Development of TTMSP to Predict the Performance of Discontinuous Natural Fibre-Polymer Composites

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ABSTRACT

Natural fiber-polymer composites are becoming increasingly important for load-bearing application due to their unique benefit of light weight and good mechanical performance. Polymers alone exhibit time dependent mechanical properties influenced by many environmental factors. More significantly, when natural fibres are present in the polymer matrices, the thermo-mechanical properties of such composites are changed by the environmental conditions and exhibit an internal and a global time dependent behavior. While durability analysis of the natural fibre-polymer composites is the main concern in real-life application, development of prediction methods is essential for evaluating their mechanical performance.

Both temperature and moisture diffusion are known to influence the time dependent mechanical properties of polymer based composites; however, conventional analysis method considers the temperature factor only. Therefore, an evaluation technique is presented in this paper to describe the nonlinear visco-elastic behavior of natural fibre-polymer composites under concurrent temperature and moisture diffusion effects. Using an analogous approach to the TTSP, time-moisture superposition will be used to identify the moisture-dependent shift factors under an assumption that the effects of temperature and moisture can be decoupled and separately determined, and reassembled later on.

INTRODUCTION

The use of natural fibres as filler in polymer-based composites has advanced rapidly over the past years because they are abundant, recyclable, biodegradable, and economically sound. Due to their economical advantage, the use of natural fiber-polymer composites in load-bearing application is widely investigated, and various researchers /1, 2/ indicated that tensile strength and flexural modulus of the composites are increased with the percentage of natural fiber/filler. Due to this nature, natural fibre fillers can also be used to tailor the performance of polymeric resins /3/. However, although it is obvious that by incorporating natural fiber in polymeric resin, the hydroscopic properties of the composites will be altered, which in turn alters the mechanical performance of the composites, a quantitative analysis of such a mechanism is not available; therefore, to quantify the hydroscopic effects on the mechanical performance of composites by formal mathematic modeling will be the primary motivation in this research.

The approach led to the time-temperature-moisture-superposition-principle (TTMSP) based on an assumption that the temperature and moisture effects can be evaluated separately. Using an analogous approach to the time-temperature-superposition-principle (TTSP) /4/, the temperature shift factor (a_T) and moisture shift factor (a_M) are separately determined for various environmental conditions, a combination of different temperature and relative humidity levels. Then the temperature and moisture effects are coupled by reestablishing their relationship through addition of their induced strain values.

All previous investigations are based on the well-known Schapery's theory on nonlinear viscoelastic materials /5, 6/, such as Hoyle *et al.* /7/, who developed a relationship of primary creep for structure applications of wood-base materials. Popelar *et al.* /8/ and Strganac *et al.* /9/ demonstrated the validity of the above mentioned Schapery's theory and its modified version as a nonlinear constitutive model of thermoplastic polymers, and proved them to be accurately characterizing the material nonlinear response. In terms of experimental analysis, Dutta and Hui /10/ used the TTSP to predict creep of fibre-reinforced plastics /FRP/ using nonlinear viscoelastic parameters (based on Schapery's theory) for their constitutive model. For hygroscopic aging effects, Sain /11/ demonstrated time-dependent mechanical properties of polymers influencing by temperature and stress with measurement of viscoelastic properties using time reflectometry. Dai /12/ indicated that flake stress relaxation rates vary with the loading strain levels that are most likely related to characteristics of free volume change in cell walls of wood flake. However, summing up from all available investigations, the effect of viscoelasticity due to hygro-thermal changes is not known.

ANALYTICAL APPROACH

Nonlinear Visco-elastic Theory

The nonlinear visco-elastic theory, also known as Schapery's theory /5/, presents a constitutive behavior, a stress-strain relation, of polymeric materials. The theory starts with a constitutive equation for uni-axial loading. According to the underlying thermodynamic theory /13/, an increment of work per unit initial volume equals the following:

$$\textit{Work per Unit Initial Volume} = \sigma\delta\varepsilon \qquad (1)$$

where σ and ε are the corresponding stress and strain of the loaded composite slabs, and all uni-axial derived theories can be applied to other stress and strain pairs as long as the virtual work condition is satisfied. Due to the load bearing nature of the composite slabs, only equations relating to their creep behaviors will be presented in this review.

The creep compliance is defined as follows:

$$D(t) = \frac{\varepsilon(t)}{\sigma} \qquad (2)$$

In equation (2) σ represents a constant applied load. The thermodynamic theory permits us to express the nonlinear material properties in strain (13) as follow:

$$\varepsilon(t) = g_0 D_0 \sigma + g_1 \int_0^t \Delta D(\psi - \psi') \frac{dg_2\sigma}{d\tau} d\tau \qquad (3)$$

where
$$D_0 \equiv D(0) \qquad (4)$$
$$\Delta D(\psi - \psi') \equiv D(\psi - \psi') - D_0 \qquad (5)$$

In Equations (4) and (5), D_o is the initial value of the creep compliance, ΔD (ψ-ψ') is the transient component of the creep compliance, and ψ is the reduced-time calculated as follows:

$$\psi = \int dt / a_\sigma \quad \text{for} \quad (a_\sigma > 0) \qquad (6)$$
$$\psi' = \psi(\tau) = \int dt / a_\sigma \qquad (7)$$

and a_σ, g_o, g_1, and g_2 are the material properties as a function of stress. Conventionally, if the applied load is sufficiently small, g_o, g_1, g_2, and a_σ can be assumed to be unity. However, in general these stress-dependent properties have specific thermodynamic significance and the changes in g_o, g_1, and g_2 reflect third and higher order dependence of the Gibb's free energy on the applied stress and can be analytically determined as follows /5/:

$$g_o = \frac{\sinh \sigma / \sigma_e}{\sigma / \sigma_e} \qquad (8)$$

$$g_1 g_2 = a_\sigma^n \frac{\sinh \sigma / \sigma_m}{\sigma / \sigma_m} \qquad (9)$$

where σ_e, σ_m, and n are constants which have values that depend on the particular material, e.g. for polyethylene, they are 400psi, 185psi, and 0.0890 /14/, respectively.

Equation (3) can be simplified since only a single step load is applied to the specimen in this study:

$$\varepsilon(t) = g_0 D_0 \sigma + g_1 g_2 \Delta D(\psi)\sigma \quad (10)$$

By substituting a constant stress into equation (3):

$$\frac{dg_2\sigma}{d\tau} = 0$$

except when τ equals to zero, it yields:

$$\varepsilon(t) = g_0 D_0 \sigma + g_1 g_2 \Delta D\left(\frac{t}{a_\sigma}\right)\sigma \quad (11)$$

Equation (11) for nonlinear creep shows that initial elastic response is particularly linear even though the creep is strongly nonlinear, and the transient component of the creep ΔD (ψ) can be modeled by the power law as /5/:

$$\Delta D\left(\frac{t}{a_\sigma}\right) = D_1\left(\frac{t}{a_\sigma}\right)^n \quad (12)$$

In the above, the constant D_l has values that depend on the particular material. Findley and Khosla /14/ had reported the creep behavior of various unfilled thermoplastics which follows very closely to the creep equation:

$$\varepsilon = \varepsilon_o^{'} \sinh \sigma / \sigma_e + m' t^n \sinh \sigma / \sigma_m \quad (13)$$

where $\varepsilon_o^{'}$ and m' are material constants having the value of 1.530% and 0.397%, respectively, for polyethylene /16/. By comparing Equations (10) and (11) with the solution of g_o, g_l, and g_2 from Equations (8) and (9), D_0 and D_1 in Equations (11) and (12) respectively can be determined as follows:

$$D_0 = \frac{\varepsilon_o^{'}}{\sigma_e} \quad \text{and} \quad D_1 = \frac{m'}{\sigma_m} \quad (14 \,\&\, 15)$$

TTSP Method

The Temperature-Time-Superposition-Principle (TTSP) method is widely used for extrapolating experimental measurements made at short times to the mechanical response of a polymeric material at extended times. It is called the method of *reduced variables*, a tool for predicting the material behavior at one certain time (or frequency) and temperature from experiments performed at some other time (or frequency) and some other temperature /17/, and thus it serves to expand the time scale.

Ferry's method of reduced variables in viscoelasticity /18/ provides an analytical method by a temperature-dependent shift factor, a_T, through a shift function. The shift function is a very sensitive function of the temperature, and the explicit form of a_T will depend upon the reference temperature T_o selected. Since this T_o is completely arbitrary, it is insightful to select some temperature which is characteristic of a polymer. Therefore, the glass transition temperature, T_g, is often taken as the reference temperature, and thus, a_T becomes a universal function of temperature /19/.

$$\log(a_t) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (16)$$

The above relation holds from T_g to (T_g + 100°C), and the constants C_1 and C_2 are the approximate universal constants with values 17.4 and 51.6 (20).

Free Volume Theory

The study of Free Volume Theory (FVT) refers to the influence of small changes of volume, which associates with modifications of molecular mobility, a "structural" contribution, for the viscoelastic materials. Since accommodations of molecule chains need sufficient inter-molecular space for differential motion that occurs with time such as to produce the viscoelastic mechanical response /21/, this time dependent characteristic is a very sensitive reaction. Thus, even if there is only a small volume change, a very large change in the time scale of macroscopic deformations can be produced. Accordingly, this volume change must directly affect the interstitial space that molecules need to respond to macroscopically imposed stress and deformations, effects of material dilatation due to solvents, temperature changes, or mechanical stresses.

Free volume is defined as the region that is accessible to the center of a molecule through a drifting motion that does not require interaction with its neighbor molecules /22/. For the purpose of deriving the FVT model, an assumption is made that all molecular motion mechanisms are affected by volume changes equally; therefore, there is no change in the phenomenological distribution functions of relaxation or retardation times /21/. Moreover, the viscoelastic equations are identical to those of linear temperature-dependent viscoelasticity except the shift function, a_M, which will be an instantaneous functional of the free volume in terms of solvent concentration, c:

$$a_M = a_M\{c\} \tag{17}$$

Doolittle had /22, 23/ empirically derived the shift function in terms of the free volume based on the phenomenological time-temperature superposition principle:

$$\log(a_M) = B\left(\frac{1}{f} - \frac{1}{f_o}\right) \tag{18}$$

where f_o is the reference (fractional) free volume at some reference temperature, in which the time-dependent (linear) material properties are measured, and f is the fractional free volume assuming a linear functional of c at any instant time:

$$f = \frac{V_f}{V} \tag{19}$$

where V_f is the free volume and V is the total volume.

For a better understanding of the FVT, it may also be visualized through a mechanical analog for viscoelastic behavior as shown in Figure 1:

Seefried and Koleske /24/ indicated that if it is assumed that the fractional free volume of the polymer increases linearly above the T_g, then the relation of T_g with f can be written as follow:

$$f = f_g + \alpha_f (T - T_g) \tag{20}$$

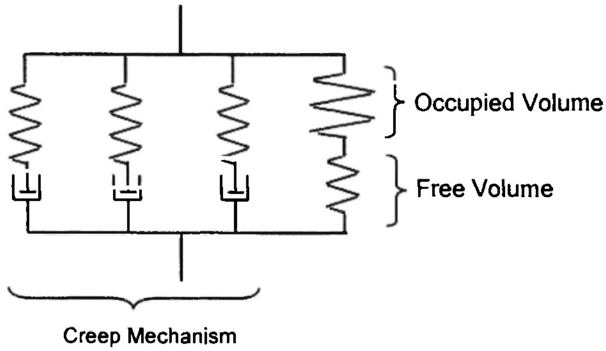

Fig. 1: Mechanical Analogue of the Constitutive Behavior of Volumetric Influence. /23/

where α_f is the thermal coefficient of expansion of the fractional free volume above T_g ($\alpha_f = 2.10 \times 10^{-4}$ K^{-1} for polyethylene at 298 K) and f_g is the free volume fraction at T_g. The combination of Equations (18) and (20) yields:

$$\log(a_M) = \frac{-B}{f_g}\left[\frac{T - T_g}{(f_g/\alpha_f) + (T - T_g)}\right] \tag{21}$$

Comparison shows that Equation (21) is identical with Equation (16) where:

$$C_1 = \frac{B}{f_g} \quad \text{and} \quad C_2 = \frac{f_g}{\alpha_f} \tag{22 \& 23}$$

EXPERIMENTAL

A flexural creep test was designed based on the standard test method of ASTM D 6112. The four-point loading configuration will be used because the plastic lumbers are expected to be relatively ductile and thus do not normally fail by the maximum strain (3%) under the three-points loading. The plastic lumber specimens tested are commercial railing products of a square shape with sides of 1.5 inch and thickness of 1/4 inch, which consists of a resin matrix of recycled HDPE and natural fiber. The cellulose fiber content of the tested plastic lumbers is about 50%. All test specimens are employed in the "as-manufactured" form in all cases.

The test rack is used to provide support of the test specimen at both ends with a span equal to sixteen times the depth of the specimen with tolerant of plus four and minus 2, and consequently the support span of the test rack in this case will be:

$$L = 16 \times 1.5\ inch = 24\ inch$$

According to the test standard, the span for the loading beam will be one-third the length of the support span and locates mid-span of the test specimen. The noses of both the support and loading beam are configured with cylindrical surfaces with a radius of 0.5 inch in order to avoid excessive indentation of the specimen. In order to allow for overhanging, at least 10% of the support span should be maintained at each end of the test specimen. Therefore, the total specimen span must be at least 30 inch at all times. Finally, the deflection of the specimen is measured at the midpoint of the load span at the bottom face of the specimen with a set of electrical displacement transducers (Figure 2) connected to an on-line computer controlled data acquisition system.

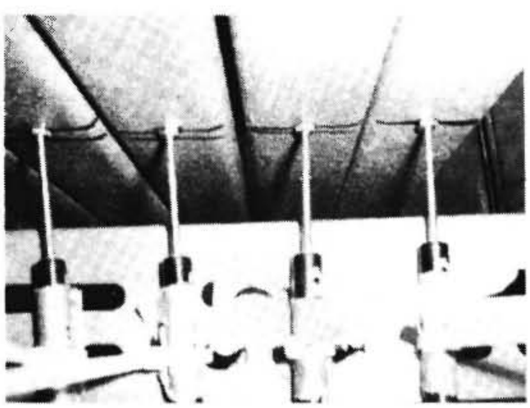

Fig. 2: Displacement Transducers.

The specimens are preconditioned in the test environment for forty-eight hours to ensure an established equilibrium condition prior to being tested. Two extreme cases of environment conditions are being tested, which are normal room condition (20°C and 34%RH) and maximum humidity (40°C and 92%RH).

The flexural creep is started by properly mounting the specimens on the creep fixture of flexural creep rack. A pre-selected load of 70 lbf (4.14 MPa) is applied rapidly and smoothly to the specimen, preferably in 1 to 5 s, and the timing is started at the onset of loading. The flexural deflection of the specimen is measured at the bottom of the test specimen at the midpoint of the load span in accordance with the approximate time schedule of 1, 6, 12, and 30 min, and 1, 2, 5, 20, 50, 100, 200, 500, 700, and 1000 hr.

RESULTS & DISCUSSIONS

The purpose of this article has been to elucidate a method that quantitatively and succinctly comprehends the complex phenomenon in plastic-natural fiber composites. However, a small part of our experimental results are shown below:

Creep Constants/Coefficients

The creep constants/ coefficients at the ambient setting i.e. 21°C and 34% relative humidity have been calculated with the help of equation #11, which may be rewritten:

$$\varepsilon(t) = g_o D_o \sigma + g_1 g_2 D_1 (t / a_\sigma)^n$$

The creep coefficients g_o, g_1, g_2, a_σ and the index value n were experimentally determined from short term creep tests (Figure 3)

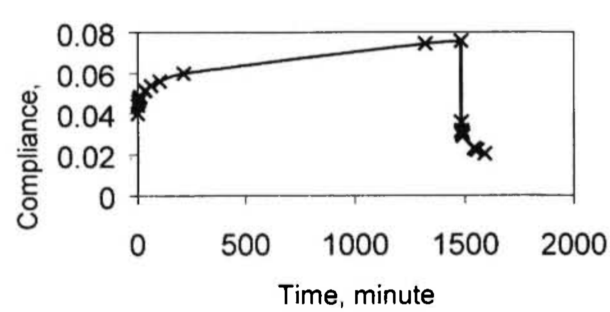

Fig. 3: Creep profile at 22% max stress level, based on three samples

Table 1
Creep coefficients at two stress levels

Stress level	g_0	g_1	g_2	a_σ	Do (%/MPa)	D_1(%/MPa/ minute $^{0.24}$)	*n
0.22 max	1.01	1.00	1.00	1.00	0.06	0.004	0.30
0.35 max	1.55	1.12	1:50	0.70	0.06	0.004	0.30

* n will vary with time

Table 1 summarizes constant values at two stress levels of the failure stress, 22% and 35%. The hallmark of creep is that g_0 and a_σ change with stress level. A higher stress indicates higher compliance (strain/stress) and a higher compliance drifts the material into the plastic/no-recovery zone. The value of "n" reflects the shape of the curve: flat or steep. The above values may not exactly tally with those obtained from equations 8, 9, 13, 14, & 15 because a composite is way more complex than a simple polymer like polyethylene. However, these equations are useful for comparing intrinsic material properties (e.g. $D_o = \varepsilon_o'/\sigma_e$). It is obvious that D_o calculated based on a property of polyethylene (matrix) will deviate from the real value D_o of composite; composite has wood particles which lower the compliance (ε/σ) dramatically.

The aforementioned coefficients describe creep in an ambient setting: at a stress level of 0.22, where the following equation will describe creep for 1000 hrs. However, the value of "n" for 1000 hrs was about 0.24 because the creep curve flattens with respect to time:

$$\varepsilon(t) = 0.06\sigma + 0.004(t)^{0.24}\sigma$$

Creep Prediction with TTMSP

Using equations (16) and (18), a_T & a_M were calculated: a_T was found to be 0.38 and a_M values are as in Table 2.

Using 20°C/34% RH as the base line creep we estimated compliance as a function of time for the conditions 40°C/93% RH and 40°C/72% RH; the experimental and predicted creep lines are delineated in Figure 4. In Figure 4, there are two shift factors, first a_T

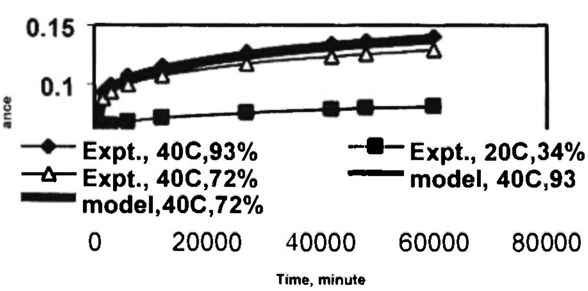

Fig. 4: Comparison of experimental creep data with predictions

Table 2
Free volume and a_M at some RH values

B	f	RH at 40° C	f_g (at T_g)	a_M
0.18	0.030	21%	0.0247	0.008 (21%-50%)
0.18	0.0347	34%	0.0247	0.120 (34%-50%)
0.18	0.0430	50%	0.0247	Not done
0.18	0.0540	93%	0.0247	0.160 (50%-93%)

and then a_M; so the effective TTMSP creep profile should assume the following equation:

$$\varepsilon(t)/\sigma = 0.06 + 0.004(t / a_T a_M)^{0.24}$$

CONCLUSION

The model of TTMSP was successfully developed based on Schapery's nonlinear viscoelastic theory. The most significant contribution of the TTMSP would be that it can provide an analytical approach to incorporate both the time-temperature and time-moisture effects in the long-term performance of the natural fibre-thermoplastic composites. The model of the time-temperature characteristic was adapted from the well-established TTSP method, and that for the time-moisture was developed based on the free volume theory of viscoelastic materials as a function of moisture content in different relative humidity levels. The shift factors for both the temperature and moisture effects were determined, the mechanical properties over time of the composites could be predicted by determining the coupling strain effects due to the combined condition.

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