TOWARDS "GREEN" VISCOELASTICALLY PRESTRESSED COMPOSITES

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Abstract
Viscoelastically prestressed polymeric matrix composites (VPPMCs) provide a means to improve mechanical properties without the need to increase composite component weight or section dimensions. In contrast with (conventional) elastically generated prestress, processing and product geometry limitations can be avoided, since fibre stretching and moulding operations are decoupled. Here, polymeric fibres are subjected to tensile creep, the applied load being removed before moulding the fibres into a matrix. The prestressed fibres impart compressive stresses (through viscoelastic recovery) to the surrounding matrix after curing, which is counterbalanced by residual tension within the fibres. Mechanical property improvements from VPPMCs based on nylon 6,6 and UHMWPE fibres have been successfully demonstrated. Of particular interest however, is whether "green" VPPMCs can be successfully manufactured. This paper reports on the first step towards green VPPMCs using biodegradable fibres based on cellulose. Here, cellulosic fibres were subjected to tensile creep conditions, prior to moulding in a polyester matrix. Although the creep conditions require further investigations to optimise prestress conditions, the VPPMCs demonstrated ~20% increase in tensile strength and modulus, when compared with control (unstressed) samples. By considering potentially suitable green resins, all-green VPPMCs may be viable in the future.

1. Introduction

Conventional glass and carbon fibre reinforcements have been widely utilised in polymeric composites, however there has been increasing awareness of their environmental and sustainability issues; i.e. the carbon dioxide emissions and energy consumption during their manufacture as well as the potential tonnage of non-degradable waste at the end of product life [1-4]. Therefore, interest in "green" fibre reinforcement as a substitute for glass or carbon fibres in various applications is increasing rapidly. Renewable and biodegradable cellulosic or regenerated cellulose fibres are of prominent importance in this regard. In addition, these fibres are readily available, cost-effective, non-toxic and have low densities [1, 3]. Darshil et al. [5] found that by substituting E-glass fibres with flax fibres in a polyester matrix, a 3.5-metre composite rotor blade (suitable for an 11 kW turbine) showed a 10% decrease in structural weight whilst maintaining operational integrity requirements. Composites based on cellulosic fibres such as flax, bamboo, hemp, and wheat straw have already been adopted in producing roofing tiles, and automotive products, i.e. door trim panels, seat foams, engine and transmission enclosures [6-9]. Fink et al. [10] demonstrated that man-made cellulose fibres can considerably enhance some thermoplastic polymers in terms of strength and stiffness.

Despite these advantages, the mechanical properties of cellulosic/cellulose fibre reinforced composites (CFRCs) are relatively poor compared with conventional carbon/glass fibre composites. Therefore investigations into strengthening CFRCs are of major importance for more extensive practical applications. Many researchers have focused on fibre surface treatment methods (coupling agent, ultraviolet, cold plasma, etc.) and achieved considerable mechanical improvements [1, 2, 4, 7, 11].

Nevertheless, these methods have environmental issues, and require expensive equipment [12, 13]. Thus investigation into a relatively simple, "green", low-cost method for mechanical improvement is required.

The concept of viscoelastically prestressed polymeric matrix composites (VPPMCs) was first published in 2000 [14]. By utilising the viscoelastic characteristics of specific fibre reinforcements, such as nylon 6,6 and ultra-high molecular weight polyethylene (UHMWPE), VPPMCs have shown significant improvements in mechanical properties compared with their unstressed control counterparts, without the need to increase section size or weight. Nylon 6,6 fibre-based VPPMCs have demonstrated up to 50% increases in tensile strength, impact strength and flexural stiffness [15-20]. For VPPMCs with UHMWPE fibres, 20–40% increases in flexural modulus and Charpy impact strength have also been reported [21, 22]. To produce a VPPMC, fibre reinforcements are stretched under a fixed tensile creep stress for a predetermined time; the stress is then released before moulding the prestressed fibres into a resin matrix. The prestressed fibres will undergo viscoelastic recovery, so that following matrix curing, compressive stresses are generated within the matrix (counterbalanced by fibre tension), leading to improved mechanical properties. One key advantage of VPPMCs is that unlike conventional elastically prestressed polymeric matrix composites (EPPMCs), the fibre stretching and moulding processes are decoupled. Thus stretching equipment can be relatively simple and there would be no geometrical limitations to VPPMC production [23].

Some studies have demonstrated the time-dependent viscoelastic behaviour of regenerated cellulose fibres over short time periods [24, 25]. This paper reports on the first study to evaluate the use of green continuous fibres for generating the prestress within a VPPMC. Here, the long-term viscoelastic recovery characteristics of regenerated cellulose fibre (viscose) was investigated and the resulting VPPMCs were studied by tensile tests.

2. Background

To investigate the viscoelastic behaviour of regenerated cellulose fibre, a strain-time assessment of creep and recovery processes has been employed in this study, being a relatively convenient method. Previous findings have demonstrated that polymeric creep and recovery can be represented by Weibull or Kohlrausch–Williams–Watts functions [26]. The time dependent creep strain $\varepsilon_{ctot}(t)$ is given by:

$$\varepsilon_{ctot}(t) = \varepsilon_i + \varepsilon_c \left[1 - \exp\left(-\left(\frac{t}{\eta_c}\right)^{\beta_c}\right)\right] \quad (1)$$

Here, ε_i is the instantaneous elastic strain; ε_c represents the time-dependent component in which η_c and β_c are the characteristic life and shape parameters respectively.

After releasing the tensile creep stress and following the instantaneous recovery strain ε_e, the recovery strain $\varepsilon_{rvis}(t)$ can be expressed as:

$$\varepsilon_{rvis}(t) = \varepsilon_r \left[\exp\left(-\left(\frac{t}{\eta_r}\right)^{\beta_r}\right)\right] + \varepsilon_f \quad (2)$$

Here, the ε_r function shows the (time-dependent) viscoelastic recovery strain with parameters η_r and β_r being the associated characteristic life and shape parameters. Permanent strain resulting from viscous flow is represented by ε_f.

If viscoelastic recovery occurs at a fixed strain, a stress will be generated as the fibre attempts contraction. This represents the principle of imparting compressive stresses within a VPPMC, following matrix solidification. The viscoelastic recovery stress, measured under a fixed strain, would not be identical to the stress locked within a VPPMC however, since the former represents ideal matrix

conditions. Nevertheless, the result provides an indication of stress magnitude. The time-dependent recovery stress, $\sigma(t)$, i.e. recovery force relative to fibre cross sectional area, can be represented as [27]:

$$\sigma(t) = \sigma_v \left[\exp\left(-\left(\frac{\Delta t}{\eta} \right)^{\beta} \right) - \exp\left(-\left(\frac{t}{\eta} \right)^{\beta} \right) \right] \quad (3)$$

Here, η and β are the associated Weibull parameters within the σ_v function, Δt is the time interval between releasing the creep stress and initiation of the recovery stress.

Previous investigations with nylon 6,6 and UHMWPE fibres demonstrated that annealed fibres exhibit significantly higher creep and recovery strain than non-annealed (as-received) fibres under identical conditions [21, 28, 29]. Thus in this paper, the influence of annealing treatment is studied.

3. Experimental procedures

3.1. Materials

The fibre reinforcement was regenerated cellulose (viscose) yarn of 600 denier consisting of 120 fibres; the cross-sectional area of each fibre was ~370 μm^2. The yarn was supplied by Xinxiang Sunshining Textiles Co. Ltd., Henan, China. The matrix material was Reichhold Polylite 32032, a clear polyester casting resin supplied by MB Fibreglass, UK, mixed with 2% MEKP catalyst.

3.2. Fibre creep, recovery and recovery stress investigations

The viscoelastic characteristics of the cellulose yarn were investigated to determine appropriate loading conditions for prestress generation. As reported in Section 2, previous stuidies with polymeric fibres have shown that annealing the yarn prior to stretching improves viscoelastic properties. Based on an investigation by Dadashian et al [30], cellulose yarns were annealed at 120 °C for 0.5 h in a fan-assisted oven; only minor changes in fibre strength and breaking extension were observed from this annealing condition in Ref. [30]. For the creep-recovery strain measurements, a stretching rig with digital cursor (± 0.01 mm precision) was used as in previous studies [19, 21, 28]. The cellulose yarn, with 250 mm marked gauge length, was suspended on the loading rig through upper and lower bobbins, typically 300–400 mm apart, the lower bobbin being mounted on a counterbalanced platform for weights to be applied. A 24 h creep duration was used, during which the strain was recorded and, following release of the tensile stress, recovery strain was also recorded in situ.

For recovery stress measurement, a bespoke force measurement rig with force sensor was employed, as previously described [27]. Following the 24-hour creep of cellulose yarn on the stretching rig, the tensile stress was released and the loose cellulose yarn (with bobbins) was transferred to the force measurement rig as quickly as possible. The initially loose yarn became progressively tightened due to viscoelastic recovery and the resulting recovery stress was monitored by the force sensor. All measurements were performed under the conditions of 20–21 °C and 35–42% RH.

From preliminary trials, a tensile stress value of 190 MPa was selected for the 24-hour creep process. Viscoelastic recovery strain and stress values were measured up to 1000 hours. For repeatability, measurements were made on two separate yarn samples, for both annealed and non-annealed cases. Eqs. (1)–(3) were applied to fit creep-recovery strain and recovery stress results from the yarns by curve fitting with *Matlab® R2015a* software.

3.3. Sample production and tensile tests

Two identical lengths of cellulose yarn (one "test", one "control") were annealed simultaneously, test yarns then being stretched under 190 MPa for 24 h as described in Section 3.2; while the control yarn was placed in close to proximity the rig, for exposure to the same environmental conditions (20–21 °C, 35–45% RH). Following stretching, both yarns were cut and folded into suitable lengths before casting. In contrast with nylon 6,6 and UHMWPE yarns in previous studies [23], the cellulose yarns were not brushed out to separate the fibres, due to the high risk of fibre damage. Two closed moulds, based on the "leaky mould" concept [31] were used to ensure the simultaneous production of test (prestressed) and control (unstressed) samples. The depth of the polished channel (10 mm wide) within each leaky mould was adjusted to produce samples of 1 mm thickness using spacers, as previously described [15]. Demoulding of composite strips was conducted ~2 h after casting; both test and control strips were then cut into required lengths to obtain sample batches, each batch consisting of two test and two control samples with sample dimensions of 200 × 10 × 1 mm, based on CRAG [32]. Prior to tensile testing, all samples were placed under steel weights in ambient conditions (19–21 °C) for ~336 h (2 weeks), to prevent possible distortion from residual stresses. Samples with three fibre volume fraction (V_f) values, i.e. 11%, 21% and 32 % were investigated. Moreover, high impact polystyrene tabs (25 mm long, 1.9 mm thick) were glued with polyester resin (as used for the matrix) at both ends of each sample. This was in accordance with CRAG [32], in order to minimise stress concentration effects in the vicinity of the clamping regions during testing.

Tensile tests were performed under room temperature (20-22 °C), on a Lloyds EZ50 universal materials testing machine, using pull-to-break mode at a loading rate of 5 mm/min [15]. The tensile modulus, strength and strain to failure (STF) were provided by stress-strain graphs.

4. Results and discussion

4.1. Cellulose fibre creep, recovery and recovery stress

Creep, recovery strains and recovery stress for both annealed and non-annealed cellulose fibres with the curve fittings are plotted against time in Fig. 1. In general, in contrast with the major differences in viscoelastic characteristics between annealed and non-annealed nylon 6,6 or UHMWPE fibres [21, 28, 29], the cellulose yarns show only minor changes from annealing. Long-term viscoelastic characteristics can be clearly observed from the curves in Fig. 1(b) for both annealed and non-annealed cellulose fibres. Importantly, the ε_f values are insignificant, indicating negligible (unwanted) permanent strain from viscous flow. Moreover, the recovery stress progressively increases as observed in Fig. 1(c); the stress outputs are predicted to be ~51 MPa and ~61 MPa for non-annealed and annealed cellulose fibres respectively as $t \rightarrow \infty$. These values are considerably greater than the value (15.4 MPa) for nylon 6,6 fibres [23]. Thus there is sufficient evidence to support the feasibility of the VPPMC technique for CFRC production. Based on correlation coefficient (r) values from the curve fittings however, greater

scatter is observed for the non-annealed cellulose yarns, especially in recovery and recovery stress (Fig. 1(b) and (c)). It is speculated that this larger variation is a result of the non-uniform stress history within the regenerated cellulose fibre, possibly induced by extrusion and drawing during manufacture [33]. It is suggested that the annealing treatment removes the previous stress history [15], leading to more consistent viscoelastic characteristics, as observed in Fig. 1. Consequently, all cellulose fibres used in composite production were annealed.

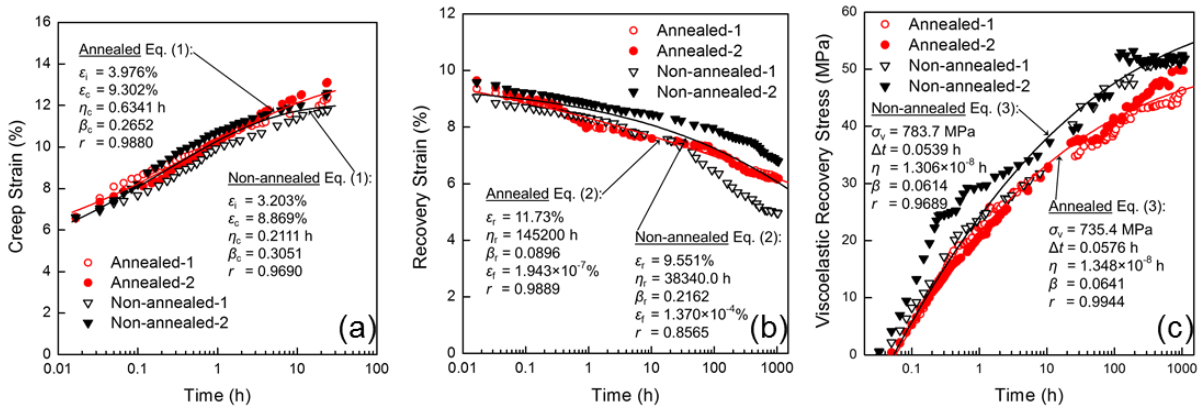

Figure 1. (a) Creep strain, (b) recovery strain (corresponding to (a)) and (c) recovery stress against time for annealed and non-annealed cellulose yarns with curve-fit parameters from Eq. (1)–(3) respectively; r is the correlation coefficient.

4.2. Tensile tests

Although tabs were employed at both ends of each sample to reduce detrimental stress concentration effects, some samples still fractured at the clamping regions. Thus, to reduce experimental uncertainty, data only from those samples that fractured near their centres were utilised for analysis. Thus sample numbers were 9 test and 9 control, 8 test and 10 control, 7 test and 5 control for V_f values of 11%, 21% and 32% respectively. Tensile strength, modulus and STF results are summarised in Fig. 2 as a function of V_f. As expected, Fig. 2(a) and (b) show that tensile strength and modulus both increase with V_f. For all three V_f values, the VPPMCs show increased strength and modulus compared with control counterpatrs. Three mechanisms are suggested to contribute to the improvement. First, during tensile testing, compressive stresses within the VPPMCs can directly resist the external tensile load, leading to improved tensile properties. Second, for (conventional) EPPMCs, it is suggested by Motahhari and Cameron [34] that the taut fibres could respond instantaneously and more collectively to external stresses. Although there is fibre waviness in our VPPMC samples, it has been suggested that this mechanism may still be effective in improving tensile properties [15]. Finally, the fracture of a fibre within a unidirectional FRC may lead to a stress wave propagating outwards, causing dynamic overstress to facilitate the fracture of neighbouring fibres [35]. It is suggested that this effect may be alleviated by compressive stresses induced by the prestressed fibres, therefore strengthening VPPMCs [15].

An optimum V_f close to 21% is shown in Fig. 2(a) and (b), where 19.6% and 19.0% increases in tensile strength and modulus are observed respectively. As previously reported for nylon 6,6 fibre VPPMCs

[15], this optimum V_f is believed to be an outcome from competing mechanisms between the fibre and the matrix. Here, too few fibres reduce the level of compressive stresses, while too many fibres would reduce matrix cross sectional area, thereby reducing the compressive stress effect. We also suggest that higher V_f values may hinder matrix permeation between fibres, further weakening compressive forces.

The STF for polyester resin is found to be 4.7% [36], which is ~1/3 that of the viscose fibre (~15%) [37]. Therefore, this may explain the increased STF with V_f for both test and control samples, as can be seen in Fig. 2(c). In addition, the STF of VPPMCs show a 50-60% decrease compared with control samples, for all three V_f values in Fig. 2(c). It can be speculated that compressive stresses within the test samples could impede sample extension during tensile tests, which lead to the observed lower STF. Also, in contrast with the taut fibres within test samples, fibres within the control samples would not be expected to respond to external tensile stresses collectively [34], so that fibre fractures are likely to proceed more progressively. This would contribute to a greater STF for control samples during the fibre fracture process [15].

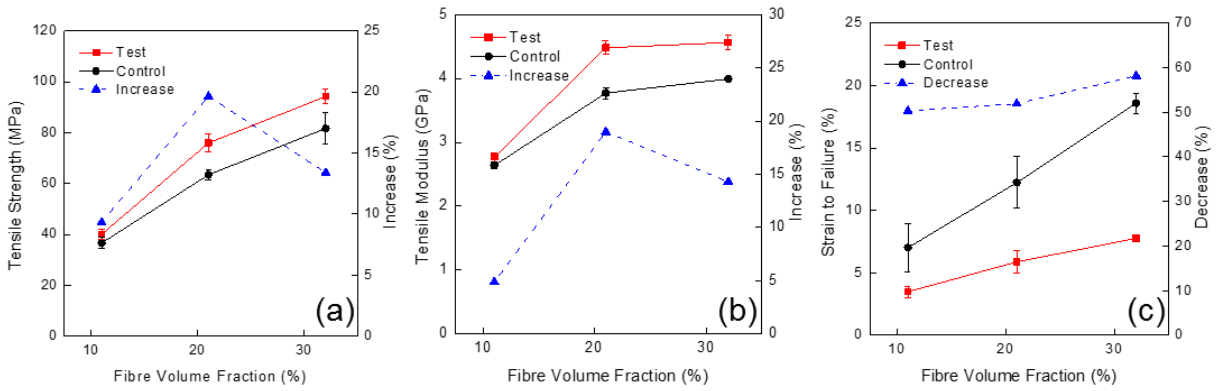

Figure 2. (a) Tensile strength, (b) modulus and (c) strain to faluire results for both test and control samples plotted against V_f. Error bars indicate the standard error.

4. Conclusions

The viscoelastic behaviour of regenerated cellulose (viscose) yarns has been investigated. Tensile tests have been performed to compare the mechanical properties between cellulose fibre based VPPMCs and their control (unstressed) counterparts. The summarised findings are:

i. By employing an appropriate creep stress, the cellulose yarns demonstrated long-term viscoelastic characteristics under both recovery strain and stress conditions. In addition, annealing prior to stretching provided the cellulose yarns with a more consistent viscoelastic behaviour, thus annealed fibres were used for VPPMC production.

ii. Tensile strength, modulus and STF increased with increasing V_f for both test and control samples. It was demonstrated that for all three V_f values (11%, 21%, 32%), greater tensile strength and modulus were observed on test samples compared with their control counterparts. This was attributed to the counteracting effects of compressive stresses and a more collective response to external tensile forces within the test samples. An optimum V_f close to 21% was indicated, where increases of ~20% were observed for both tensile strength and modulus. A 50-60% decrease in STF was observed for test samples at all three V_f values.

Our study has demonstrated improvements in tensile properties by applying the concept of viscoelastically prestress to CFRCs. Cellulose fibres, being renewable and biodegradable, open up opportunities for "green" VPPMC production, by substituting polyester resin with a green matrix material, such as PLA or vegetable oil-based epoxy.

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