep, the subsequent viscoelastic recovery rate can be expected to increase if temperature is raised and this corresponds with time-temperature superposition principles. For many polymers, the effect enables accelerated ageing to be undertaken, if the appropriate shift factor, α_T , is known. Here, α_T equates an elevated temperature to a shift in time (ageing). From published data on creep [25] and stress relaxation [26] for nylon 6,6 fiber, a linear relationship between $\log \alpha_T$ and temperature allows α_T to be obtained over a suitable temperature transition. Thus, $\log \alpha_T$ was found to be 3.577 at 60°C relative to 20°C; i.e., rates of creep, stress relaxation, or some other measure of viscoelastic activity would be 3,776 times faster at 60°C relative to 20°C [14].

By subjecting samples of viscoelastically recovering nylon 6,6 yarn to periods of 60°C, this α_T value was used to acquire the accelerated ageing data in Fig. 1. As stated

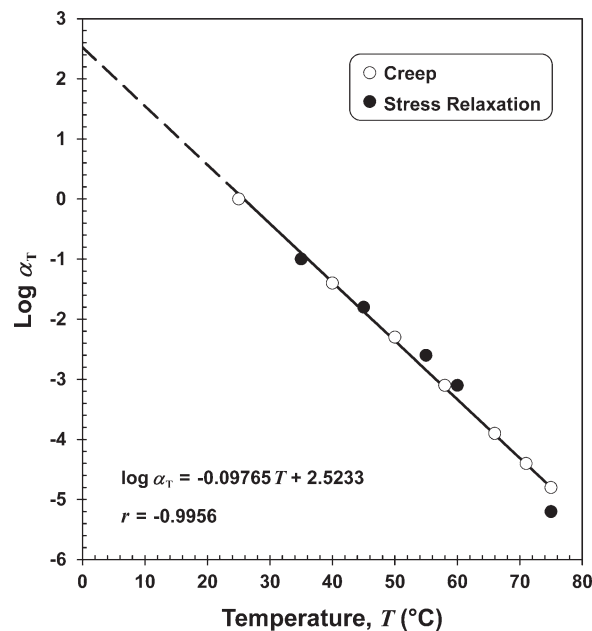


FIG. 2. Plot of the time-temperature shift factor, α_T , as a function of test temperature (data range 25–75°C) using published data for creep [25] and stress relaxation [26] in nylon 6,6 fiber. Reference temperature ($\log \alpha_T = 0$) was 25°C. The line-fit and equation are from linear regression; r is the correlation coefficient. This is revised from a previous plot (data range 25–60°C) [14].

earlier however, recovery strain measurements beyond the equivalent of 100 years at 20°C become impractical; hence, Charpy impact testing of aged VPPMC samples becomes the most viable option. In previous work [15], batches of VPPMC samples and their control counterparts were subjected to periods of 60°C for more than 3 months, prior to Charpy impact testing at 20°C. These results demonstrated no deterioration in impact performance over a duration equivalent to 20°C for 1,000 years or 40°C for 20 years. In the current work, this time-temperature envelope for VPPMC durability is extended further, by up to 20-fold.

To provide a significant increase in accelerated ageing within an acceptable period (~ 3 months) requires the ageing temperature to be higher than 60°C. Figure 2 shows the previously adopted $\log \alpha_T$ versus temperature plot (25–60°C) [14] extended to show data from creep and stress relaxation [25, 26] up to 75°C. This enables $\log \alpha_T$ to be determined at 70°C relative to 20°C. Linear regression to 75°C gives a slightly steeper gradient of -0.09765 in Fig. 2, compared with -0.08943 to 60°C [14] and the resulting $\log \alpha_T$ value for a 20–70°C transition is 4.8825. Therefore, viscoelastic activity would be 76,300 times faster at 70°C relative to 20°C. Thus by subjecting VPPMC samples (with control counterparts) to 70°C for 2,298 h (i.e. ~ 3.2 months), the prestress effect from viscoelastic recovery mechanisms will be aged to the equivalent of 20,000 years at 20°C, based on data from Fig. 2. By using the parameter values shown in Fig. 1, Eq. 1 at 1.753×10^8 h (20,000 years) predicts $\varepsilon_{\text{vis}}(t)$

to be very low, i.e., 0.036%; nevertheless, this is still ~ 400 times greater than ε_f .

EXPERIMENTAL

Fiber reinforcement was from continuous untwisted multi-filament nylon 6,6 yarn (140 filaments, 27.5 μm filament diameter), supplied by Goodfellow Cambridge, UK. The nylon yarn was annealed in a fan-assisted oven (150°C, 0.5 h); this was essential for long-term viscoelastic recovery, as shown in Fig. 1. Moreover, to enable direct comparison, nylon yarn designated for unstressed “control” samples was also annealed at the same time. Nylon yarn designated for (prestressed) “test” samples was attached to a bespoke stretching rig and subjected to 340 MPa tensile creep stress for 24 h, while equivalent (annealed) control yarn was positioned in close proximity to the stretching rig for exposure to the same ambient conditions (19.5–21°C, 30–50% RH). On releasing the creep load, each yarn was folded, cut into lengths of ~ 500 mm and combed (brushed) into flat ribbons ready for molding.

The matrix material was a clear-casting polyester resin, as used in recent work [16, 20, 21, 27], i.e., Cray Valley Norsodyne E9252, mixed with 1% MEKP catalyst, supplied by CFS Fibreglass, UK. Gel-time (room temperature) was ~ 0.25 h. Unidirectional continuous fiber composites were open-cast in two aluminum molds, the process being completed within 0.5 h of the fiber stretching procedure. Each mold had a 10 mm wide channel for casting a 460 mm strip of test and control materials simultaneously from the same resin mix, to produce one batch. Following demolding (after ~ 2 h), the composite strips were each cut into five equal (80 mm) lengths and held under a weighted steel strip for 24 h to prevent any risk of stress-induced sample distortion.

Each batch consisted of five test and five control samples, the sample dimensions being 80 \times 10 \times 3.2 mm, all with a fiber volume fraction, V_f , of 2.2%. These were stored at room temperature (19–22°C) in polythene bags for 336 h (2 weeks) prior to them being subjected to accelerated ageing. A muffle furnace was used for accelerated ageing; this was calibrated for operation at 70°C and checked for long-term temperature stability ($\pm 0.5^\circ\text{C}$). Composite samples were placed as a single layer on an aluminum tray within the muffle furnace to ensure a uniform heat distribution. This arrangement enabled three batches (i.e., 15 test and 15 control samples) to be subjected to 70°C for 2,298 h. Following this heat treatment, the samples were stored in polythene bags at room temperature for a further 336 h prior to impact testing.

A Ceast Resil 25 Charpy machine with 7.5 J hammer, operating in accordance with BS EN ISO 179, was used for impact testing at 3.8 ms^{-1} . In common with earlier Charpy-based studies using open-cast nylon fiber/polyester matrix samples with a low V_f [10, 12–16], fibers tended to settle towards the bottom of the mold prior to

TABLE 1. Charpy impact test results from the three batches of composite samples, aged in terms of viscoelastic recovery, to an equivalent of 20,000 years at 20°C: 5 (prestressed) test and 5 (unstressed) control samples per batch..

Batch	Batch mean impact energy (kJ m^{-2})		Increase in energy (%)
	Test \pm SE	Control \pm SE	
1	43.5 \pm 3.0	34.5 \pm 1.3	26.1
2	53.4 \pm 1.0	33.9 \pm 1.4	57.4
3	45.8 \pm 5.9	34.1 \pm 1.4	34.2
Mean \pm SE	47.5 \pm 3.3	34.1 \pm 1.3	39.3 \pm 9.4

SE is the standard error of the mean.

curing. Thus samples were tested with the fiber-rich side facing away from the Charpy hammer and a diagram of this configuration has been previously published [10, 12, 13]. Testing was performed at 20°C and, as with the previous work on accelerated ageing [15], a 24 mm span was used.

RESULTS AND DISCUSSION

Impact Energy Absorption

Table 1 summarizes the Charpy impact data from the three batches of composite samples. Although the test samples show notable batch-to-batch variations, there is clearly an increase in impact energy absorbed (test samples relative to control counterparts) for all three batches, giving a mean increase of 39.3 \pm 9.4%. This compares well with the average energy increase (38.9 \pm 4.5%) obtained from three composite batches that had not been subjected to accelerated ageing, produced (with the same materials) and impact tested (at 336 h) under the same conditions [16]. Therefore, the results in Table 1 suggest that (i) viscoelastically induced prestress from the nylon fibers remains active after the accelerated ageing process, and (ii) there appears to be no deterioration in the increased energy absorption from this prestress mechanism.

Composite samples from Ref. 16 were identical to those produced for the current work, except that V_f was 3.3%. This gave mean Charpy impact values of 90.6 \pm 2.3 kJ m^{-2} (test samples) and 65.4 \pm 2.1 kJ m^{-2} (control samples), i.e., these are almost double the corresponding values in Table 1. Thus although Table 1 and Ref. 16 show a similar prestress generated increase in impact energy absorption ($\sim 39\%$), the 50% higher nylon fiber content in Ref. 16 enabled both test and control samples to absorb almost twice the impact energy due to the inherent toughness of the fibers; i.e., an effect independent of prestress mechanisms.

Further evidence of viscoelastically induced prestress remaining active for the impact-tested samples in Table 1 is shown in Fig. 3. Here, the debonded region is much

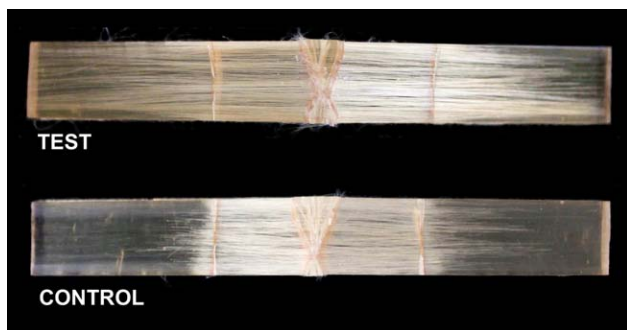


FIG. 3. Typical test (prestressed) and control (unstressed) samples after Charpy impact testing from the batches aged to an equivalent of 1.753×10^8 h (20,000 years) at 20°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

greater in the test sample, extending almost over the full sample length; in contrast, debonding within the control sample is mainly confined to the region bounded by the vertical crack in the vicinity of the Charpy anvil shoulders, either side of the sample center. These effects were observed for all samples evaluated in this study.

The region of impact-induced debonding being much greater in the test samples is consistent with observations from previous Charpy impact studies of nylon fiber-based VPPMCs [10, 12–16, 27]. Earlier investigations on these VPPMCs eventually led to the conclusion that prestress induced increases in impact energy absorption may arise from four mechanisms [15]: (i) matrix compression impeding crack propagation, (ii) matrix compression attenuating dynamic overstress effects, (iii) residual fiber tension causing a more collective response to external loads, and (iv) residual shear stresses at the fiber-matrix interface regions promoting energy absorbing fiber debonding over transverse fracture. A more recent study [16] suggests that (iv) is the principal mechanism, i.e., prestress enhanced residual shear stresses between fibers and matrix are triggered to promote fiber-matrix debonding (over transverse fracture) when they are subjected to externally imposed shear stresses caused by the impact process. This shear stress triggering mechanism has also been observed in glass fiber EPPMCs [4].

The Long-Term Performance of VPPMCs

The above findings demonstrate that the benefits from prestress in nylon fiber-based VPPMCs show no deterioration up to the equivalent of 20,000 years at a constant 20°C, thereby verifying the prevalence of viscoelastic activity predicted at this age by *Eq. 1* in the “Background” section. As reported in the “Introduction” section, VPPMCs have a potentially major limitation, in that viscoelastic activity is temperature-sensitive and, although this can be exploited for accelerated ageing purposes, it is clear that the long-term performance of these composites must be quantified by ambient temperature as well as time.

Figure 4 shows the new time-temperature boundary (i.e., 20,000 years at 20°C) established from this work. In

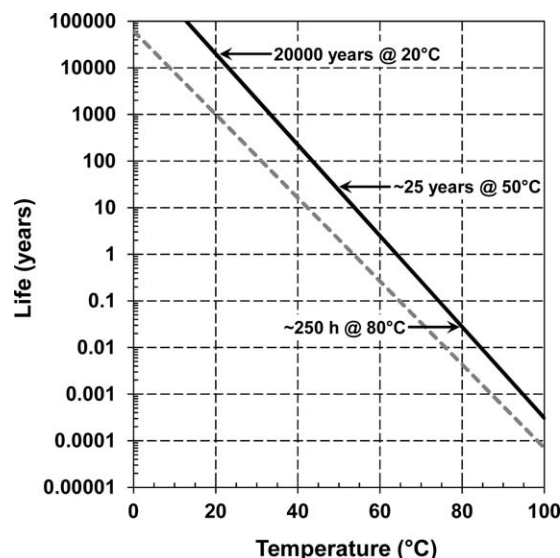


FIG. 4. VPPMC life as a function of ambient temperature (black line), based on the new time-temperature boundary, i.e., 20,000 years at 20°C. The broken (gray) line represents the previously established boundary (1,000 years at 20°C) from Ref. 15.

accordance with Fig. 2, increasing the ambient temperature will reduce the duration over which VPPMCs are known not to deteriorate. For comparison, the previously established boundary [15] is also shown (1,000 years at 20°C). The slightly steeper fall-off with temperature of the new boundary arises from the gradient value in Fig. 2 being $\sim 9\%$ larger than the original value [14] used for the previous boundary in Ref. 15. It is notable however that the new boundary indicates these VPPMCs would, for example, show no deterioration in impact performance after ~ 25 years at a constant 50°C ambient temperature. Clearly, this would make VPPMC technology viable for many, if not most practical applications.

It is also evident from Fig. 4 that the use of high temperature matrix curing cycles for VPPMC processing remains somewhat restricted, despite the new raised boundary. That said, at 80°C for example, the known limit of duration from Fig. 4 would be ~ 250 h. Thus several hours exposure to a moderately raised curing temperature should be possible, while maintaining an acceptable (subsequent) duration of operation. It is worth noting here that low temperature curing resins are of interest for applications such as aerospace, as they would allow autoclave-free curing and cheaper tooling [28, 29]; therefore future developments in resins and composites manufacture may reduce the need for high temperature curing cycles.

Elastic or Viscoelastic Prestressing?

Structurally, since VPPMCs require polymeric fibers with suitable viscoelastic characteristics, mechanical properties such as strength and stiffness can be expected to be inferior to EPPMCs based on glass or carbon fibers, especially when compared with nylon 6,6 fibers. Nevertheless,

as reported in the “Introduction” section, VPPMCs have now been demonstrated with UHMWPE fibers, which are ~ 4 times stronger and >20 times stiffer than nylon 6,6 fibers [20, 21]; hence, their mechanical performance is competitive with glass and carbon fibers. VPPMC strength and stiffness properties can also be enhanced by commingling nylon 6,6 fibers (for prestress) with other mechanically superior fibers, such as Kevlar [27]. Since however, VPPMCs require prestressing fibers that are heat-sensitive (such as nylon 6,6 or UHMWPE), it may be expected that applications involving high thermal loadings would favor the use of EPPMCs.

Compared with EPPMCs, VPPMCs are a relatively recent development and this article demonstrates that their longevity, even at elevated ambient temperatures, represents a practical product life (e.g., ~ 25 years at 50°C). Conversely, we are not aware of any published studies on the longevity of EPPMCs; only Zhigun [1] refers to EPPMC sheets being stored at room temperature for 3 months prior to evaluation. As reported in the “Introduction” section, the potential influence of localized creep at the fiber-matrix interface regions is particularly important here: in contrast with prestress being maintained by viscoelastic activity in VPPMCs, the prestress within EPPMCs may deteriorate with age. Although high temperature curing can be used (whilst prestressing loads are maintained) in EPPMC production, it can be speculated that elevated temperatures in service will exacerbate the fiber-matrix creep effect, thereby shortening the useful life of EPPMCs.

CONCLUSIONS

By using time-temperature superposition principles, nylon 6,6 fiber-based VPPMC samples have been subjected to accelerated ageing. The VPPMC samples (together with control counterparts) were maintained at a constant 70°C for 2,298 h (~ 3.2 months), which is equivalent to an exposure of 20,000 years at 20°C in terms of viscoelastic recovery within the nylon fibers. This is a 20-fold increase in ageing, over previous work. Charpy impact results from these samples suggest that viscoelastically generated prestress from the nylon fibers remains active after the accelerated ageing process, since there is no deterioration in increased impact energy absorption ($\sim 40\%$) from this prestress mechanism. The results have enabled a new time-temperature envelope to be established, which indicates that VPPMCs based on nylon 6,6 fibers should show no deterioration in impact performance after ~ 25 years at a constant 50°C ambient temperature.

In contrast, the longevity of EPPMCs remains open to speculation. As previously reported, progressive localized matrix creep at the fiber-matrix interface regions may cause a deterioration in elastically generated prestress with time; we also suggest that the effect could be exacerbated by exposure to elevated ambient temperatures.

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