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THE EFFECT OF WATER ON THERMAL STRESSES IN POLYMER COMPOSITES

Roy M. Sullivan
Structures and Dynamics Laboratory
George C. Marshall Space Flight Center
Marshall Space Flight Center, AL

ABSTRACT

The fundamentals of the thermodynamic theory of mixtures and continuum thermochemistry are reviewed for a mixture of condensed water and polymer. A specific mixture which is mechanically elastic with temperature and water concentration gradients present is considered. An expression for the partial pressure of water in the mixture is obtained based on certain assumptions regarding the thermodynamic state of the water in the mixture. Along with a simple diffusion equation, this partial pressure expression may be used to simulate the thermostructural behavior of polymer composite materials due to water in the free volumes of the polymer. These equations are applied to a specific polymer composite material during isothermal heating conditions. The thermal stresses obtained by the application of the theory are compared to measured results to verify the accuracy of the approach.

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INTRODUCTION

In their application as thermal protection barriers, polymer composite materials are subjected to severe heating conditions. The success of these materials as thermal protectants is contingent upon a thorough understanding of the thermostructural behavior so that sound design practices may be employed. Water and other volatiles may be entrapped in the polymer during curing or they may be adsorbed from the surroundings prior to their use. Since it is common for these volatiles to be present in the polymer, it is also essential to characterize how they will alter the thermostructural response of polymer composite materials.

Over the past few years, there have been many attempts to model, in an explicit manner, the thermostructural response of phenolic resin composites as they are heated to high temperatures*. These attempts have been based on and derived from the porous media theory. Although some have included the effect of water on the thermomechanical response, the primary emphasis has been to simulate the effect of thermal decomposition of the polymer on the structural behavior of the composite. These attempts have been successful in the sense that they have demonstrated the direct dependence of the transient

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* These works are too numerous to list all the important contributions. For a fairly comprehensive list see the works of Sullivan and Salamon (1992), McManus (1990) and Wu and Katsube (1994).

thermomechanical response on the diffusion process. The shortcoming with the porous media approach is the inability to accurately relate the stresses in the polymer chains to the chemical state of the volatile species.

The present effort approaches this problem from the perspective that the polymer and the water in its free volumes constitute a miscible mixture. In this study, we will review the principles of the thermodynamic theory of mixtures as discussed in the works by Bowen (1967), deGroot (1963) and Prigogine (1955). Specifically, we are interested in how these principles apply to a binary mixture of polymer and water where both temperature and water mass concentration gradients are present. We will restrict our attention to a mixture where the deformation states are assumed to remain infinitesimal and we will assume that no chemical reactions occur which would cause the generation or consumption of any of the chemical species. From this review and under the assumption of an isothermal body, a simple diffusion equation is obtained which can be used to calculate the diffusion of water through the polymer.

Using very simple mechanical considerations, the expression for the total stress for an elastic mixture may be written as the sum of the partial stresses. The expression for the partial pressure of water in the mixture is developed from thermodynamic considerations under the assumption of constant composition. We approximate the partial entropy of water in the mixture using the specific entropy of pure, condensed water. The resulting expression for the partial pressure of water in the mixture is a function of the partial density of water and the temperature.

In the final section, the diffusion equation and the partial pressure expression are employed to model the thermal stress response of carbon phenolic composite specimens under uniform heating conditions. The diffusion equation is used to determine the local partial density of water in the specimen as a function of spatial location and temperature. From these results, the volume average partial density in the specimens is determined for each temperature. Using the volume average partial density and the expression for the partial stress, the volume average partial stress of water is calculated. Comparisons are made between the calculated thermal stresses and measured stresses in order to exercise the theory and determine its accuracy. This work is an extension of the work originally published in Sullivan (1994).

REVIEW OF THERMOCHEMISTRY AND FORMULATION OF THE THEORY

Preliminaries and Basic Assumptions

Figure 1 illustrates the architecture of a reinforced polymer composite. The sketch shows the reinforcing fiber bundles embedded in the polymeric resin, the polymer free volumes and the polymer network crosslink juctions. The enlarged view illustrates the relation between polymer free volumes and occupied volumes. The volume which the water occupies is only a fraction of the total polymer free volume. The occupied volume fraction may be defined as

$$\varphi^{oc} = \frac{V^{oc}}{V^{t}} \tag{1}$$

where V^{oc} is the volume occupied by water molecules and V^{t} is the total volume which is the sum of the volume occupied by polymer, the volume occupied by water and the volume which is unoccupied.

Treating the polymer and water in the free volumes as a mixture, the density of this mixture ρ is the sum of the partial densities of the individual constituents, namely

$$\rho = \rho_w + \rho_p \tag{2}$$

where ρ_w and ρ_p represent the partial density of water and polymer, respectively. In this study, we will assume that only the water constituent is volatile, that no chemical reactions occur which would cause the generation or consumption of either of the chemical species and that the deformations states remain infinitesimal. Therefore, the density of the polymer ρ_p remains constant and the density of the mixture varies only with the partial density of water in the mixture ρ_w. The partial density of water is given by

$$\rho_w = \varphi^{oc} \rho_w^{oc} \tag{3}$$

where ρ_w^{oc} is the density of water inside the occupied volume which we shall refer to as the *occupational density* of the water.

We will assume, as our primary postulate, that the thermodynamic state of water in the free volumes can be approximated by the thermodynamic state of pure condensed water. This assumption is based on the notion that the motion of the water molecules upon heating will be restricted by the presence of the polymer segments in the same manner that the motion of water molecules in pure condensed water are restricted by their neighboring water molecules*. We may therefore approximate the partial entropy of water in the mixture by the specific entropy of pure, condensed water. The occupational density of water in the free volumes will be assumed to be equal to the density of pure, condensed water under the same temperature and pressure conditions.

The occupied volume fraction depends upon the frequency of water molecules in the polymer. This will be a function of the affinity for storage of water in the polymer, the relative humidity of the surroundings and the temperature of the surroundings. For nonequilibrium or transient conditions, the occupied volume fraction is tied directly to the diffusion process and in this case it is also a function of time. For this reason, a diffusion equation is included as part of the theoretical formulation.

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* In the case of water in phenolic polymers, the forces between the polymer molecules and the water molecules are of the same nature as the forces between adjacent water molecules in pure, condensed water. In pure condensed water, the forces are dipole-dipole forces between adjacent water molecules and, in the case of water and phenolic polymer, the forces are dipole-dipole forces between the water molecules and the hydroxyl group in each polymer repeating unit.

Conservation Laws for a Binary Mixture in a Continuous System

Let us consider a miscible mixture of polymer and condensed water occupying some arbitrary volume Ω. Within this volume, the temperature, stress and partial density of the water may be continuous functions of the spatial coordinates X_i and the time variable t. The conservation laws which govern the variation of the temperature, stress and partial density inside this mixture are the conservation of energy, momentum and water mass, respectively. Following the usual approach in continuum mechanics, the conservation laws are written for the entire volume in the form of volume integrals using Gauss' theorem (Chung, 1988 and Fung, 1965). The local form of these laws are then extracted from the volume integrals.

For the binary mixture of polymer and water with water concentration and temperature gradients present, the local form of the conservation laws are written

Conservation of Water Mass: $\dot{\rho}_w + \text{div}\,\breve{J}_w = 0$ (4)

Conservation of Linear Momentum: $\text{div}\,\breve{\sigma} = 0$ (5)

Conservation of Energy: $\rho\,\dot{u} = \text{tr}\,(\breve{\sigma}\,\dot{\breve{e}}) - \text{div}\,\breve{J}_q + \rho\,r$ (6)

where $\dot{\rho}_w$ is the local time derivative of the partial density of water, $\breve{\sigma}$ is the Cauchy stress tensor for the mixture, $\dot{u}$ is the time derivative of the specific internal energy, $\dot{\mathbf{e}}$ is the time derivative of the infinitesimal strain tensor and r is the heat supplied per unit mass. The vectors $\tilde{\mathbf{J}}_w$ and $\tilde{\mathbf{J}}_q$ are the water mass flux and heat flux vectors, respectively. In equations (4) to (6), *div* denotes the divergence operator. Also, in equation (5), body forces have been ignored.

The local entropy balance equation is

$$\rho\,\dot{s} + \mathrm{div}\,\tilde{\mathbf{J}}_s = \sigma + \frac{\rho\,r}{T_a} \tag{7}$$

where $\dot{s}$ is the local time derivative of the entropy of the mixture per unit mass, $\tilde{\mathbf{J}}_s$ is the entropy flux vector, σ is the local rate of entropy production and T_a is the absolute temperature. For the present case, the entropy flow vector $\tilde{\mathbf{J}}_s$ may be written in terms of the heat and mass fluxes as

$$\tilde{\mathbf{J}}_s = \frac{\tilde{\mathbf{J}}_q - \mu_w \tilde{\mathbf{J}}_w}{T_a} \tag{8a}$$

and the local entropy production rate σ is given by (Katchalsky and Curran, 1965)

$$\sigma = \frac{1}{T_a}\tilde{\mathbf{J}}_q \cdot \tilde{\mathbf{X}}_q + \frac{1}{T_a}\tilde{\mathbf{J}}_w \cdot \tilde{\mathbf{X}}_w. \tag{8b}$$

In equation (8a), μ_w is the chemical potential of the water in the mixture. The vectors $\tilde{\mathbf{X}}_q$ and $\tilde{\mathbf{X}}_w$ are the forces responsible for the heat and mass fluxes, respectively. Mathematically, they are written $\tilde{\mathbf{X}}_q = -\,\mathrm{grad}\,T$ and $\tilde{\mathbf{X}}_w = -\,\mathrm{grad}\,\mu_w$ where *grad* denotes the spatial gradient operator.

The local form of the second law of thermodynamics is known as the Claussius-Duhem inequality and it states that the local rate of entropy production for any admissible thermodynamic process must be nonnegative (Coleman and Gurtin, 1967). Therefore, for the two simultaneous processes, there is the restriction that

$$\mathbf{J}_q \cdot \mathbf{X}_q + \mathbf{J}_w \cdot \mathbf{X}_w \geq 0.$$

The Flow Equations in a Continuous System

For a continuous system where heat and mass fluxes occur simultaneously, the simplest relation between the flux vectors $\mathbf{J}_q$ and $\mathbf{J}_w$ and their corresponding force vectors $\mathbf{X}_q$ and $\mathbf{X}_w$ are the linear relations

$$\begin{aligned} \mathbf{J}_q &= L_{qq}\mathbf{X}_q + L_{qw}\mathbf{X}_w \\ \mathbf{J}_w &= L_{wq}\mathbf{X}_q + L_{ww}\mathbf{X}_w \end{aligned} \qquad (9)$$

where L_{ij} is the set of arbitrary constitutive coefficients known as the phenomenological coefficients (Katchalsky and Curran, 1965). The Claussius-Duhem inequality imposes the restriction on the matrix of constitutive coefficients L_{ij} that the determinant must be nonnegative, $|L_{ij}| \geq 0$. Furthermore, Onsager (1931) established that $L_{ij} = L_{ji}$, $i \neq j$, giving for the present case that $L_{qq} L_{ww} \geq L_{qw}^2$.

Under isothermal conditions, the second expression in equations (9) reduces to

$$\mathbf{J}_w = - L_{ww} \operatorname{grad} \mu_w . \tag{10}$$

Choosing the variables $\tilde{\mathbf{e}}$, T and ρ_w as independent, the chemical potential may be written as a function of these variables, namely $\mu_w = \mu_w (\tilde{\mathbf{e}}, T, \rho_w)$. However, if the strain tensor has a negligible effect on the chemical potential, then, for an isothermal body, equation (10) takes a form similar to Fick's law. This is commonly written as

$$\mathbf{J}_w = - D \operatorname{grad} \rho_w \tag{11}$$

where D is the diffusivity coefficient which is a function of temperature. For isothermal bodies with water mass fluxes, the Claussius-Duhem inequality imposes the restriction that the diffusivity coefficient must be nonnegative.

Substituting equation (11) into equation (4), we obtain the familiar equation for the diffusion of moisture through an isothermal body which is nondeformable or one where the deformation states do not effect the chemical state. This is

$$\dot{\rho}_w - \operatorname{div} (D \operatorname{grad} \rho_w) = 0. \tag{12}$$

A Simple Thermomechanical Model

In order to develop an expression for the total stress at each spatial location in the mixture, we consider the mechanical analog shown in Fig. 2 which consists of a spring in a parallel arrangement with a piston and cylinder device. The spring represents the collective stiffness of the polymer network as well as any additional stiffness provided by reinforcing fibers. The cylinder contains pure, condensed water.

Since we have assumed a miscible mixture, the force in the piston and the force in the spring act over the same area*. The total stress of the mixture is therefore the sum of these forces divided by the infinitesimal area. Mathematically, this is simply

$$\tilde{\boldsymbol{\sigma}} = \tilde{\boldsymbol{\sigma}}^{p} + \tilde{\boldsymbol{\sigma}}^{w} \qquad (13)$$

where $\tilde{\boldsymbol{\sigma}}^{p}$ is the partial stress tensor of the polymer and $\tilde{\boldsymbol{\sigma}}^{w}$ is the partial stress

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* We follow the traditional approach in solid mechanics where the Cauchy stresses are defined as the internal forces acting over an infinitesimal area. This area is assumed much larger than the atomic dimensions, so the forces in the lattice network are assumed to be evenly distributed over the infinitesimal area. Therefore, in the present case, the partial stress of the polymer is the force in the polymer network evenly distributed over the total or bulk area of the mixture and the partial stress of the water is the force exerted by the water in the free volumes evenly distributed over the bulk area.

tensor for the water, given by $\tilde{\sigma}^w = -\tilde{I}\,P^w$ where $\tilde{I}$ is the identity matrix and P^w is the partial pressure of water in the mixture.

The differential of the partial stress of the polymer can be expanded in terms of the independent variables $\tilde{\varepsilon}$, T and ρ_w as

$$d\tilde{\sigma}^p = \left\{\frac{\partial \tilde{\sigma}^p}{\partial \tilde{\varepsilon}}\right\}_{T,\rho_w} d\tilde{\varepsilon} + \left\{\frac{\partial \tilde{\sigma}^p}{\partial T}\right\}_{\tilde{\varepsilon},\rho_w} dT + \left\{\frac{\partial \tilde{\sigma}^p}{\partial \rho_w}\right\}_{T,\tilde{\varepsilon}} d\rho_w \qquad (14)$$

where the subscripts on the brackets indicate differentiation with those variables held constant. In the model of Fig. 2, the force in the spring is independent of the density of water in the cylinder when temperature and strain are held constant. Thus, the expression for the polymer partial stress increment, equation (14), reduces to

$$d\tilde{\sigma}^p = \left\{\frac{\partial \tilde{\sigma}^p}{\partial \tilde{\varepsilon}}\right\}_{T,\rho_w} d\tilde{\varepsilon} + \left\{\frac{\partial \tilde{\sigma}^p}{\partial T}\right\}_{\tilde{\varepsilon},\rho_w} dT. \qquad (15)$$

Recognizing the first term in brackets as the fourth-order stiffness tensor $\tilde{C}^p$ and the second term as the negative product of the stiffness tensor and the tensor of thermal expansion coefficients $\tilde{\beta}^p$, equation (15) may be written

$$d\tilde{\sigma}^p = \tilde{C}^p\,d\tilde{\varepsilon} - \tilde{C}^p\,\tilde{\beta}^p\,dT. \qquad (16)$$

Substituting equation (16) into the differential form of equation (13) and employing $d\tilde{\sigma}^w = -\tilde{I}\,dP^w$ leads to

$$d\tilde{\boldsymbol{\sigma}} = \tilde{\mathbf{C}}^{p}\, d\tilde{\boldsymbol{\varepsilon}} - \tilde{\mathbf{C}}^{p}\, \tilde{\boldsymbol{\beta}}^{p}\, dT - \tilde{\mathbf{I}}\, dP^{w}. \tag{17}$$

An Expression for the Partial Pressure of Water in the Mixture

We are now left with the task of determining the variation of the partial pressure of water with temperature. To this end, let us now consider a homogeneous mass of pure condensed water as shown in Fig. 3 which is heated through a continuous series of equilibrium states. As heat is applied and the temperature increases, we will simultaneously apply a pressure such that the water molecules may not leave the condensed phase and enter the vapor phase. The expression for the chemical potential in terms of pressure and temperature for such a mass is

$$d\mu_w = v_w\, dP - s_w\, dT \tag{18}$$

where v_w is the specific volume of pure water and s_w is the specific entropy. Since there is no water mass transferred between phases, the chemical potential of the water does not vary as it is heated, $d\mu_w = 0$. Imposing this restriction on equation (18) leads to

$$\int_{P_o}^{P} v_w\, dP = \int_{T_o}^{T} s_w\, dT \tag{19}$$

where P is the pressure which is required such that no evaporation of the water occurs during the increase in temperature.

For a condensed phase, the specific entropy may be regarded as being independent of the pressure (Prigogine and Defay, 1954). This is evident by examining the thermodynamic surface of equilibrium states in the condensed region. For example, in the temperature versus specific entropy diagram, the lines of constant pressure collapse to one curve in the condensed region. Therefore, in the purely condensed phase, the specific entropy is only a function of the temperature (Kestin, 1966) and equation (19) can be written

$$\int_{P_o}^{P} v_w \, dP = \int_{T_o}^{T} s_w \, dT = f\,(T). \qquad (20)$$

We now return our attention to the condensed mixture of polymer and water and consider the case where this mixture is heated under constant composition conditions. In this case, the expression for the chemical potential of water in the mixture is (Guggenheim, 1933)

$$d\mu_w = V_w \, dP - S_w \, dT \qquad (21)$$

where V_w is the partial volume of water in the mixture and S_w is the partial entropy. Under the same restriction that $d\mu_w = 0$, we now have

$$\int_{P_o}^{P} V_w \, dP^w = \int_{T_o}^{T} S_w \, dT. \qquad (22)$$

If the partial entropy of water in the mixture is approximated by the specific entropy of pure condensed water, equation (22) may be written as

$$\int_{P_o}^{P} V_w \, dP^w = \int_{T_o}^{T} s_w \, dT = f\,(T). \tag{23}$$

Performing the integration of the left hand side of equation (23) with V_w independent of pressure leads to an expression for the partial pressure of water which is

$$P^w = P_o^w + \rho_w \int_{T_o}^{T} s_w \, dT \tag{24}$$

where P_o^w is the partial pressure at T_o and where we have made the substitution $V_w = 1/\rho_w$.

The assumption that V_w is independent of the pressure follows from the previous assumption that the thermodynamic state of the water is equal to the thermodynamic state of pure, condensed water and by our choice of equation (12) as the diffusion equation. The partial density, by equation (3), is the product of the occupational density and occupied volume fraction. If we consider that for condensed water, any variation in the specific volume requires large increments in the applied pressure and if we assume that the partial pressure variations are not large enough to cause significant changes in the occupational density, then we may assume that the occupational density does not vary with partial pressure. Furthermore, since the occupied volume fraction is governed by equation (12) and since equation (12) is independent of pressure, the occupied volume fraction will be independent of the partial pressure. These considerations justify the assumption that the partial density and therefore the partial volume is independent of the partial pressure.

Integrating equation (17) and substituting equation (24) for the partial pressure, the total stress expression is

$$\tilde{\sigma} = \tilde{\sigma}_o + \int_{\tilde{e}_o}^{\tilde{e}} \tilde{C}^p \, d\tilde{e} - \int_{T_o}^{T} \tilde{C}^p \, \tilde{\beta}^p \, dT - \tilde{I} \, \rho_w \int_{T_o}^{T} s_w \, dT \tag{25}$$

where $\tilde{\sigma}_o$ is the initial total stress at temperature T_o and strain state $\tilde{e}_o$.

DEMONSTRATION AND VERIFICATION OF THE THEORY

Test Description

We will now apply the principles and equations which have been established in the previous section to simulate the thermomechanical response of a specific polymer composite material under a specific set of heating conditions. The material which is chosen for this simulation is carbon phenolic. Carbon phenolic is a general class of laminated, composite materials which are constructed with carbon fabric which has been impregnated with a phenolic resin.

We will simulate the conditions imposed during the tests reported in Hubbert (1989) where cylindrical specimens made of FM5055 carbon phenolic were heated uniformily at a constant rate of 5.5 ^{o}C/sec. The specimens were 1.27 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 (Fig. 4). As the specimens were heated, the stress required to maintain zero 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.

In Fig. 5, the measured restraining stress is plotted versus temperature. The results are shown for specimens with three different initial moisture contents. The amount of water in the specimens has two effects on the measured thermal stresses. The most obvious effect is that the magnitude of the restraining stress is proportional to the initial moisture content in the specimen. In addition, water is known to lower the glass transition temperature in glassy polymers (Meares, 1965). For carbon phenolic, this effect is illustrated in Fig. 5 where we have identified the approximate glass transition temperatures for the 0% and 4% moisture conditions. The glass transition temperature for the 8% initial moisture specimen is more difficult to identify since, in this case, the partial stress of water becomes more significant and obscures the glass transition effect on the measured stress.

Analysis Approach

Since the specimens were heated uniformily, the temperature is independent of the spatial coordinates. Furthermore, we will assume that the response of the specimens is axisymmetric with symmetry about the r-z plane and that the diffusion of water occurs only in the radial direction (Fig. 4). The variables $\breve{\sigma}$ and ρ_w are therefore independent of θ. We will also assume that these variables are independent of z so that $\breve{\sigma} = \breve{\sigma}(r, t)$ and $\rho_w = \rho_w(r, t)$.

The axisymmetric, one-dimensional form of equation (12), with diffusion in only the radial direction, is

$$\dot{\rho}_w - \frac{1}{r}\left\{\frac{\partial}{\partial r}\left(r\, D_r \frac{\partial \rho_w}{\partial r}\right)\right\} = 0 \tag{26}$$

where D_r is the diffusivity of water in the radial direction. The boundary and initial conditions which are imposed are

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

respectively where a is the radial dimension of the specimen and ρ_w^o is the initial partial density. The initial partial density is approximated as the product of the initial moisture content and the dry density of the composite. In the case of carbon phenolic, we'll approximate the dry density as 1.5 g/cc.

In Fig. 6, the diffusivity of FM5055 carbon phenolic in the direction parallel to the fabric plane is plotted versus temperature. The hollow circles represent measurements made by Stokes (1990). The solid line represents the diffusivity versus temperature description which will be used for this simulation. It was obtained by a linear fit through the measured data points.

The diffusion equation 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.

Results

Figures 7a and 7b are plots of the calculated partial density of water versus radial location at various temperatures obtained from the numerical solution of equation (26). Figure 7a shows the partial density for the 4% moisture specimen and 7b shows the values for the 8% moisture specimen. In both cases, the partial density is initially uniform. As time and temperature increase, the diffusivity increases according to the model in Fig. 6. Driven by the density gradient, the radial diffusion of water begins to occur to a noticable extent at temperatures above 350 ^{o}C when the diffusivity has reached a sufficient value. Diffusion continues until approximately 475 ^{o}C when, as the numerical results indicate, there is very little water left in the specimens and therefore the density gradients at all spatial locations approach zero.

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* A detailed discussion of the method is given in Zienkiewicz (1982) and Segerlind (1984). A discussion of its application to axisymmetric diffusion equations is given in Lee, Salamon and Sullivan (1994).

The volume average partial density of water may be determined as a function of time by the relation

$$\overline{\rho_w}(t) = \int \rho_w(r, t)\, dV \Big/ \int dV. \tag{27}$$

For this specific problem, where the partial density is only a function of time and the radial coordinate and where the time variable is related to the temperature variable by a constant, equation (27) may be written specifically as

$$\overline{\rho_w}(T) = \frac{1}{a^2} \int \rho_w(r, T)\, r\, dr. \tag{28}$$

The volume average partial density in the specimen was calculated using equation (28) and the numerical results of Figs. 7. The average densities are plotted for the two initial moisture conditions in Fig. 8.

We may approximate the volume average partial pressure of water in the specimen using the volume average densities of Fig. 8 and the expression for the partial pressure given in equation (24). In Fig. 9, the average partial pressure is plotted versus temperature for the two initial moisture conditions. From room temperature to 350 °C, the partial pressure increases with temperature since the partial density remains constant and since the specific entropy is a positive function of the temperature. The increase in the partial pressure with temperature is governed by the integral term in equation (24). As the diffusion of water occurs above 350 °C, the partial pressure drops with the drop in partial density and falls to zero when the partial density falls to zero. At all temperatures, the partial pressure of water for the 8% initial moisture case is twice that of the 4% initial moisture case.

The present approach may be verified by comparing the total stress given by equation (25) to the total stress measured by Hubbert for both the 4% and 8% conditions. We may rewrite equation (25) as

$$\tilde{\sigma} = \tilde{\sigma}^{p} + \tilde{\sigma}^{w}_{o} - \tilde{I}\,\rho_{w} \int_{T_o}^{T} s_{w}\, dT \qquad (29a)$$

where

$$\tilde{\sigma}^{p} = \tilde{\sigma}^{p}_{o} + \int_{\tilde{e}_o}^{\tilde{e}} \tilde{C}^{p}\, d\tilde{e} - \int_{T_o}^{T} \tilde{C}^{p}\, \tilde{\beta}^{p}\, dT \qquad (29b)$$

and where $\tilde{\sigma}^{p}_{o}$ and $\tilde{\sigma}^{w}_{o}$ are the initial partial stress of the polymer and initial partial stress of water, respectively. Setting $\tilde{\sigma}^{w}_{o}$ equal to zero, the total stress component in the axial direction, according to equation (29a), is

$$\sigma_{zz} = \sigma^{p}_{zz} - \overline{\rho_{w}} \int_{T_o}^{T} s_{w}\, dT. \qquad (30)$$

In equation (30), we have replaced the partial density with the volume average partial density.

The measured restraining stress for the 0% condition shown in Fig. 6 is a direct measurement of the polymer partial stress component σ^{p}_{zz}. The second term on the right hand side of equation (30) is the volume average partial pressure which has been plotted in Fig. 9 for the two moisture conditions. Superimposing the measured restraining stress profile for the 0% condition with the two pressure profiles of Fig. 9, the total stress profiles for the 4% and 8% moisture conditions may be determined. These are plotted in Fig. 10 along with the measured values.

There are slight discrepencies between the calculated and the measured total stresses near the glass transition temperature. This results from simply superimposing the two profiles together. The polymer partial stress profiles have not been adjusted to account for the effect of moisture content on the glass transition behavior of the polymer. In spite of these slight discrepencies, the measured and calculated total stress profiles compare quite well for both moisture conditions.

DISCUSSION AND CONCLUSIONS

From the framework of continuum thermochemistry and the thermodynamics of mixtures, we have developed an analytical approach for modeling the transient thermomechanical response of polymer composite materials which are influenced by the diffusion of water through the polymer. A diffusion equation and an equation for the partial pressure of water are obtained and have been applied to model the time and temperature dependent thermal stresses in carbon phenolic composite specimens under isothermal heating conditions.

In the application of this theory, we have not solved the momentum equation, equation (4), explicitly. Rather, we relied on a volume average approach and certain assumptions regarding the symmetry of the thermostructural response. In spite of this, we have obtained a close agreement between the measured thermal stresses and those obtained by the numerical and analytical methods.

The diffusion model which was used for this simulation has been extrapolated from measurements made at lower temperatures. The accuracy of the diffusion model at higher temperatures can not be fully verified in this problem since the specimens failed before the total stress measurements could indicate when the exodus of moisture occurs. The diffusivity model is verified, in part, since the exodus of moisture must occur at temperatures higher than the failure point and since the partial pressures calculated with this diffusivity model are consistent with this observation.

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Figure 1. Sketch showing the architecture of a polymer composite material.

Figure 2. Sketch of the mechanical analog.

Figure 3. Sketch of a homogeneous mass of pure, condensed water with applied pressure necessary to prevent evaporation.

Figure 4. Sketch of the carbon phenolic specimens and heating conditions imposed during the tests by Hubbert (1989).

Figure 5. Plot of the measured restraining stresses versus temperature for three different initial moisture conditions.

Figure 6. Plot of the moisture diffusivity versus temperature in the direction parallel to the fabric plane.

Figure 7. Partial density of water as a function of radial location for various temperatures.

(a) 4% initial moisture condition
(b) 8% initial moisture condition

Figure 8. Volume average partial density of water as a function of temperature for the two initial moisture conditons.

Figure 9. Volume average partial pressure of water as a function of temperature for the two initial moisture conditons.

Figure 10. Measured and calculated restraining stress in the axial direction plotted versus temperature for the two initial moisture conditions.

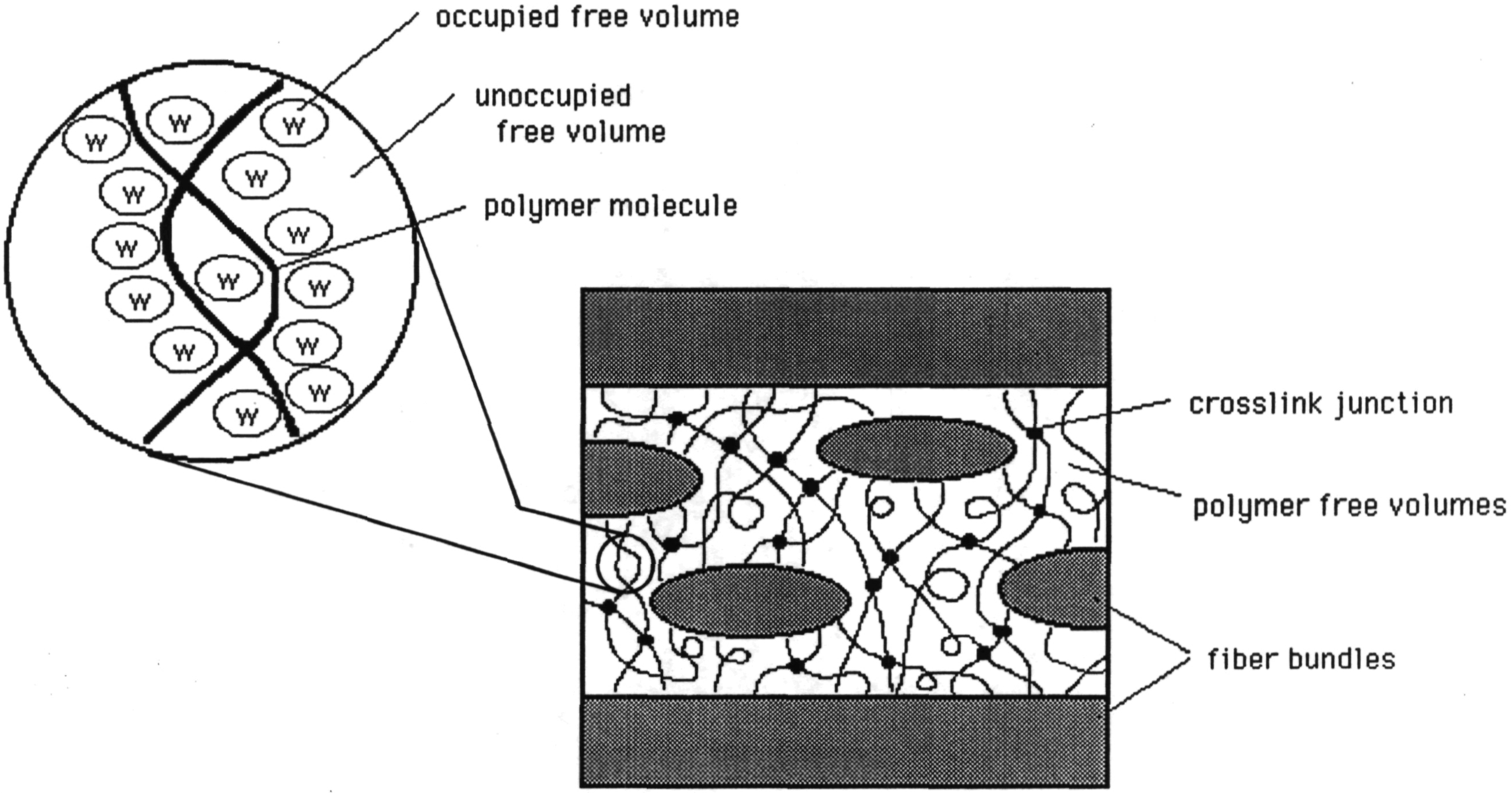


Figure 1. Sketch showing the architecture of a polymer composite material.

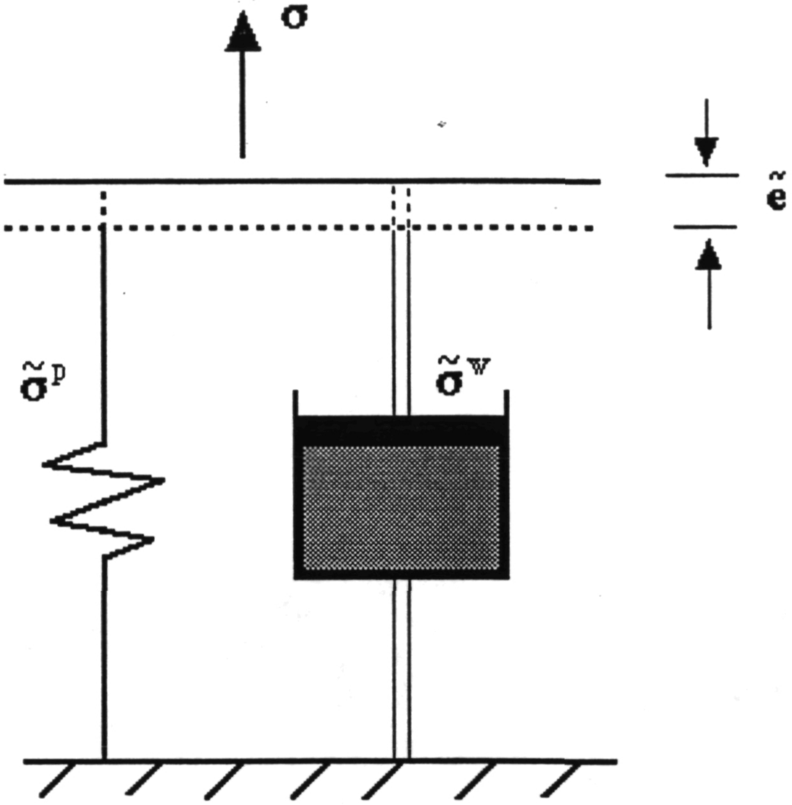


Figure 2. Sketch of the mechanical analog.

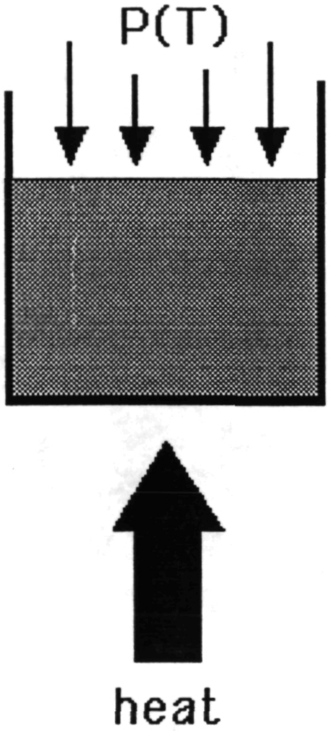
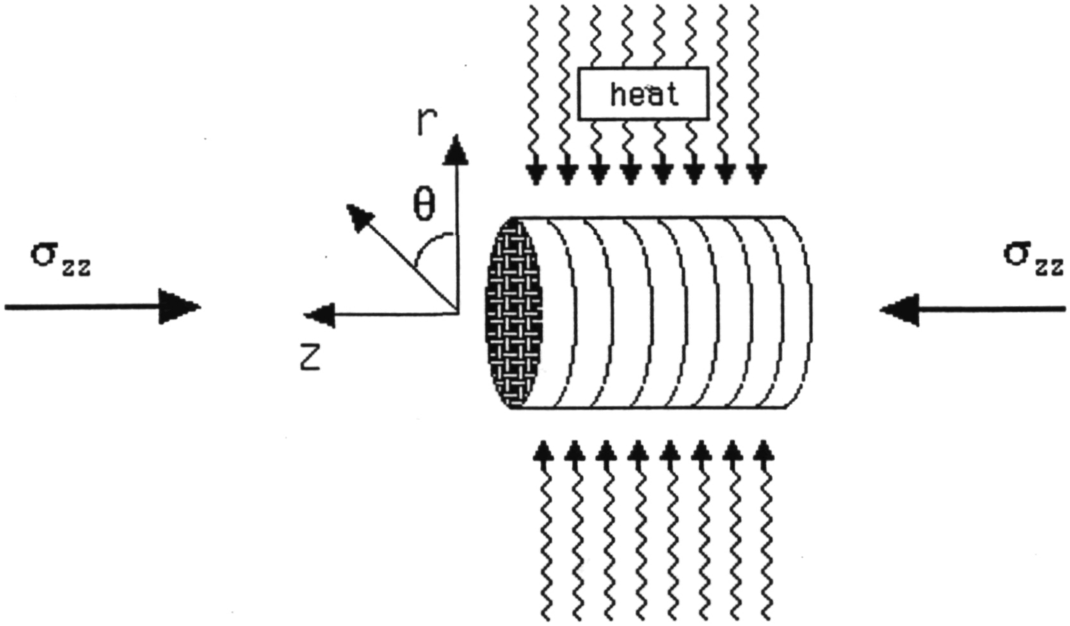


Figure 3. Sketch of a homogeneous mass of pure, condensed water with applied pressure necessary to prevent evaporation.



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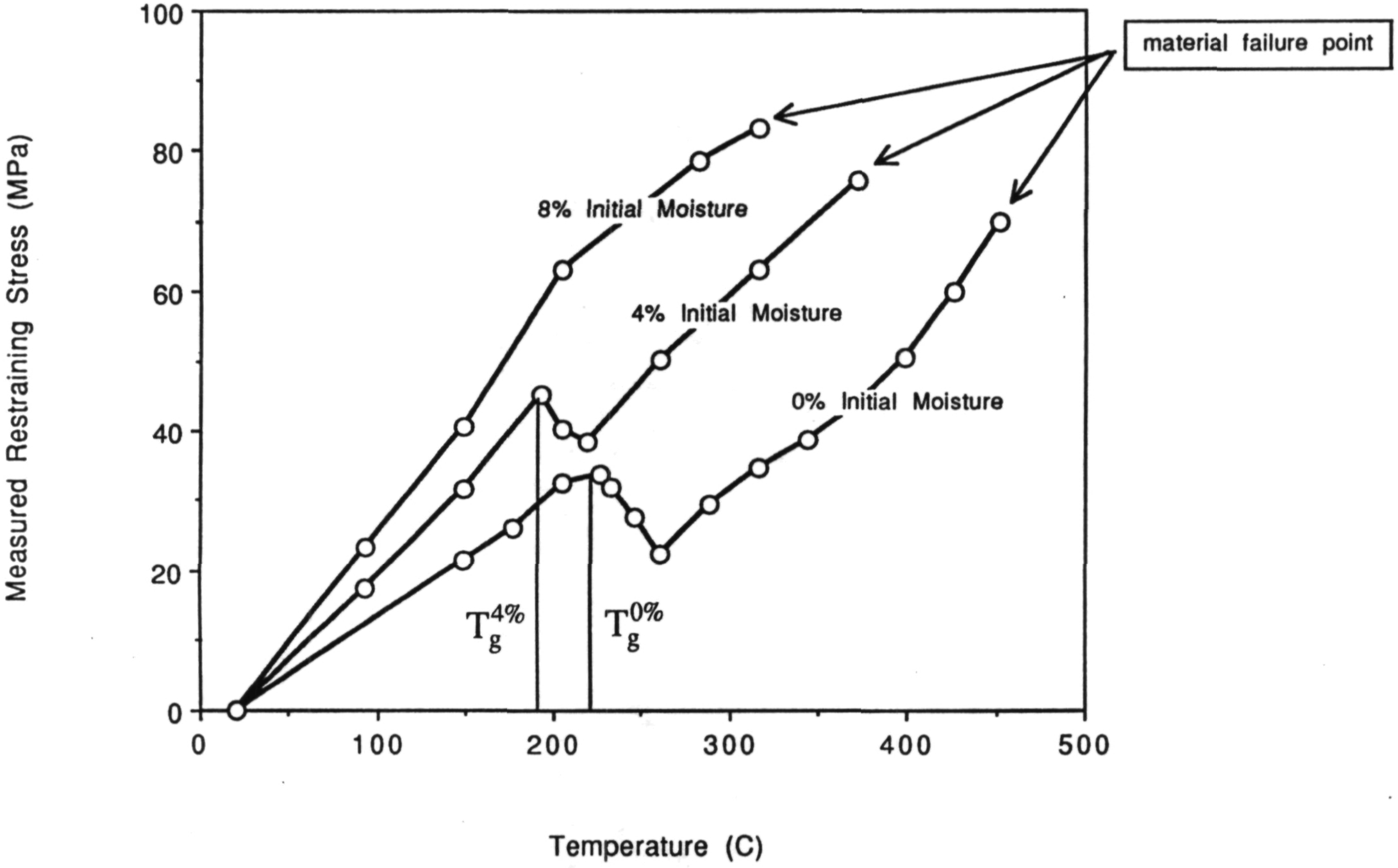


Figure 5. Plot of the measured restraining stresses versus temperature for three different initial moisture conditions.

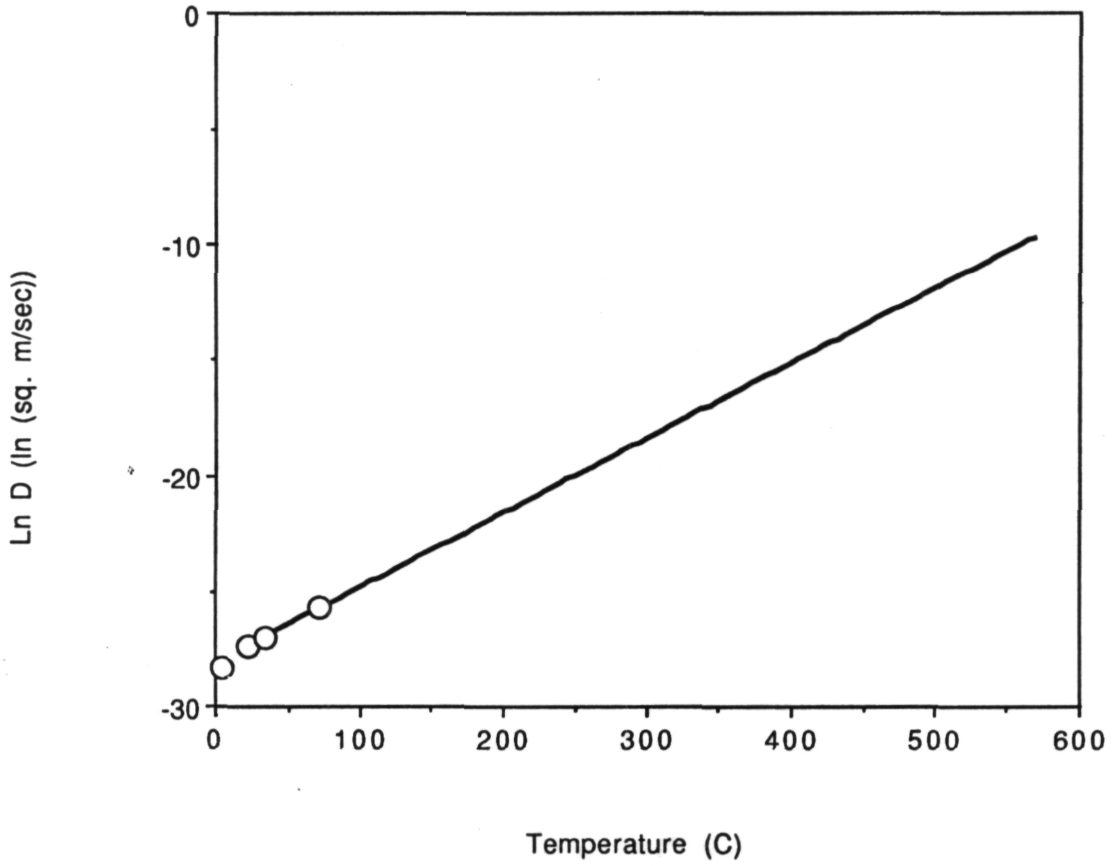
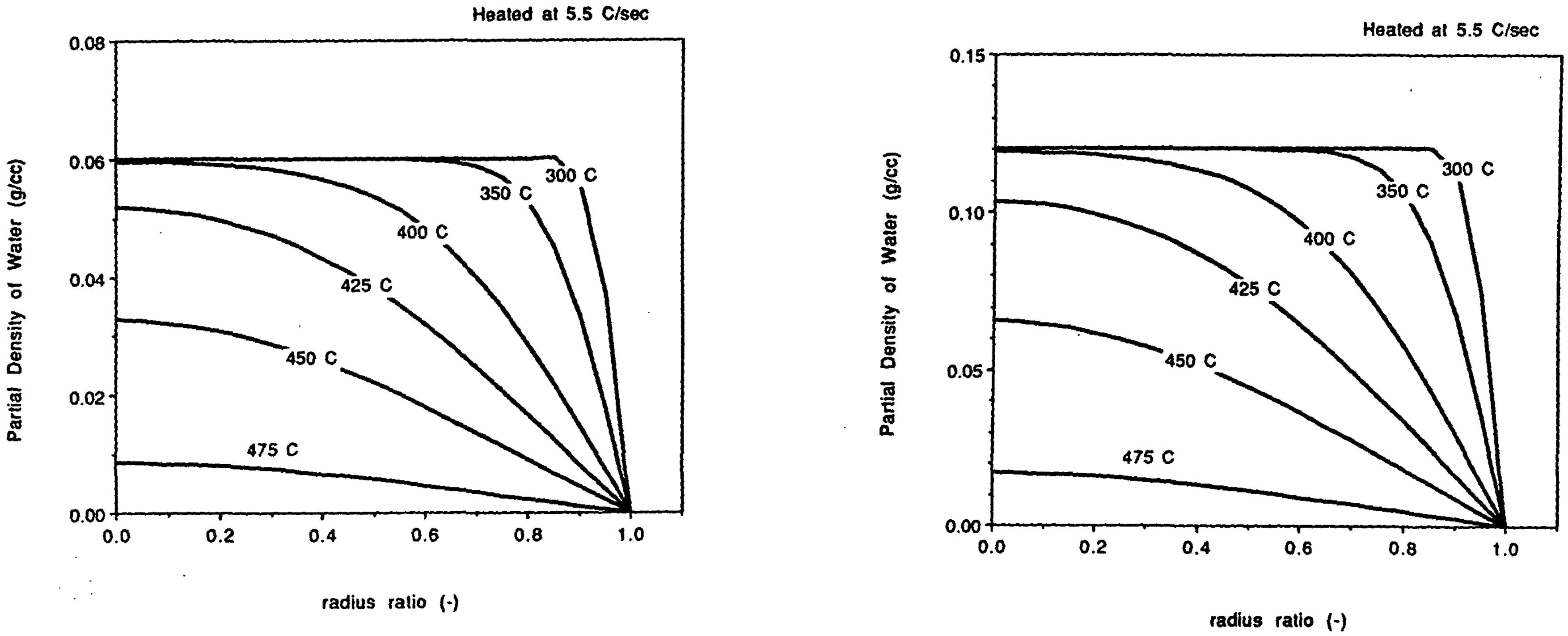


Figure 6. Plot of the moisture diffusivity versus temperature in the direction parallel to the fabric plane.



(a) 4% initial moisture condition

(b) 8% initial moisture condition

Figure 7. Partial density of water as a function of radial location for various temperatures.

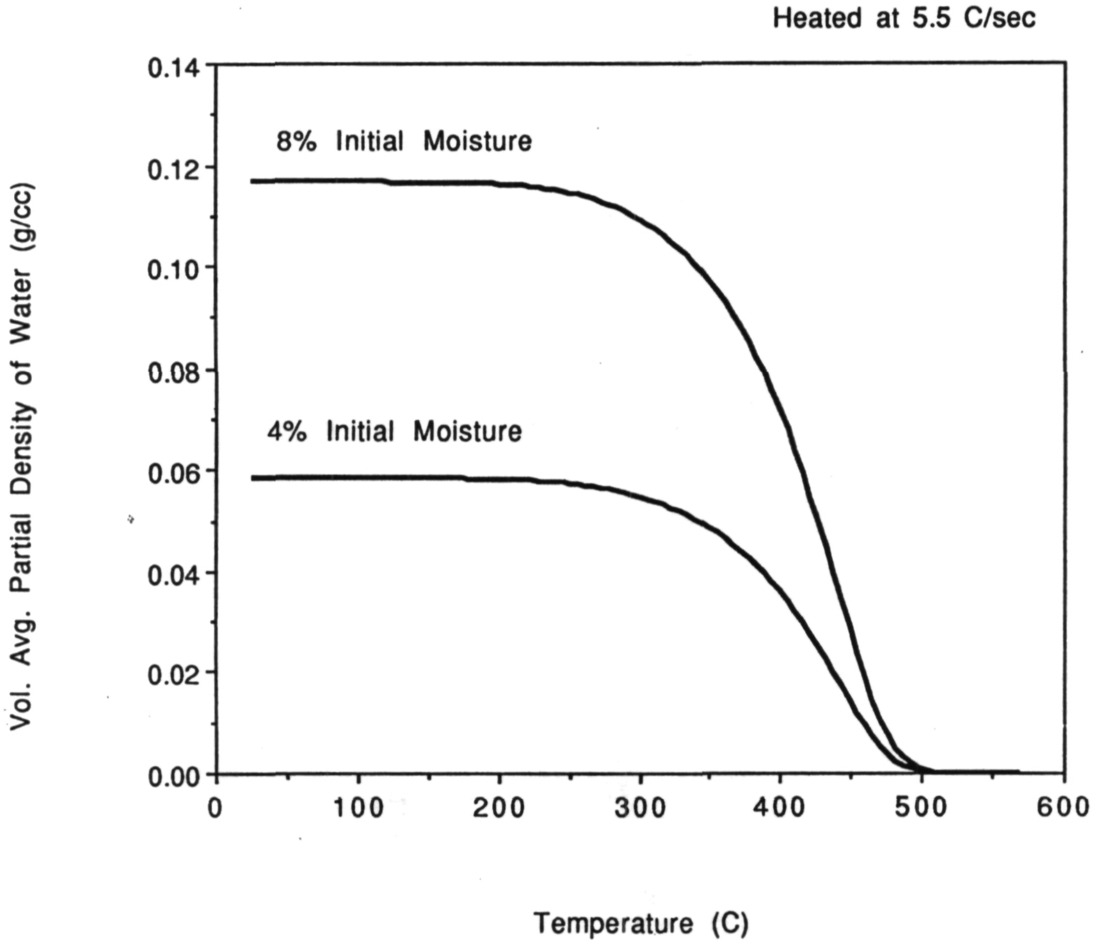


Figure 8. Volume average partial density of water as a function of temperature for the two initial moisture conditons.

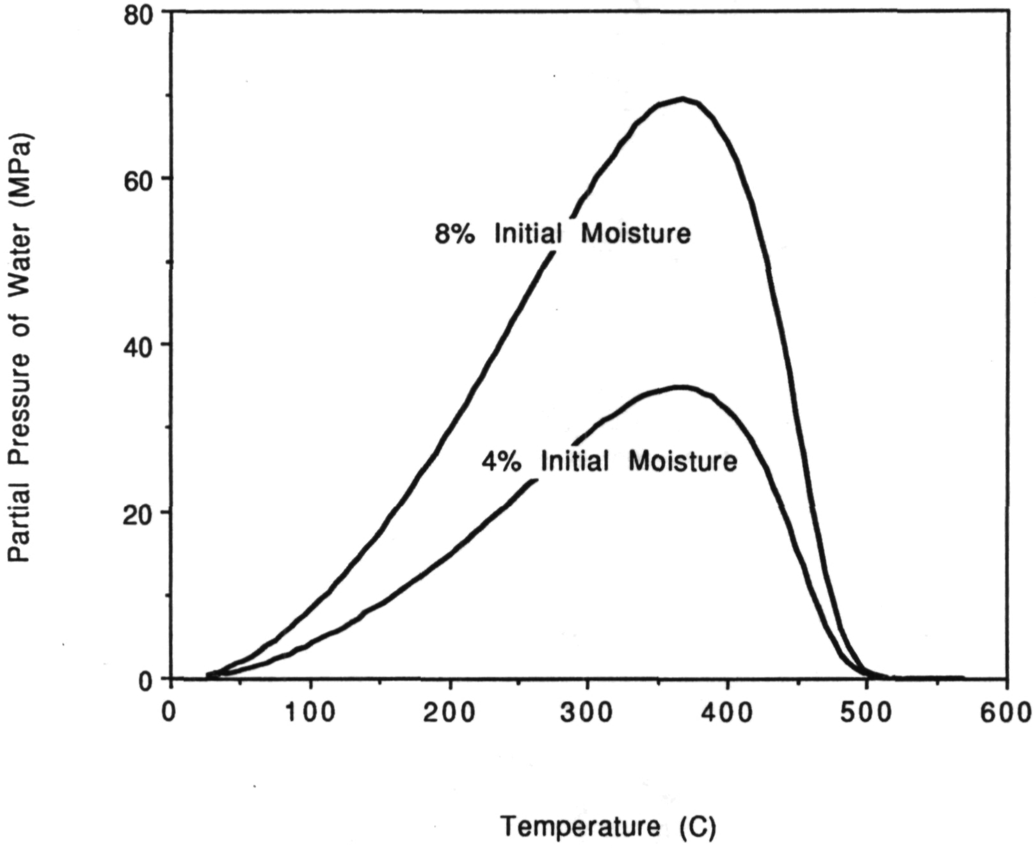
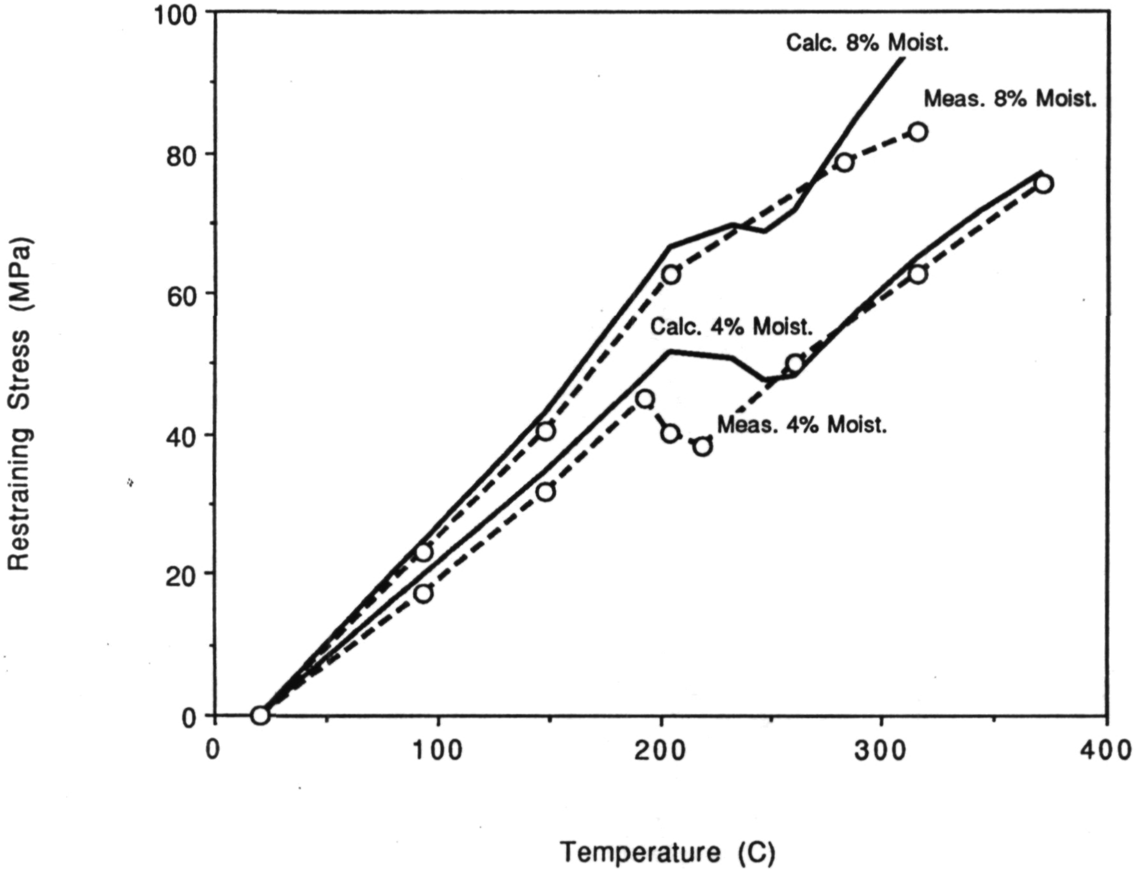


Figure 9. Volume average partial pressure of water as a function of temperature for the two initial moisture conditons.



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