Development of constitutive model for composites exhibiting time dependent properties

L Pupure\(^1\), R Joffe\(^{1,2,3}\), J Varna\(^1\) and B Nyström\(^2\)

\(^1\)Material Science, Luleå University of Technology, S-97187 Luleå, SWEDEN
\(^2\)Materials and Manufacturing, Swerea SICOMP, S-94126 Piteå, SWEDEN

E-mail: liva.rozite@ltu.se, roberts.joffe@ltu.se, janis.varna@ltu.se, birgitha.nystrom@swerea.se

Abstract. Regenerated cellulose fibres and their composites exhibit highly nonlinear behaviour. The mechanical response of these materials can be successfully described by the model developed by Schapery for time-dependent materials. However, this model requires input parameters that are experimentally determined via large number of time-consuming tests on the studied composite material. If, for example, the volume fraction of fibres is changed we have a different material and new series of experiments on this new material are required. Therefore the ultimate objective of our studies is to develop model which determines the composite behaviour based on behaviour of constituents of the composite. This paper gives an overview of problems and difficulties, associated with development, implementation and verification of such model.

1. Introduction

Natural fibre composites exhibit good mechanical properties [1-3] but until now they have been used mainly for non-structural applications [4-6]. Only during the few past years the development of natural fibre composites for structural applications has gained the momentum. Most of the work in development of these materials was focused on the composites with synthetic thermosetting matrices [7-8]. Very recently several commercial bio-based thermosetting resins (Tribest, EpoBioX etc.) have been introduced, allowing production of whole bio-based composites. Properties of polymers derived from soybean oil and protein fillers have been reported in [9], a critical review of bio-based thermosets is presented in [10]. The latest results [11-12] demonstrated that these composites are comparable with glass fibre reinforced polymers in terms of stiffness. However due to variability of fibre properties [13-15] and limited filament length it is complicated to arrange and control fibre alignment in composites as well as ensure stable, predictable composite properties. Therefore, another type of reinforcement with natural origin has caught attention of researchers – Regenerated Cellulose Fibres (RCF). These fibres are continuous with constant, reproducible cross-section and properties (see Figure 1.) however they exhibit highly non-linear time-dependent behaviour. Thus, in order to accurately describe these materials and predict their properties RCF have to be treated as material with time-dependent properties. In the same way as synthetic fibres, RCF can be aligned and used in composite manufacturing. Also the transverse failure mechanisms are similar (Figure 1a) – crack propagation along the interface of the fibre and in the matrix is similar to glass fibre composites.

\(^3\) To whom any correspondence should be addressed.
The nonlinear visco-elastic material model developed by Schapery [16-17] has been successfully applied to randomly oriented short bio-based composites [18-19] and synthetic long fibre composites [20]. However in order to apply this model, large number of time-consuming experiments must be carried out. As soon as the fibre orientation distribution or the fibre content changes new series of tests are required. Therefore it would be more convenient to use multiscale modelling, obtaining the higher scale material model on the basis of material models of constituents and their geometrical parameters in the composite. There are number of problems associated with development, implementation and verification of such model. These issues are discussed in this paper.

The used bio-based materials (resins and fibres) are relatively new and limited amount of information is available, especially when it comes to the long term performance. Most of the thermo-mechanical characteristics of these materials have to be obtained experimentally.

2. Model: Theory and experiments

2.1. Theoretical background

The theory of nonlinear viscoelastic materials used in this study was developed by Schapery [16-17], in this theory are obtained using expansion of the Gibb’s free energy in viscoelasticity related internal state variables and using for them linear evolution laws with respect to thermodynamic forces. For anisotropic materials subjected to general loading case the resulting constitutive equations include many stress invariant dependent material parameters/functions to be experimentally identified. All these stress dependent functions are also affected by temperature and humidity, but in fixed environmental conditions they can be considered as stress dependent only.

In uniaxial tensile loading case, one-dimensional model [16-17] may be used, that contains only three stress invariant dependent functions, which characterize the nonlinearity. The model has been modified to account for microdamage $d(\sigma_{\text{max}})$ [21]. The final form of the material model for one-dimensional case is as follows:

$$
\varepsilon = d(\sigma_{\text{max}}) \left[ \varepsilon_0 + g_1 \int_0^t \Delta S(\psi - \psi') \frac{d(g_z,\sigma)}{d\tau} + \varepsilon_{pl}(t, \sigma) \right]
$$

(1)

The “reduced time” in equation (1) is given as:

$$
\psi = \int_0^t \frac{dt'}{a_\sigma} \quad \text{and} \quad \psi' = \int_0^t \frac{dt'}{a_\sigma}
$$

(2)
In equation (1) \( \varepsilon_0 \) represents elastic strain in undamaged composite which, generally speaking, may be nonlinear function of stress. \( \Delta S(\psi) \) is the transient component of the viscoelastic creep compliance at low stress, which characterize time dependent part of the Viscoelastic (VE) response. According to the theory it does not depend on stress level. The \( g_1 \) and \( g_2 \) are stress dependent material properties and \( a_\sigma \) is the shift factor. These three functions in fixed conditions depend on stress only.

It was shown by Schapery [17] that the viscoelastic creep compliance at low stress has the form of Prony series,

\[
\Delta S(\psi) = \sum_i C_i \left( 1 - \exp \left( - \frac{\psi}{\tau_i} \right) \right)
\]  

In equation (3) \( C_i \) are constants and \( \tau_i \) are called retardation times.

For sufficiently small stresses, a linear viscoelastic region, where the VE-strains are proportional to the stress level, may exist. By normalizing the introduced constants and including the normalization constants in \( C_i \) it can be assumed that at very low stress \( g_1 = a_\sigma = 1 \). Regarding \( g_2 \), the assumption \( g_2 = 1 \) can be used at the lowest stress level investigated, which makes its value undetermined at lower stress values (including when stress is approaching to zero). Using these assumption equation (1) becomes the strain-stress relationship for linear viscoelastic, nonlinear viscoplastic materials. The physical meaning of the damage related function \( d(\sigma_{\text{max}}) \) in equation (1) was revealed in [22] analysing the elastic strain term.

The last term in equation (1) accounts for irreversible Viscoelastic (VP) strains that develop at high stresses and increase with the time of loading. In [21,23] the development of VP strains was successfully described by functions presented in [24]. In this model VP-strain grows during loading with specified time dependence and dependence on the applied stress given by:

\[
\varepsilon_{VP}(\sigma, t) = C_{VP} \left\{ \int_0^{t^*} \left( \frac{\sigma(t)}{\sigma^*} \right)^M d\tau \right\}^m
\]

\( C_{VP} \), \( M \) and \( m \) are constants to be determined, \( t/t^* \) is normalized time where \( t^* \) is an arbitrary chosen characteristic time constant and \( \sigma^* \) is an arbitrary chosen stress constant. In this study \( t^* = 7200 s \) and \( \sigma^* = 1 \text{MPa} \) are assumed. It should be noted that equation (4) slightly differs from the original form: \( t^* \) and \( \sigma^* \) have been introduced to have \( C_{VP} \) dimensionless (if \( C_{VP} \) is presented in \%, the calculated VP-strain values in equation (4) will be also in \%).

When stress is kept constant, as in a creep test, \( \sigma = \sigma_0 \) and the integration in equation (4) is trivial. The VP-strain dependence of the creep test length, \( \Delta t_1 \) obeys the following power function:

\[
\varepsilon_{VP}(t_1) = C_{VP} \left( \frac{\sigma_0}{\sigma^*} \right)^{M_m} \left( \frac{\Delta t_1}{t^*} \right)^m
\]

If the material behaviour can be described by equation (4), the time dependence of VP-strains in constant stress creep test should follow a power function with respect to time as predicted by equation (5):
\[
\varepsilon_{VP}(t_i) = A \left( \frac{\Delta t_i}{t_i^*} \right)^m
\]  

(6)

where A has power law dependence on the applied stress level in the creep test:

\[
A = C_{VP} \left( \frac{\sigma}{\sigma^*} \right)^{\ln m}
\]  

(7)

In order to obtain VP constants \( C_{VP} \), \( M \) and \( m \), multiple step creep and strain recovery tests must be performed. When the VP strain analysis is finished and model parameters determined, it is possible to subtract the VP-strain from the total strain, in order to obtain pure VE response. For VE analysis one step creep tests must be performed.

2.2. Experimental procedures

Even thou identification of parameters in the described model requires wide range of experiments, in this paper only experimental procedures referred in the “Discussion” section will be described.

2.2.1. Materials

The RCF produced by special type of the viscose process “Cordenka 700 Super 3” (Cordenka GmbH, Germany) are used as reinforcement in this work. Some of the characteristics of these fibres are available from manufacturer [25] as well as reported in [26-27].

Epoxidized pine oil based resin EpoBioX (Amroy, Finland) with Amroy Ca35Tg curing agent (mixing ratio 100:27) was used. This resin is approximately 75% bio-based. Resin plates were manufactured by use of resin transfer moulding. The resin was infused at room temperature and at low flow speed and then cured for 2h at 80°C.

Fibre preforms were manufactured by winding fibre roving on steel plate using filament winding machine (2 layers). Afterwards these preforms were impregnated using vacuum infusion with resin heated to 50°C. After impregnation plates were cured for 2h at 80°C. The composites had volume fraction of fibres \( V_f = 67.1\% \) (average value of \( V_f \) is obtained from image analysis of micrographs).

2.2.2. Conditioning

Since bio-based materials are very sensitive to moisture, the influence of humidity was analysed. Non conditioned samples (NC) were tested as received (at room environment: relative humidity, RH≈24%, room temperature RT≈23°C). The conditioned samples were stored in an environment with controlled humidity until moisture content in materials reached equilibrium. Two RH levels, 41% and 70%, were used. Prior to conditioning, the specimens were kept in the oven at 50°C until they reached a constant mass. The fixed level of relative humidity was achieved by use of saturated solution of different salts. The weight of samples was regularly measured to ensure that moisture content reached saturation level.

2.2.3. Tensile tests

Quasi-static tensile tests of composites were performed in displacement controlled mode at 2mm/min (strain rate ≈2%/min) on electromechanical tensile machine Instron 3366 equipped with 10 kN load cell and pneumatic grips. Standard Instron extensometers 2620-601 (50mm base) were used to measure longitudinal strain. Fibre bundle tensile tests (gauge length of bundles 100 mm) were also performed on Instron 4411 in displacement controlled mode with loading rate 10mm/min (=10%/min strain rate). The machine was equipped with mechanical grips and 500N load cell. Every bundle was fitted with end tabs - flat pieces of wood were glued at the each bundle end (Araldite 2011 two component epoxy adhesive was used). Since it was not possible to perform direct strain measurement
on bundles, the displacement of the cross-head of the tensile machine was used to calculate strain. In order to obtain actual strain value, machines compliance was measured and taken into account.

Tensile creep with following strain recovery tests for resins and composites were performed using creep rig with dead weight. Creep test on bundles were performed with the same set up as for quasi-static tensile tests. Two types of creep tests were performed: a) single step; b) multiple step. In the latter case a load is applied in steps. Each loading step was followed by recovery period, where no load is applied. Recovery interval was 8 times longer than loading interval. Multiple step creep test consisted of loading intervals with duration of 10, 20, 30 and 60 min. Single step creep tests were performed in one step with loading interval 120 min. The irreversible strains at the end of the recovery period (if present) were taken as VP-strain.

**Figure 2.** Schematic drawing of the relaxation test: a) with constant applied strain and b) strain as a function of time keeping constant viscoelastic strain.

3. **Discussion**

3.1. **Complications with model formulation and parameter identification**

The developed model is in the form of \( \varepsilon(\sigma) \) (strain as a response to applied stress) and all the nonlinearity parameters in the model have to be determined as dependent on stress. Therefore all tests performed in order to obtain parameters for model must be stress controlled, which would be multiple-step and one-step creep tests at different load levels. The validation of the model also requires stress controlled tensile tests. These tests with different load rates are more difficult to perform than strain controlled experiments. It is also more common to perform strain/displacement controlled tensile tests. In addition most of codes for numerical structural analysis and also most of analytical micromechanics models (rule of mixtures, concentric cylinder assembly model) and even the classical laminate theory require constitutive model where stresses are expressed as a function of strains. The above arguments motivate development of a model in form \( \sigma(\varepsilon) \). It is expected that due to the viscoelastic nature of the response the stress would be expressed through convolution integral with respect to the strain ramp and the relaxation function which is strain dependent. In order to obtain parameters for such a model, relaxation tests should be performed where viscoelastic (VE) strain should be kept constant. If material has no viscoplastic (VP) strains, then these tests are simple to perform – constant strain level in sample must maintain for certain time. However most of the materials have also VP strain component and performing relaxation test where VE strain is kept constant becomes very challenging. While the applied strain is maintained at the same level, as the time progresses, also VP strain will develop and VE strain will reduce with time (Figure 2a)). Therefore in order to obtain accurate results from relaxation tests, the overall applied strain level must be increased to compensate for development of VP strains, so that VE strain is constant during the test (Figure 2b)). Since the VP strain development depends on the stress-time dependence, see equation (4), which is not known before the test is finished, the VP strain time dependence can not be predicted even if the law for VP strains is identified in creep and strain relaxation tests. One way to access VP strain problem in the relaxation experiment is to perform this test several times. After first test some approximate information about VP strains will be available (the final value obtained experimentally after recovery and the stress-time
dependence has been measured. The subsequent experiment should be modified by accounting for VP strain. However, this approach would only complicate the experimental program and increase the number of tests needed to obtain parameters. Fortunately in some cases VP strains can be neglected. For some materials it is possible to condition samples in a sequence of creep tests until amount of the new developed VP strain is negligible.

Assuming that the viscoelastic model in form of $\sigma(\epsilon)$ is found, the application of it for any strain controlled ramp is straightforward: by integration of the time dependent viscoelastic strains over the required time interval. It is more difficult (impossible) to deal in this way with viscoplastic strain because these strains are intrinsically caused by stresses and not the opposite. Viscoplastic strain value at certain instant of time depends on the stress history.

In a case when the applied strain has viscoelastic as well as viscoelastic part the best way is to use a discrete form of the material model using small strain increments to simulate the strain ramp. In this approach the stress in the time instant $t_{k+1}$ is found knowing the strain and stress at $t_k$. This implies that the viscoplastic strain at $t_k$ has been calculated using equation (4). The calculation is a multi-step procedure: a) at a given applied strain at $t_{k+1}$ the viscoelastic strain is estimated as the difference between the applied and the viscoplastic strain at $t_k$; b) the viscoelasticity model is used to find stresses at $t_{k+1}$; c) the found stress is used in the viscoplasticity law to find the viscoplastic strain at $t_{k+1}$. If the time step is small the accuracy is sufficient.

A general assumption that a region of linear viscoelasticity exists at low stresses and in the linear VE region functions $g_1 = g_2 = a_\sigma = 1$ has been used in many studies [19]. However, in thermodynamics there is neither requirement of the existence of linear region nor $g_1 = g_2 = a_\sigma = 1$.

The requirement is that at very low stresses these functions have constant values and that the compliance there can be expressed in Prony series. Since the above constants are always multiplied by $C_i$ in Prony series, for convenience one may include these constant values at zero in still unknown $C_i$ and have at zero stress $g_1 = g_2 = a_\sigma = 1$. It should be noted that experimentally these conditions can be fulfilled for $g_1$ and $a_\sigma$ but not for $g_2$. The reason is that the lowest stress level used in creep and strain recovery test for finding parameters cannot be zero. It has certain finite value $\sigma_1$, to be able to perform reliable strain measurements and it is not known a priori if it belongs to a linear region or not. Inspecting the creep and strain recovery expressions for this first test, one can see that in expressions $C_i$ is always multiplied by $g_2$ and therefore it is not possible to find both of them during the fitting procedure: one can find only the product. Certainly, one can define $g_2(\sigma_1) = 1$ and determine $C_i$ values which are stress state independent. Using tests at different stress levels we find $g_2(\sigma)$ (which is actually $g_2(\sigma)/g_2(\sigma_1)$). Obviously, there is no way to find the $g_2$ values for $\sigma < \sigma_1$ because there are no test results. The only clear thing is that at zero stress there is no reason to expect $g_2 = 1$ (since in fact it is $g_2(0)/g_2(\sigma_1)$).

Another problem linked to these stress dependent functions in the material model is lack of physically based information regarding the shape of these functions. In different papers, different types of functions are presented [17-18] and the approach has been based on fitting accuracy rather than physical meaning.

3.2. Complications with material behaviour

Although RCF are continuous and have resemblance with filaments of other man-made fibres (glass, carbon etc.), mechanical behaviour of these fibres is completely different. Since RCF is of natural origin, they are very sensitive to surrounding environment. As can be seen in Figure 3a), where simple tensile tests for bundles at different relative humidity levels are presented, they are very sensitive to moisture. The stress-strain curves are about 20-30% lower at high RH. This behaviour of fibres reflects also in behaviour in composites (Figure 3b).
Figure 3. Stress-strain curves at different RH levels for a) nonimpregnated RCF bundles and b) RCF/EpoBioX composites.

Obviously, in order to develop a model which is based on properties of constituents, moisture content in constituents and its effects must be studied. As described below, the equilibrium moisture content in constituents, which is different in the fibre and in the matrix, depends on the relative humidity and also on the moisture diffusion related conditions at the fibre/matrix interface.

From the conditioning experiments moisture content at specific RH level was found and values are presented in Table 1. Theoretically, moisture content in composite is related to the moisture in constituents by a simple rule-of-mixture (ROM) expression:

\[
C^w_c = C^w_f W_f + C^w_m W_m
\]  

(8)

where \(C^w\) is moisture content and \(W\) is weight fraction. Indices \(c\), \(m\) and \(f\) are for composite, matrix and fibre. Weight fraction of fibre can be calculated:

\[
W_f = \frac{\rho_f}{\rho_c} V_f
\]  

(9)

Where \(\rho\) represents densities. Density of composite can be also found from ROM:

\[
\rho_c = \rho_f V_f + \rho_m V_m
\]  

(10)

Density of EpoBioX resin \(\rho_m = 1.06 \text{ g/cm}^3\) and RCF fibres \(\rho_f = 1.50 \text{ g/cm}^3\). Values for moisture content in composite calculated according to equation (8) are also presented in Table 1. It can be seen, that the composite has less moisture, than we obtained theoretically. This means, that at given RH fibres absorb less moisture, when they are in composite. Hence, in order to verify at certain RH the composite model, which is based on properties of constituents must be tested at correct environmental conditions. According to these results, fibres must be conditioned and tested at lower RH level, than composite and matrix. It is possible to back-calculate moisture content in fibres that are embedded in matrix by using equation (8): \(C^w_f = 3.16\%\).

We can plot the RH-moisture content relationship for fibre bundles by using the two data points in Table 1 and assuming, that at RH=0\%, the moisture content in RCF is 0. As shown in Figure 4 we obtain almost linear relation between RH level and moisture content in RCF. From Figure 4 we can read that moisture content \(C^w_f = 3.16\%\) corresponds to RH=21\%, which is approximately RH in the room at the time of testing.
Table 1. Moisture content in material at different RH levels

| Material                | RH=41% | RH=70% |
|-------------------------|--------|--------|
| RCF                     | 6.41%  | 10.40% |
| EpoBioX                 | 0.28%  | 0.82%  |
| RCF/EpoBioX (experimental) | 2.41%  | 5.91%  |
| RCF/EpoBioX (theoretical)  | 4.82%  | 7.91%  |

Figure 4. Moisture content in RCF as a function of RH level.

RCF also exhibit highly non-linear time-dependent behaviour. It is clearly visible in Figure 5a), where curves from loading-unloading tests are presented. It is also obvious that the slope of the stress-strain curve from loading and unloading differs a lot. None of these slopes represent the elastic modulus of the material, but the unloading slope even in the low strain region is more affected by the viscoelastic behaviour. For the composite the hysteresis loop is much smaller than for RCF bundles; however there is noticeable difference in loading/unloading slopes of stress-strain curve, as shown in Figure 5b).

Figure 5. Stress-strain curves for a) loading-unloading test for fibre bundle and b) composite stress-strain response in small stress region
4. Conclusions
Experimental and theoretical challenges related to development of material model for regenerated cellulose fibre (RCF) reinforced composites with bio-matrix are identified and potential solutions are suggested.

The theoretical model suggested for description of the composite time dependent behaviour is based on multiscale analysis: Schapery’s type nonlinear viscoelastic models generalized for viscoplastic strains and damage are developed separately for fibre and for matrix characterization and used to find the response of the composite which is also nonlinear viscoelastic and viscoplastic with damage.

In order to use this approach the material models for constituents developed in formulation where the stress is the independent variable have to be inverted to form where stress is calculated as a function of the strain ramp.

Two directions towards this goal are identified and critically analysed: a) using series of relaxation tests at different applied strain levels instead of creep test; b) incremental formulation of the earlier developed models based on creep tests with following inversion to calculate stress versus the applied strain.

The fibre behaviour is very complex with large viscoplastic and viscoelastic strains and hysteresis loops developing in high stress cycling. The model development is further complicated by the high moisture sensitivity of the RCF composite constituents. It is demonstrated that the fiber stress-strain response at different moisture contents has to be analysed before the composite model can be applied for a certain relative humidity.

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