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A micromechanical approach to the viscoelasticity of unidirectional hybrid composites

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Combination of the well-known rule of mixtures and the classical theory of linear viscoelasticity leads to a stress/strain relation that effectively predicts the viscoelastic behaviour of hybrid composites in uniaxial extension. From this theory, it is shown that the rule of mixtures does not apply directly to the dynamic quantities \( E_d \) and \( \tan \delta \), whereas it can be used directly to correlate the storage and loss moduli of the composite to the properties of its components. The stress/strain relation is experimentally verified under isothermal conditions for a unidirectional, hybrid polyethylene-aramid/epoxy system both in constant strain rate and dynamic forced vibration experiments. The micromechanical model leads to numerical predictions which are in good agreement with experimental data on composite materials in various compositions.

Key words: composite materials; hybrids; polyethylene fibres; aramid fibres; epoxy resin; viscoelasticity; modelling

High performance polyethylene (HP-PE) fibres, produced by solution (gel)-spinning and subsequent drawing\(^1\,^2\), possess unique properties in terms of high strength-to-weight and modulus-to-weight ratios. The toughness and the viscoelastic character of HP-PE fibres renders them eminently suitable for applications where impact resistance\(^3\) and vibrational damping properties\(^4\) are required. However, due to the one-dimensional microstructure of HP-PE, namely, extended polyethylene chains with relatively weak intermolecular van der Waals’ interactions, the compressive and shear strengths are not impressive. Moreover, HP-PE fibres are inherently unstable with respect to long-term static loads (creep). Consequently, not much research is being considered on structural applications of HP-PE fibre-reinforced composites.

To compensate for these weaknesses of HP-PE, hybridization of HP-PE composites with carbon fibres offers interesting possibilities\(^5\,^6\,^7\,^8\). However, when elastic carbon fibres are combined with fibres like HP-PE that possess a pronounced time-dependent behaviour, the hybrids inevitably display viscoelastic behaviour, with vibrational damping properties that are better and long-term properties that are worse than the carbon-reinforced composites.

It is generally accepted that the longitudinal tensile modulus of hybrid composites obeys the rule of mixtures (ROM)\(^9\). The carbon–HP-PE system also displays this type of behaviour, for the initial as well as the long-term modulus\(^9\). Moreover, it has been shown that dynamic quantities such as storage and loss moduli display the same behaviour, whereas \( \tan \delta \) does not obey the ROM.

As demonstrated by Hashin, for a composite based on a viscoelastic matrix and elastic fibres, the classical theory of linear viscoelasticity can easily be incorporated in the ROM\(^1\). In this study, the same basic modelling is applied to unidirectional composites based on viscoelastic fibres, in an attempt to derive a mathematical relation that can be used to evaluate the viscoelastic behaviour of these materials on the basis of the properties of their components. The relation is experimentally verified using the HP-PE-aramid/epoxy system, where all components display significant viscoelastic behaviour. Following the same procedure the hybrid system HP-PE-carbon/epoxy, which is more interesting in terms of mechanical properties, can be modelled more easily because of the elastic character of the carbon fibres.

For the sake of simplicity the study is performed for isothermal loading conditions (30°C) while the viscoelastic characterization is restricted to relatively short loading times (0.01 s \( t \) \( \leq \) 10 000 s). The components are regarded to be linearly viscoelastic in a first approximation, whereas the ROM is applied to relate the viscoelastic behaviour of the hybrid to the properties of its components.
EXPERIMENTAL DETAILS

Materials

The fibres used in this study were an HP-PE fibre (Dyneema SK60, 400 den) supplied by DSM High Performance Fibers BV, and an aramid fibre (Twaron-HM, 1500 den) supplied by Akzo. A common epoxy system, Ciba-Geigy's Araldite LY556/HY917/DY070, based on bisphenol A with an anhydride curing agent, was used as the principal matrix.

Unidirectional (UD) composites were prepared by a modified pultrusion process. Bundles containing aramid and/or HP-PE yarns were immersed in a bath of epoxy resin and pulled into moulds with PTFE inserts squeezing out the surplus resin and trapped air. The samples were cured for 4 h at 80°C and post-cured at 110°C for 12 h. Using this pultrusion technique, circular specimens with a diameter of 1.2 mm were prepared. The volume fraction of HP-PE and/or aramid fibres was varied, whereas the total volume fraction of fibres was 30 to 40%. The composites obtained by this procedure are denoted by the HP-PE volume fraction vs. the aramid volume fraction; 0.163/0.195, for instance, is a composite consisting of 16.3% HP-PE fibre and 19.5% aramid fibre.

For characterization of the pure epoxy matrix, epoxy films of about 0.1 mm thickness were prepared by curing in a hot press for 4 h at 80°C at a pressure of 5 bar and post-curing for 12 h at 110°C.

Mechanical testing

Stress-relaxation and tensile experiments were performed on a Frank 81565 tensile tester equipped with a thermostatically controlled oven and an extensometer. All static mechanical experiments were performed at a constant temperature of 30°C. For stress-relaxation and tensile experiments fibre samples with a length of 255 mm were prepared. To avoid slippage in the clamps, the fibre samples were provided with adhesively bonded cardboard tabs. The UD composite specimens had an overall length of 300 mm. To improve clamping, the ends of the specimens were provided with adhesively bonded cardboard tabs. The UD composite specimens had an overall length of 300 mm. To improve clamping, the ends of the specimens were provided with glass tubes (diameter 6 mm, bore 1.5 mm, length 50 mm), which were adhesively bonded to the specimen. The specimens were clamped by enclosing the glass tubes in specially shaped grips that applied the load directly to the glass tubes. All samples, except the epoxy films, were previously conditioned by loading at a constant strain level of 1% for a period of 1 min.

In the tensile experiments, HP-PE fibre, aramid fibre and epoxy were loaded up to failure at a strain rate of 0.001 s⁻¹. The composite materials, however, were loaded only to a strain level of 1%, again at a strain rate of 0.001 s⁻¹.

The dynamic properties of the HP-PE fibre in uniaxial extension were studied using dynamic mechanical thermal analysis (DMTA MK2 from Polymer Laboratories), at frequencies of 0.2 to 3 Hz and temperatures between 0 and 90°C. The samples were 20 mm long and had a cross-sectional area of about 0.01 mm². To avoid buckling of the fibre as a result of the dynamic strain amplitude (0.05%), a static load of 150 MPa was applied.

Dynamic experiments on aramid fibre, epoxy and the composite materials were performed on a Zwick Rel servo-hydraulic tensile tester (20 kN) adapted for application of 'white' noise strain excitation (Fig. 1). The internal function generator of the servo-hydraulic system was disconnected and replaced by a combination of a low frequency noise generator and an adjustable DC voltage generator, creating the possibility to change the applied static strain and dynamic strain amplitude separately. The generated noise signal consisted of 256 frequencies in the range 0 to 10 Hz, where all frequencies contributed with equal amplitude (so-called 'white' noise). Stress output and strain input were transformed into dynamic quantities using an HP 98785A fast Fourier analyser in the frequency range 0.1 to 5 Hz. The samples used for these dynamic experiments were identical to those used for stress-relaxation and tensile tests. During the experiment the static strain level was maintained at 0.5%, whereas the dynamic strain amplitude was 0.1%. The temperature was controlled at 30°C.

COMPONENT CHARACTERIZATION

Linearity

In the characterization of the mechanical properties, all components — HP-PE, aramid and epoxy — are regarded to be linearly viscoelastic in a first approximation. In the case of HP-PE fibre this assumption is correct in dynamic and/or short-term loading situations, whereas significant non-linearities are observed in long-term loading situations. Phenomenologically speaking, this non-linear deformation behaviour originates from a combined contribution of a reversible
viscoelastic and a plastic flow process to the deformation of the fibre\(^{13}\). The plastic deformation process dominates at long loading times and/or high temperatures. As this study focuses on short-term and dynamic loading situations, the contribution of the plastic deformation process can be neglected, for under these conditions the reversible viscoelastic contribution will dominate the deformation behaviour.

Although aramid fibre is known to possess non-linear characteristics\(^{14}\), the deformation behaviour of the Twaron-HM fibre is approximately linear up to failure. This was studied by performing stress–relaxation experiments at strain levels up to 1.75\%. As can be observed in Fig. 2, the stress–relaxation isochrone, constructed for a loading time of 300 s, is approximately proportional to strain over the entire strain region covered experimentally. Hence, a linear viscoelastic approach to the deformation behaviour of Twaron-HM seems to be justified.

Non-linear effects in the low modulus epoxy matrix were ignored as these will be negligible compared with the mechanical properties of the composite.

**Viscoelastic modelling**

For a linear viscoelastic material, the Boltzmann superposition principle\(^{15}\) applied to uniaxial extension leads to:

\[
\sigma(t) = \int_0^t E(t-t') \dot{e}(t') \, dt'
\]  
(1)

This convolution integral provides a mathematical equation that relates viscoelastic stress to strain under various loading conditions. The time-dependent behaviour is characterized by a viscoelastic function, in this case the stress–relaxation modulus \(E(t)\). For prediction of the mechanical behaviour of a viscoelastic material using Equation (1), a mathematical description of this viscoelastic function is needed that covers a sufficiently wide time/frequency range.

The stress–relaxation moduli of HP-PE, aramid and epoxy, measured at 30\(^\circ\)C and 1\% strain, are plotted double logarithmically against time in Fig. 3. It can be observed that all materials display a power law relaxation in time, where:

\[
E(t) = Ct^{-n}
\]  
(2)

This analytical approximation of the stress–relaxation behaviour leads to comprehensive expressions for the dynamic modulus \(E_d\) and the loss angle \(\delta\) as a function of the angular frequency \(\omega\):

\[
E_d(\omega) = C \Gamma (1-n) \omega^n
\]  
(3)

\[
\delta(\omega) = n \pi/2
\]  
(4)

where \(\omega = 2\pi f\) and \(\Gamma(\cdot)\) is the gamma-function.

However, as the power law approximation for the stress–relaxation moduli has been verified experimentally only for 100 s < \(t\) < 4000 s, Equations (3) and (4) will predict the dynamic behaviour for 2.5 \(\times\) \(10^2\) rad s\(^{-1}\) < \(\omega\) < 2.5 \(\times\) \(10^2\) rad s\(^{-1}\). Especially upon extrapolation to the high frequency side, the power law approximation can be expected to deviate markedly from the actual material behaviour, as has been shown for HP-PE fibres\(^{13}\). However, for aramid and epoxy the power law approximation holds over a sufficiently wide frequency range. This is shown in Fig. 4, where the experimental values of the dynamic modulus (Fig. 4(a)) and \(\tan \delta\) (Fig. 4(b)) are compared with the power law prediction (Equations (3) and (4)). The power law coefficients for aramid and epoxy (Table 1), used to predict the
Fig. 4 (a) Dynamic moduli and (b) tan δ of aramid fibre and epoxy vs. angular frequency (solid lines), measured at 30°C, using the 'white' noise forced vibration set-up. The symbols represent experimental data from stress-relaxation experiments, transformed to dynamic quantities (see text) using the power law approximation (dashed lines).

Table 1. Power law coefficients for aramid and epoxy, as derived from the stress–relaxation data in Fig. 4

<table>
<thead>
<tr>
<th>Material</th>
<th>C (GPa s^n)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aramid</td>
<td>119.4</td>
<td>0.010</td>
</tr>
<tr>
<td>Epoxy</td>
<td>2.9</td>
<td>0.025</td>
</tr>
</tbody>
</table>

dynamic quantities, were derived from the stress–relaxation data in Fig. 3.

Introduction of Equation (5) into Equation (1) leads to the following expressions for the storage modulus $E'(\omega)$ and the loss modulus $E''(\omega)$:

$$E'(\omega) = E_\infty + \int_{-\infty}^{\infty} H(\tau) \omega^2 \tau^2 / (1 + \omega^2 \tau^2) \, d(\ln \tau)$$

$$E''(\omega) = \int_{-\infty}^{\infty} H(\tau) \omega^2 \tau^2 / (1 + \omega^2 \tau^2) \, d(\ln \tau)$$

The dynamic modulus $E_d(\omega)$ and the phase angle $\delta(\omega)$ are related to the storage and loss moduli by:

$$E_d^2(\omega) = E'(\omega)^2 + E''(\omega)^2$$

$$\tan \delta(\omega) = E''(\omega) / E'(\omega)$$

The dynamic properties of the HP-PE fibre were experimentally evaluated by means of isothermal frequency scans in the range 0 to 90°C. The results are shown in Fig. 5, where the values of the dynamic modulus $E_d$ (Fig. 5(a)) and $\tan \delta$ (Fig. 5(b)) are plotted double logarithmically against the angular frequency $\omega$ for all temperatures covered experimentally. Master curves of $E_d$ and $\tan \delta$, constructed by horizontal shifting and matching of adjacent curves, are presented in Fig. 6 for a reference temperature of 30°C. It was shown that time-temperature superposition is allowed for HP-PE fibres and master curves obtained in this way can be used quite effectively to predict the actual fibre behaviour up to loading times of $10^4$ s.

The procedure used to derive the continuous relaxation spectrum $H(\tau)$ is based on an approximate relation, suggested by Booij and Palmen, between the relaxation time spectrum, the dynamic modulus and the phase angle $\delta$:

$$H(\tau = \omega^{-1}) = (E_d(\omega)/\tau_\infty) \sin(2\tau(\omega))$$

The relation provides a first estimate of the distribution of relaxation times in the time scale between $\tau_{\min} = \omega_{\max}^{-1}$ and $\tau_{\max} = \omega_{\min}^{-1}$, where $\omega_{\min}$ and $\omega_{\max}$ represent the lower and upper limits of the frequency range covered by the master curves in Fig. 6. Next the spectrum is extrapolated and adjusted on the basis of the predictions it yields on the basis of Equations (6)–(9) for the functions $E_d$ and $\tan \delta$ over the experimentally covered frequency range. The distribution of relaxation times $H(\tau)$ obtained by this procedure is presented in Fig. 7. The spectrum covers a frequency interval from $\ln \tau = -8$ to $\ln \tau = 10$ (Equation (5)), whereas an equilibrium modulus $E_\infty$ of 25.65 GPa was needed to obtain a reasonable description of the master curves of $E_d$ and $\tan \delta$ (solid lines in Fig. 6).

Model verification (components)

To evaluate the viscoelastic functions obtained in the previous section, model predictions of constant strain rate stress build-up experiments (0.001 s$^{-1}$) were
Fig. 5 (a) Dynamic modulus and (b) tan δ of HP-PE fibre vs. angular frequency at temperatures from 0 to 90°C: +, 0°C; Δ, 10°C; ●, 20°C; ×, 30°C; △, 40°C; ●, 50°C; V, 60°C; ■, 70°C; □, 80°C; ▼, 90°C

Fig. 6 Master curves of the dynamic modulus (△) and tan δ (●) vs. the logarithm of the angular frequency for a reference temperature of 30°C. The solid lines represent the numerical predictions using the continuous relaxation spectrum of Fig. 7.

Fig. 7 The continuous relaxation spectrum \( h(t) \) of HP-PE fibre at a reference temperature of 30°C (equilibrium modulus = 25.65 GPa)

Fig. 8 Numerical prediction (solid lines) of constant strain rate experiments (0.001 s\(^{-1}\)) of HP-PE fibre, aramid fibre and epoxy, compared with experimental data at 30°C (symbols) compared with experimental data. The power law approximation used for aramid and epoxy leads to an analytical solution for these tensile experiments, where:

\[
\sigma(t) = \frac{\dot{\varepsilon}}{1-n} \cdot \tau^{1-n}
\]  

Using the continuous relaxation spectrum derived for HP-PE, a numerical prediction of the tensile behaviour was made on the basis of Equations (1) and (5) and the data of the continuous spectrum as represented in Fig. 7. The results of the model predictions are presented in Fig. 8, where a good agreement with the experimental data can be observed.

The numerical prediction of the stress–relaxation modulus of HP-PE is compared with experimental data in Fig. 3. As can be observed, the model prediction is in good agreement with the experimental data.

MICROMECHANICAL APPROACH TO HYBRID COMPOSITES

Modelling

In the case of continuous fibre reinforcement, the deformation behaviour of unidirectional composites in uniaxial extension can be considered as the result of matrix and fibres acting in parallel. This leads to the
well-known ROM which relates the Young’s modulus of an $n$-components composite to the Young’s moduli of the components by:

$$E_{\text{comp}} = \sum_{i=1}^{n} v_i E_i$$

(12)

where $E_{\text{comp}}$ is the Young’s modulus of the composite, and $E_i$ represents the Young’s modulus of the $i$th component. The volume fraction of the $i$th component is represented by $v_i$. In conformity with the ROM, it can easily be deduced that the stress–relaxation modulus of the composite is related to the stress–relaxation moduli of its components in the following manner:

$$E_{\text{comp}}(t) = \sum_{i=1}^{n} v_i E_i(t)$$

(13)

where $E_{\text{comp}}(t)$ represents the viscoelastic function of the composite. An expression for the dynamic quantities of the composite can be derived by a Laplace transform of Equation (1), which leads to:

$$\delta_{\text{comp}}(s) = \frac{E_{\text{comp}}(s)}{s} \delta(s)$$

$$= \delta_{\text{comp}}(s) \delta(s)$$

(14)

where $\delta_{\text{comp}}(s)$ represents the transfer function of the composite and $s$ equals $j\omega$. As the Laplace transform is a linear transformation, the transformation of Equation (1) after introduction of Equation (13) into Equation (1) leads to:

$$\delta_{\text{comp}}(s) = \sum_{i=1}^{n} v_i \delta_i(s) \delta(s)$$

(15)

By definition:

$$\delta_{\text{comp}}(s) = E_{d,\text{comp}}(s) \exp\left[ j\omega \delta_{\text{comp}}(s) \right]$$

$$= E_{d,\text{comp}} \cos(\delta_{\text{comp}}) + j E_{d,\text{comp}} \sin(\delta_{\text{comp}})$$

$$= E'_{\text{comp}}(s) + j E''_{\text{comp}}(s)$$

(16)

where $E_d$, the dynamic modulus, equals $|\delta|$, $\delta$ is the loss angle (arg $\delta$) and $E'$, $E''$ represent storage and loss moduli of the composite, respectively. As the transfer functions of the components can be described in a similar way, Equations (15) and (16) lead to:

$$E'_{\text{comp}} = \sum_{i=1}^{n} v_i E'_i$$

(17)

$$E''_{\text{comp}} = \sum_{i=1}^{n} v_i E''_i$$

(18)

and

$$E_{d,\text{comp}} = \left[ \left( \sum_{i=1}^{n} v_i E'_i \right)^2 + \left( \sum_{i=1}^{n} v_i E''_i \right)^2 \right]^{0.5}$$

(19)

$$\delta_{\text{comp}} = \arctan \left[ \left( \sum_{i=1}^{n} v_i E''_i \right) / \left( \sum_{i=1}^{n} v_i E'_i \right) \right]$$

(20)

From Equations (19) and (20) it should be noted that the ROM cannot be applied directly to relate the dynamic modulus $E_{d,\text{comp}}$ and the loss angle $\delta_{\text{comp}}$ of the composite to the dynamic moduli and the loss angles of its components.

Model verification (composites)

The validity of this simple micromechanical approach was evaluated in constant strain rate (0.001 s$^{-1}$) and dynamic (‘white’ noise) experiments. The model prediction of the constant strain rate experiments was obtained by applying the ROM to the tensile predictions of the components, represented in Fig. 8. This procedure is in fact equivalent to numerical integration of Equation (1) after introduction of Equation (13) into Equation (1). As can be observed in Fig. 9, the model predictions are in good agreement with the experimental data.

Numerical predictions of the dynamic quantities $E_d$ and $\tan \delta$ of the composite were obtained using Equations (19) and (20). For aramid and epoxy $E'$ and $E''$ were calculated from the power law predictions of $E_d$ and $\tan \delta$ (Equations (3) and (4)), using the coefficients given in Table 1. For HP-PE the storage and loss moduli, $E'$ and $E''$, were calculated by numerical integration of Equations (6) and (7). The results are presented in Figs 10(a) and 10(b), where a good agreement between the model predictions and the experimental data can be observed.

To illustrate the importance of small differences in $\tan \delta$, it is indicatively noted that an increase in $\tan \delta$ from 0.015 to 0.06, being typical values at a frequency of 1 Hz for aramid and HP-PE fibres respectively, implies that free vibrations in the HP-PE fibre will fade out four times faster.

CONCLUSIONS

Combination of the ROM and the classical theory of linear viscoelasticity leads to a stress/strain relation that effectively predicts the mechanical behaviour of hybrid composites in uniaxial extension under various loading conditions. Although the stress/strain relation was verified only in a rather limited frequency range, it is inherently able, even on the basis of the component characterization performed in this study, to describe...
As the ROM can be applied directly to determine the longitudinal tensile, storage and loss moduli of composites, the use of the stress/strain relation presented in this paper might seem a cumbersome procedure. However, it supplies a comprehensive mathematical basis for a fast numerical evaluation of the vibrational damping properties of UD composites in various compositions.

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