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THE EFFECT OF WATER ON THE THERMAL EXPANSION BEHAVIOR OF FM5055 CARBON PHENOLIC

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ABSTRACT

The effect of water on the thermal expansion behavior of FM5055 carbon phenolic is studied using a theory of mixtures approach. A partial pressure expression for the water constituent was obtained based upon certain assumptions regarding the thermodynamic state of water as it resides in the free volumes of the polymer. A simple constitutive model is used to simulate the polymer strain due to the application of the partial pressure of water. The resulting theory is applied to model the effect of moisture on the thermal expansion of FM5055 carbon phenolic specimens. The application of the theory results in calculated strains which were in close agreement with the measured strains.

INTRODUCTION

The thermal expansion behavior of phenolic polymer composite materials is significantly influenced by the amount of moisture which exists in the composite prior to heating. The effect of water has been measured in studies by Stokes and Koenig 1990 and Stokes 1990a. The presence of water in the free volumes of the polymer during heating has two primary effects: it lowers the glass transition temperature of the polymer and it generates internal stresses in the polymer network due to thermal excitation of the water in a confined volume. These internal stresses, in turn, affect the apparent thermal expansion behavior.

In a recent study, Sullivan (1995) used a mixtures approach to model the effect of water on thermal stresses in polymer composites. Sullivan developed a partial pressure expression for the water based on certain assumptions regarding the thermodynamic state of water as it resides in the free volumes of the polymer. The objective of the present paper is to apply the partial pressure expression for water developed in Sullivan (1995) to model the effect of water on the thermal expansion behavior of FM5055 carbon phenolic. This will require a slight modification of the theory since in that work it was assumed that the mixture was elastic and since the thermal expansion strain measured by Stokes (1990a) has irreversible as well as elastic components. In the present work, we will employ a simple constitutive model which has both elastic and irreversible components to simulate the polymer strain under the application of the partial pressure of water. In the final section, the resulting theory is applied to simulate the effect of water on the thermal expansion of FM5055 carbon phenolic specimens. We simulate the conditions imposed during the tests conducted by Stokes (1990a).

THEORETICAL DEVELOPMENT

The Diffusion Equation

We study the physics of heating a polymer composite material containing water in the free volumes of the polymer from within the framework of the mixtures theory. In this regard, we may conceive of the water in the free volumes and the polymer network itself as constituting a binary, miscible mixture. The theory developed in Sullivan (1995) assumes that the strain states of the mixture remain infinitesimal and therefore the mixture occupies a fixed control volume. The partial density of water in the mixture ρ_w is therefore only dependent upon the mass concentration of water in the free volumes.

Within this mixture, the local mass concentration of water may vary with spatial location. The variation of the moisture content with space and time depends upon the process of diffusion of water through the polymer network. The differential equation governing the flow of water through the polymer network is written

$$\dot{\rho}_w - \text{div}(D \text{grad } \rho_w) = 0 \quad (1)$$

where D is the diffusivity coefficient and $\dot{\rho}_w$ is the local time derivative of the partial density of water.

In equation (1), the forces which drive the diffusion of water through the polymer are due only to the concentration gradients. The choice of equation (1) as the diffusion equation implies that the effect of stress on the diffusion process can be neglected. This is not true as a general rule. However, for the purpose of the present simulation, this assumption will be sufficient. We will see the consequences of this assumption when the theory is applied in the following sections and the numerical results are compared to measurements.

An Expression for the Partial Stress of Water

The total stress of the mixture $\bar{\sigma}$ is the sum of the partial stresses, that is

$$\bar{\sigma} = \bar{\sigma}^p + \bar{\sigma}^w \quad (2)$$

where $\bar{\sigma}^p$ is the partial stress tensor of the polymer and $\bar{\sigma}^w$ is the partial stress tensor of the water. Equation (2) is merely Dalton's law of partial pressures (Guggenheim, 1933) which was originally intended for gaseous mixtures. Its application here is more general since we will apply equation (2) to a mixture of condensed phases.

In the most general sense, the partial stresses are functions of the independent variables $\bar{\epsilon}$, T and ρ_w . However, for our purposes here we will assume that the partial stress of water is independent of the strain state. Therefore, we have that

$$\bar{\sigma}^w = \bar{\sigma}^w(T, \rho_w). \quad (3)$$

From (3), the differential increment in the partial stress of the water may be written in the expanded form as

$$d\bar{\sigma}^w = \left\{ \frac{\partial \bar{\sigma}^w}{\partial T} \right\}_{\rho_w} dT + \left\{ \frac{\partial \bar{\sigma}^w}{\partial \rho_w} \right\}_T d\rho_w \quad (4)$$

where the subscripts on the brackets indicate differentiation with those variables held constant. Assuming that the second term in (4) is negligible in comparison to the first term, (4) becomes simply

$$d\bar{\sigma}^w = \left\{ \frac{\partial \bar{\sigma}^w}{\partial T} \right\}_{\rho_w} dT. \quad (5)$$

We must now determine the relation between the partial stress of water and increments in temperature as the polymer and water mixture are heated under constant composition conditions. For this purpose, we start with Gibbs expression (Guggenheim, 1933)

$$d\mu_w = V_w dP - S_w dT \quad (6)$$

where μ_w is the chemical potential of water in the mixture, V_w is the partial volume and S_w is the partial entropy. If we assume that as this mixture is heated, the chemical potential of the water does not vary then (6) becomes

$$V_w dP = S_w dT. \quad (7)$$

Integrating both sides of (7), while taking the partial volume independent of the pressure, and substituting $\rho_w = 1/V_w$, we obtain

$$P_w = P_w^0 + \rho_w \int_{T_0}^T S_w dT \quad (8)$$

where P_w^0 is the partial pressure of water at temperature T_0 . Substituting the specific entropy of water s_w for the partial entropy, equation (8) becomes

$$P_w = P_w^0 + \rho_w \int_{T_0}^T s_w dT. \quad (9)$$

In arriving at equation (8), we integrated the left side of (7) with the partial volume independent of pressure. This is justified since the partial density and therefore the partial volume are only dependent upon the diffusion process and since by using equation (1) we are assuming that the diffusion occurs independent of the partial pressure.

Constitutive Relations for the Polymer Strain

At temperatures below the glass transition temperature, the polymer is in a *glassy* state and behaves as a linear elastic solid. At temperatures above the glass transition temperature, the polymer behaves *rubbery* exhibiting both elastic as well as irreversible deformations during loading (Meares, 1965). In the rubbery state, we specify that the dilatational response is linear elastic and that the distortional strain response has elastic and irreversible components.

The polymer strain components e_{ij} may be written in terms of the deviatoric \hat{e}_{ij} and dilatational e parts as

$$e_{ij} = \hat{e}_{ij} + \frac{1}{3} e \delta_{ij}. \quad (10)$$

where we now specify that¹

$$e = e^e \quad \hat{e}_{ij} = \hat{e}_{ij}^e + \hat{e}_{ij}^i. \quad (11)$$

Substituting equations (11), equation (10) is written

$$e_{ij} = \hat{e}_{ij}^e + \hat{e}_{ij}^i + \frac{1}{3} e^e \delta_{ij}. \quad (12)$$

¹ The mechanical model described by the second expression in (11) is similar to a Maxwell solid since the distortional strain is simply the sum of the elastic and irreversible components.

We will assume that the polymer is isotropic in its mechanical response. The constitutive relations for the elastic response are given by the relations for an isotropic elastic solid which are

$$\epsilon_{ij}^e = \frac{1}{2G} \sigma_{ij}^p \quad e^e = \frac{1}{3K} \sigma_{kk}^p \quad (13)$$

where the repeated indices imply summation. In (13), G and K are the elastic shear and the elastic bulk modulus of the polymer, respectively and σ_{ij}^p is the polymer deviatoric stress components. For the irreversible strain, we use the constitutive relation

$$\epsilon_{ij}^ir = \int \frac{1}{2\eta} \sigma_{ij}^p dt \quad (14)$$

where η is the viscosity of the polymer and t is the time variable. Substituting equations (13) and (14) into (12) yields for the polymer strain

$$e_{ij} = \frac{1}{2G} \sigma_{ij}^p + \frac{1}{9K} \sigma_{kk}^p \delta_{ij} + \int \frac{1}{2\eta} \sigma_{ij}^p dt \quad (15)$$

where the last term is zero when the temperature is below the glass transition temperature.

APPLICATION TO THE FREE THERMAL EXPANSION EXPERIMENT

Test Description

We will now apply the equations established in the previous section to model the effect of water on the thermal expansion of FM5055. We will simulate the conditions imposed during the tests reported in Stokes (1990a) where cylindrical specimens made of FM5055 carbon phenolic were heated uniformly at a constant rate of 5.5°C/sec. The specimens were 0.635 cm in diameter and 2.54 cm in length and were fabricated such that the direction transverse to the fabric plane was aligned with the axial direction of the specimen (Figure 1). As the specimens were heated, the strain in the axial direction was measured as a function of temperature. The oven chamber in which the specimens were heated was maintained at zero percent relative humidity.

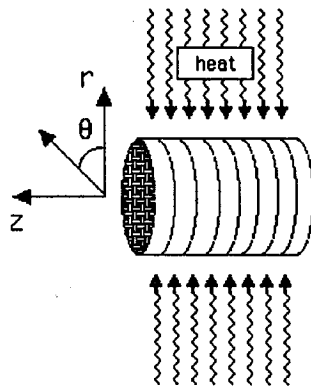


FIGURE 1. SKETCH OF CARBON PHENOLIC SPECIMEN FROM STOKES (1990a).

Stokes (1990a) measured the transverse thermal expansion strain for specimens containing three different initial moisture contents: 0%, 4% and 8% initial moisture. The measured results from Stokes are shown in Figure 2.

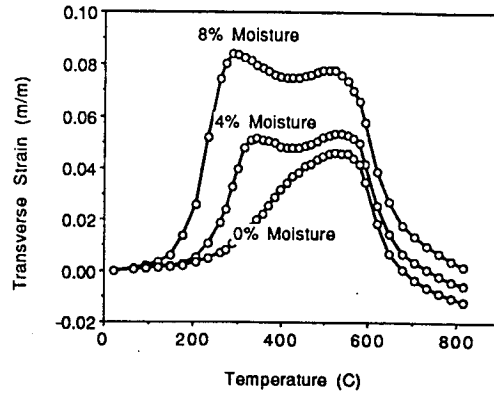


FIGURE 2. THERMAL EXPANSION MEASURED BY STOKES (1990a).

The strain response due to water may be isolated by subtracting the strain response for the 0% moisture specimen from the response for the 4% and 8% moisture specimens. This yields the two strain profiles shown in Figure 3 which we shall refer to as the *moisture-induced thermal expansion*.

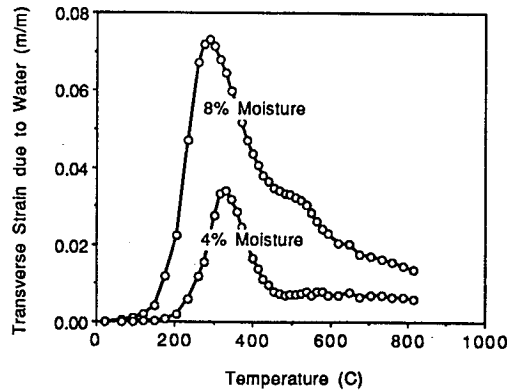


FIGURE 3. MOISTURE-INDUCED THERMAL EXPANSION VERSUS TEMPERATURE.

Diffusion Equation Solution

We will assume that the diffusion of water in the cylindrical specimens occurs in only the radial direction. For cylindrical coordinates, the one-dimensional form of (1), with diffusion in only the radial direction, is written

$$\dot{\rho}_w - \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(r D_r \frac{d\rho_w}{dr} \right) \right\} = 0 \quad (16)$$

where D_r is the diffusivity of water in the radial direction.

The boundary and initial conditions which are imposed are

$$\rho_w(a, t) = 0 \quad \text{and} \quad \rho_w(r, 0) = \rho_w^i,$$

respectively where a is the radial dimension of the specimen and ρ_w^i is the initial partial density of water in the specimen. The initial partial density is estimated as the product of the initial moisture content and the dry density of the composite. In the case of FM5055, we'll approximate the dry density as 1.5 g/cc.

The diffusion equation, (16), is solved numerically under the imposed boundary and initial conditions using the finite element method. The Galerkin weighted residual method was used to cast the diffusion equation into a matrix equation which is necessary for the numerical solution. Linear, one-dimensional elements were used to discretize the domain of the problem and to implement the finite element method.

Minimechanics and the Effect of Carbon Fibers on the Response

Due to the presence of the carbon fiber reinforcement, the average strain in the polymer is one-dimensional: $e_{rr} = e_{\theta\theta} = 0$. The average stress state in the polymer due to the partial pressure of water is therefore

$$\sigma_{ij}^p = \begin{bmatrix} -P_w & 0 & 0 \\ 0 & -P_w & 0 \\ 0 & 0 & P_w \end{bmatrix}. \quad (17)$$

Now since the stress tensor and the deviatoric stress tensor are related by

$$\delta_{ij} = \sigma_{ij} - \frac{1}{3} \sigma_{kk} \delta_{ij} \quad (18)$$

the polymer deviatoric stress tensor is

$$\delta_{ij}^p = \begin{bmatrix} -\frac{2}{3}P_w & 0 & 0 \\ 0 & -\frac{2}{3}P_w & 0 \\ 0 & 0 & \frac{4}{3}P_w \end{bmatrix}. \quad (19)$$

Substituting equations (17) and (19) into (15), we obtain for the transverse strain component, $i=z$ and $j=z$,

$$e_{zz} = \frac{(1+2\nu)}{E} P_w + \frac{2}{3} \int \frac{1}{\eta} P_w dt \quad (20)$$

where E and ν are the Young's modulus and Poisson's ratio for the polymer, respectively and are related to G and K by the familiar relations

$$G = \frac{E}{2(1+\nu)} \quad K = \frac{E}{3(1-2\nu)}. \quad (21)$$

Once again, the last term in (20) is zero at temperatures below the glass transition temperature.

Description of the Material Constants

The variation of the moisture diffusivity with temperature is illustrated in Figure 4. The moisture diffusivities measured by Stokes (1990b) are plotted as hollow circles and the moisture diffusivity model which is used for the simulation is shown as a solid line. The solid line is merely a linear fit through the two extreme measured data points and extrapolated to higher temperatures.

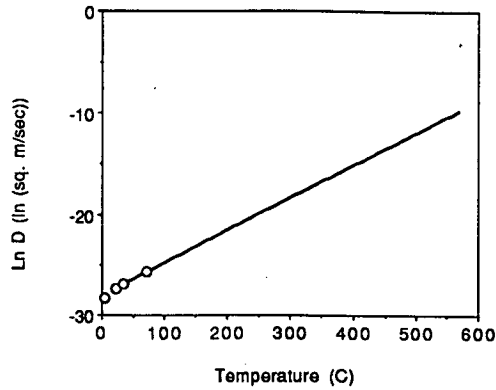


FIGURE 4. DIFFUSIVITY VERSUS TEMPERATURE.

The variation of the elastic Young's modulus with temperature is illustrated in Figure 5. The values measured by Stokes (1990a) are plotted as hollow circles and hollow squares for the 4% and 8% moisture specimens, respectively. The description of the modulus variation with temperature, which is used for this simulation, is shown as a solid and dashed line for the 4% and 8% moisture specimens, respectively.

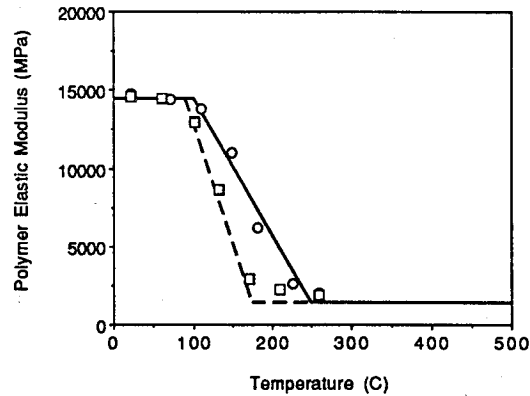
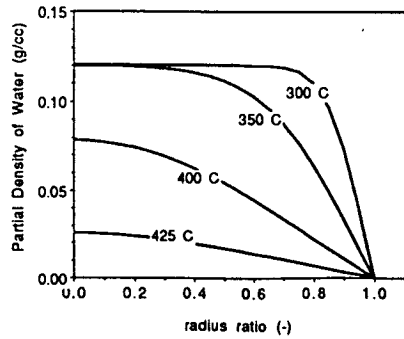


FIGURE 5. ELASTIC MODULUS VERSUS TEMPERATURE.

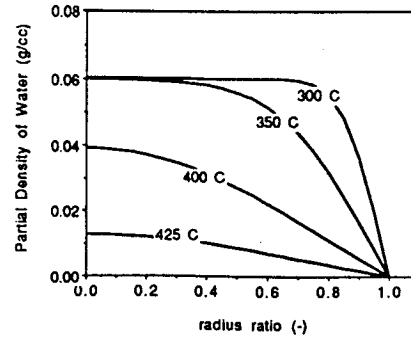
In addition, we use a constant value of 0.3 for the polymer Poisson's ratio and a constant polymer viscosity of 100000.0 MPa-sec for this simulation.

RESULTS

The numerical solution of the diffusion equation under the imposed boundary and initial conditions yields the local partial density of water in the specimens as a function of radial location and time. Figure 6a and 6b show the results for the 8% and 4% moisture conditions, respectively. Initially, the partial density is uniform throughout the specimen. As the temperature increases, the diffusivity increases according to the model illustrated in Figure 4. The radial diffusion of water begins to occur at approximately 300°C when the diffusivity has reached a sufficient value. Diffusion continues until approximately 450°C when there is no water left in the specimens.



a. 8% INITIAL MOISTURE



b. 4% INITIAL MOISTURE

FIGURE 6. PARTIAL DENSITY OF WATER VERSUS RADIAL LOCATION.

A volume average partial density may be calculated at each temperature by $\bar{\rho}_w = \int \rho_w dV / V$ where V is the volume of the specimen. For this specific problem, where the partial density is only a function of the radial location and time and where the time variable is related to the temperature variable by a constant, the volume average partial density is expressed specifically as

$$\bar{\rho}_w(T) = \frac{1}{a^2} \int \rho_w(r, T) r dr . \quad (22)$$

The volume average partial density is calculated at each temperature using equation (22) and the results shown in Figures 6. The volume average partial density of water for the two initial moisture conditions are shown in Figure 7.

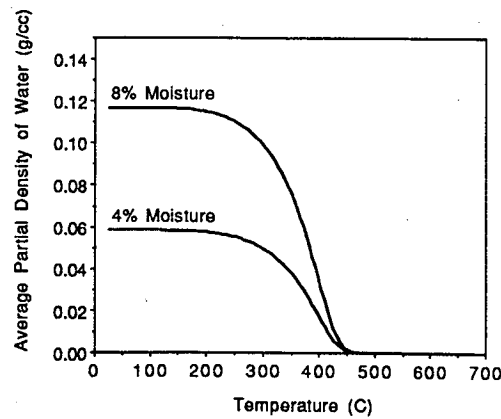


FIGURE 7. VOLUME AVERAGE PARTIAL DENSITY VERSUS TEMPERATURE.

The average partial pressure of water in the specimens is calculated using equation (9) with P_w^0 set equal to zero and using the volume average partial density shown in Figure 7. The numerical values for S_w are obtained from Keenan, et al. (1969). The variation of S_w with temperature is specified by the path along the liquid portion of the saturation curve (Kestin, 1966). The average partial pressure for the two moisture conditions are shown in Figure 8. The partial pressure increases with temperature from room temperature to 325°C since the specific entropy of water is a positive function of temperature. The increase in the partial pressure with temperature is governed by the integral term in equation (9). As the diffusion of water occurs above 325°C, the partial pressure drops with the drop in the partial density and falls to zero at approximately 450°C when the average partial density becomes zero.

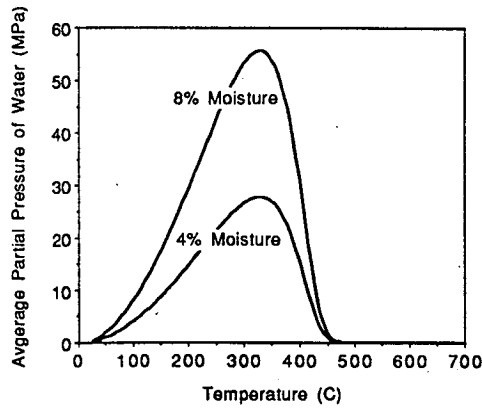


FIGURE 8. VOLUME AVERAGE PARTIAL PRESSURE VERSUS TEMPERATURE.

The transverse strain is calculated from equation (20) using the partial pressures of Figure 8 and the elastic modulus description illustrated in Figure 5. The results are shown in Figure 9 along with the moisture-induced strain profiles from Figure 3 which are plotted as hollow circles and hollow squares. For both moisture conditions, there is close agreement between the calculated and measured peak strains. Also, for the 4% moisture condition, the calculated inelastic strain is the same as that which was measured. For the 4% moisture condition, the calculated peak strain temperature is consistent with the measured peak strain temperature. For the 8% moisture condition, however, the calculated peak strain temperature lags the measured by 50°C.

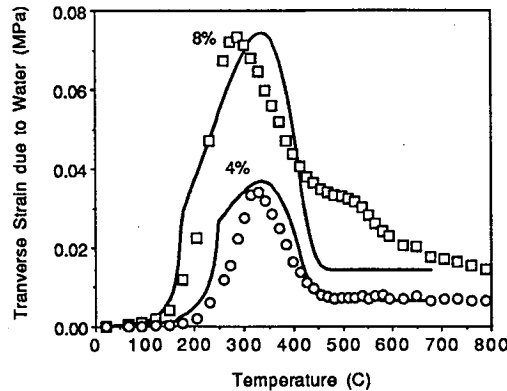


FIGURE 9. CALCULATED AND MEASURED STRAIN VERSUS TEMPERATURE.

DISCUSSION AND CONCLUSIONS

The partial pressure expression developed in Sullivan (1995) has been applied to model the effect of water on the thermal expansion behavior of FM5055 carbon phenolic. The strains obtained through application of the theory compared fairly well with those measured by Stokes (1990a). This provides another verification of the accuracy of the partial pressure expression and the assumptions which were used in the development.

The accuracy of the model may be improved further with a few modifications. For example, the slope of the calculated strain between the glass transition temperature and the peak strain temperature is not consistent with the slope of the moisture-induced strains. This may be due to the very simple constitutive model which was employed for this simulation. Alternative constitutive models should be investigated in future studies.

Furthermore, as we have previously stated, the choice of equation (1) to model the diffusion process implies that the diffusion of water is independent of the stress state. Consequently, the numerical results obtained from the solution of (1) yield the same diffusion rate for both moisture conditions (Figures 6 and 7). The moisture-induced strains in Figure 3, however, indicate that the diffusion of water occurs faster in the 8% moisture specimen than in the 4% specimen. This is due to the higher partial pressures in the 8% moisture specimen which cause higher stress gradients and an increase in the diffusion rate. At higher heating rates, the effect of stress on the diffusion rate will become more significant. In future studies, a stress-dependent diffusion equation should be employed to account for this effect.

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