

# Effect of Time at Temperature on the Ply-Normal Modulus of Carbon Phenolic

Roy M. Sullivan\*

NASA John H. Glenn Research Center at Lewis Field, Cleveland, Ohio 44135

Eric H. Stokes<sup>†</sup>

Southern Research Institute, Birmingham, Alabama 35211

and

Eric H. Baker<sup>‡</sup>

Connecticut Reserve Technologies, Cleveland, Ohio 44135

DOI: 10.2514/1.J050960

The effect of heating rate and time at temperature on the ply-normal tensile modulus of carbon cloth phenolic is investigated. The results of previous experimental studies reveal that slower heating rates and longer times at temperature result in a higher tensile modulus. It is speculated that the heating rate effect is due to a combination of moisture diffusion and the effect of water on the glass transition of the phenolic polymer. An equation is proposed that defines the value of the ply-normal modulus as a function of temperature and moisture content. Numerical solutions for moisture diffusion in the ply-normal tensile specimen are performed, and the equation for the ply-normal modulus is applied to calculate the modulus as a function of temperature and heating rate. The numerical results are successful in simulating the measured effect of heating rate and time at temperature on the ply-normal modulus. The validity of the supposition that the heating rate and time at temperature effect is due to the combination of moisture diffusion and plasticization of the phenolic polymer is demonstrated.

## Nomenclature

$c_w$	=	current moisture content
$c_w^f$	=	final moisture content
$c_w^o$	=	initial moisture content
$D_f$	=	moisture diffusivity in in-plane direction, cm <sup>2</sup> /h
$D_{ij}$	=	moisture diffusivity tensor, cm <sup>2</sup> /h
$D_n$	=	moisture diffusivity in normal direction, cm <sup>2</sup> /h
$D_o$	=	preexponential coefficient for moisture diffusivity, cm <sup>2</sup> /h
$D_{ij}^p$	=	tensor of diffusion constants based on pressure gradient driven diffusion, g/(cm · h · MPa)
$E_a$	=	activation energy for moisture diffusivity, kcal/mole
$E_n$	=	Young's modulus in ply-normal direction, MPa
$J_{w_i}$	=	components of moisture flux vector, g/(cm <sup>2</sup> · h)
$p_w$	=	partial pressure of water, MPa
$R$	=	universal gas constant, kcal/mole · °K
$T$	=	temperature, °C or °K
$T_m$	=	midpoint temperature, °C
$\rho_p$	=	partial density of polymer, g/cm <sup>3</sup>
$\rho_w$	=	partial density of water, g/cm <sup>3</sup>

## I. Introduction

FIBER-REINFORCED phenolic matrix composites have been used for decades as ablative heat shields in many military and aerospace applications. Carbon cloth phenolic (CCP) is a laminated, carbon fabric-reinforced phenolic matrix composite used as the

thermal insulation in solid rocket motor nozzles. The CCP insulation protects the metallic structural components of the nozzle assembly from the high-temperature exhaust gases during motor operation. While in service as solid rocket motor nozzle insulation, CCP composites are exposed to very high surface heat fluxes. Flame surface temperatures can be as high as 2700°C, and since CCP composites are extremely good insulators, severe thermal gradients will occur in the CCP insulation. Thermal gradients in excess of several 1000 degrees per centimeter can develop within the CCP insulation.

As the CCP is heated from room temperature to very high temperatures, the phenolic matrix experiences a number of physical and chemical changes. Like all other amorphous polymers, the phenolic matrix will experience a transition from a brittle mechanical behavior in the glassy state to a rubbery behavior above the glass transition temperature. At higher temperatures, the phenolic polymer will experience decomposition, where the polymer is converted to a carbon char. Ultimately, oxidation of the char and chemical ablation occurs at the flame surface. Surface ablation also occurs due to mechanical erosion. Glass transition, polymer decomposition, and oxidation will each occur at a specific temperature range. As such, there is not only a thermal gradient within the insulation, there is also a material state gradient within the insulation. In addition, the location of these gradients changes with time. The regions of glass transition and polymer decomposition, which initially develop very close to the flame surface, will penetrate deeper into the insulation as time progresses. The CCP insulation must be designed with sufficient thickness so that, at the end of motor operation, a certain minimum thickness of insulation is not heat affected.

The high temperatures and severe thermal gradients sometimes result in localized material failures. The most common failure is delamination. Static motor firings and thermal and thermostructural analysis of the CCP insulation design is required for flight certification. Through testing and analysis, the CCP insulation is designed to provide sufficient thermal insulation and to minimize the probability of a structural failure.

Thermostructural analysis is performed with the finite element method. Thermal gradients are modeled through discretization and by assigning temperatures to elements based on the depth from the heated surface. Gradients in the state of the material are modeled by

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\*Materials Research Engineer, Structures and Materials Division, 21000 Brookpark Road, Mail Stop 49-7.

<sup>†</sup>Senior Research Engineer, Materials Research Department, 757 Tom Martin Drive.

<sup>‡</sup>Research Associate, Structures and Materials Division, 21000 Brookpark Road, Mail Stop 49-7.

inputting material properties as a function of temperature and by assigning material properties to the elements based on the current element temperature. Obviously, an accurate measure of the mechanical properties and their dependence on temperature is necessary in order to obtain an accurate prediction of the stress states within the CCP insulation.

A complicating factor in the analysis of CCP insulation components is that the high-temperature mechanical properties are also a function of the heating rate. Lander [1] was one of the first to observe the effect of heating rate on the mechanical properties of CCP composites. Specifically, he studied the effect of time at temperature, the inverse of the heating rate, on the Young's modulus in the bias direction, which is the direction within the fabric plane, 45 deg from the fiber direction. Lander [1] heated CCP specimens to temperatures between 149°C (300°F) and 538°C (1000°F) and varied the amount of time the specimens were held at temperature before applying the mechanical load. He found that, within the range of temperatures between 204°C (400°F) and 316°C (600°F), the initial Young's modulus in the bias direction increased and the strain to failure decreased with the length of hold time. Lander [1] suggested a few possible reasons for the time-at-temperature effect. The most compelling of these was the suggestion that water will act to plasticize the polymer and that, due to the effect of diffusion, less water is present in the material as the hold time is increased.

The effect of heating rate on the mechanical properties is not typically included in the thermostructural analysis of CCP insulation. The underlying cause of the heating rate effect has not been definitively determined; thus, equations for calculating the mechanical properties based on the relevant physics are not available. In this paper, the supposition that the time-at-temperature effect on the mechanical behavior is due to the effects of moisture diffusion and plasticization is investigated. The main focus will be on the initial Young's modulus in the direction normal to the fabric plane, a material direction that is referred to as the ply-normal direction. In the next section, the results from more recent experimental studies, which measured the effect of heating rate and time at temperature on the ply-normal modulus of CCP, are reviewed. The following section presents the results from a series of experimental studies that were conducted to measure the effect of water in CCP. Specifically, these studies measured 1) the effect of moisture on the glass transition temperature, 2) the effect of moisture on the ply-normal tensile modulus at two specific temperatures, and 3) the rate of moisture diffusion and its dependence on temperature. Next, an equation is proposed to calculate the ply-normal modulus based on the temperature and moisture content. A series of numerical solutions are performed to predict moisture diffusion in the ply-normal tensile specimens and determine the moisture content as a function of temperature and heating rate. Using these results, the equation for the ply-normal modulus is applied to predict the modulus as a function of temperature and heating rate. The paper concludes with a discussion of the results and a discussion on how this approach can be incorporated into a structural analysis scheme for predicting the stress states that cause delamination in CCP insulation.

## II. Ply-Normal Tensile Tests

McCurdy [2] measured the ply-normal tensile mechanical behavior of carbon phenolic as a function of temperature using a round dog bone specimen with a diameter of 1.02 cm (0.40 in.) in the gauge section. He performed his experiments on FM5055 carbon phenolic, which is a particular carbon phenolic made using 91LD phenolic resin. The carbon fabric was derived from rayon yarn

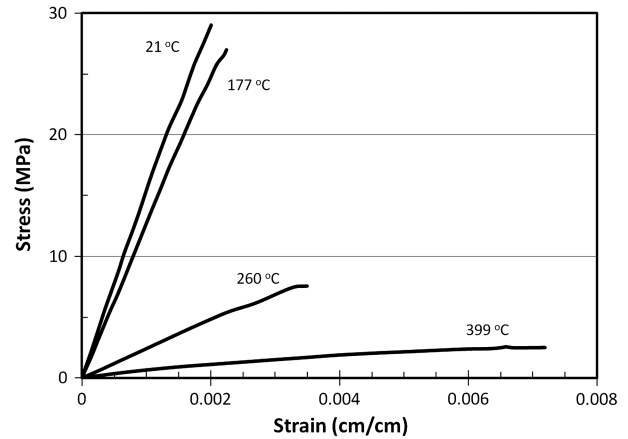


Fig. 1 Average ply-normal stress-strain response of FM5055 CCP at 21, 177, 260, and 399°C (from McCurdy [2]).

supplied by Avtex Rayon. McCurdy [2] heated the specimens to a variety of temperatures at a rate of 1.11°C/s (2°F/s). When the specimens reached the test temperature, they were loaded at a constant stress rate of 6895 kPa/min (1 ksi/min) until the specimens failed. The strain was recorded continuously from load initiation to specimen failure. The average ply-normal stress-strain behavior at 21, 177, 260, and 399°C reported by McCurdy [2] is shown in Fig. 1. These results illustrate the effect of temperature on the mechanical behavior in amorphous polymers. The mechanical behavior transitions from a glassy (brittle) behavior at room temperature to a rubbery behavior above the glass transition temperature. The initial modulus, which is the tangent to the stress-strain curve at the point of initial loading, gradually decreases as the material is heated from room temperature to temperatures above the glass transition. There is also a dramatic increase in the strain to failure in this same temperature range.

Dunkin [3] also measured the ply-normal tensile mechanical behavior of carbon phenolic specimens as a function of temperature using a round dog bone specimen with a 1.02 cm (0.40 in.) diameter in the gauge section. He performed his experiments on MX4926 carbon phenolic, which is made using SC1008 phenolic resin. The carbon fabric was derived from a rayon yarn supplied by the North American Rayon Corporation. The specimens were heated to temperature at a rate of 0.55°C/s (1°F/s). When the specimens reached temperature, they were loaded mechanically at a rate of 6895 kPa/min (1 ksi/min). The initial modulus was determined in a similar manner as McCurdy [2]. In both McCurdy [2] and Dunkin [3], the heating rates were slow enough to assume that the temperatures within the specimens were uniform.

Dunkin [3] conditioned the specimens in a 40% relative humidity (RH) environment at 41°C (105°F) before conducting the tensile tests. The volatile content in the specimens was determined by vacuum drying some of the specimens at 110°C (230°F) and measuring the weight loss. He found that the moisture conditioned specimens contained an average volatile content of 4.2% by weight. There was no attempt to precondition the specimens to a specific moisture content in the study by McCurdy [2].

Table 1 is a summary of the average initial ply-normal modulus reported by McCurdy [2] and Dunkin [3]. Notice that there is good agreement between the measured initial modulus obtained from these two studies. The specific phenolic resin does not seem to have a significant effect on the measured ply-normal modulus. The only

Table 1 Summary of the average measured ply-normal initial modulus versus temperature from McCurdy [2] and Dunkin [3]

	Modulus (GPa)								
	21°C	121°C	177°C	204°C	260°C	260°C 3 min hold	316°C	399°C	482°C
Dunkin [3] 0.55°C/s	15.79	—	11.03	6.69	4.55	—	0.83	0.41	0.43
McCurdy [2] 1.11°C/s	15.44	12.62	12.27	—	2.48	7.65	—	0.62	0.55

significant discrepancies between the two sets of results are the measurements at 260°C.

There was also a series of tests reported in McCurdy [2] that attempted to measure the effect of time at temperature on the ply-normal mechanical behavior. In these tests, specimens were heated to 260°C at a rate of 1.11°C/s. The specimens were held at 260°C for approximately 3 min before the mechanical load was applied. The average initial modulus for these tests is also included in Table 1. Note the significant difference in the measured average initial modulus for the specimens that were held for 3 min at 260°C before load application and the specimens that were loaded within a short amount of time after reaching the test temperature.

### III. Experimental Studies on Moisture in Carbon Cloth Phenolic

#### A. Effect of Moisture on Ply-Normal Thermal Expansion and Modulus

The effect of water in lowering the glass transition temperature in amorphous polymers has been reported by many previous authors (Couchman and Karasz [4], Delasi and Whiteside [5], McKague et al. [6], Reimschuessel [7], and Ellis and Karasz [8]). It is widely accepted that glass transition is the result of a thermally activated increase in the mobility and flexibility of the polymer segments. The glass transition temperature is the temperature at which there is sufficient thermal energy to overcome the secondary forces between the polymer molecules and permit rotational and translational movement of chain segments (Ebewele [9]). The absorption of moisture and other diluents by the polymer increases the distance between polymer molecules. This reduces the intermolecular forces between polymer molecules, and it reduces the thermal energy required for glass transition. Thus, the glass transition temperature is reduced.

Stokes [10] measured the effect of moisture content on the ply-normal thermal expansion behavior of FM5055 carbon phenolic. Cylindrical specimens with a 0.635 cm (0.25 in.) diameter were fabricated so that the ply-normal direction was coincident with the specimen axial direction. The specimens were heated at 5.55°C/s (10°F/s), and the axial growth was measured continuously as a function of temperature. The specimens were preconditioned to various moisture contents by placing them in relative humidity conditioning environments until their weight equilibrated. Constant relative humidity conditioning environments were created with saturated salt solutions, as described in Stokes [11].

Stokes [10] measured the thermal expansion of specimens with 2, 4.5, 6.1, 8.5, and 8.9% moisture. The ply-normal thermal expansion in the vicinity of the glass transition temperature is plotted in Fig. 2. The initiation of glass transition occurs at the temperature at which the thermal expansion curve begins to deviate from the initial linear portion of the thermal expansion curve. The effect of moisture in lowering the glass transition temperature is obvious in Fig. 2. Notice

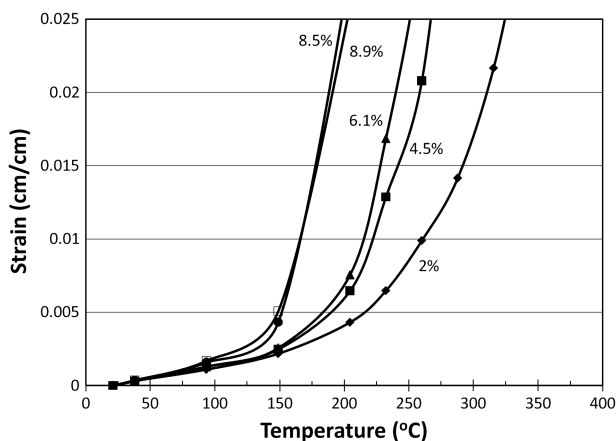


Fig. 2 Thermal expansion versus temperature for initial moisture contents of 2, 4.5, 6.1, 8.5, and 8.9% (from Stokes [10]).

that the thermal expansion curves for 4.5 and 6.1% moisture appear to have the same glass transition initiation temperature. The same is true for the 8.5 and 8.9% curves. A good estimate of this temperature for 2, 4.5, and 8.5% moisture is 175, 150, and 125°C, respectively.

Stokes [10] also measured the effect of water on the ply-normal mechanical behavior of FM5055 carbon phenolic specimens at temperatures near the glass transition. The mechanical behavior was measured using round dog bone specimens with a 1.02 cm diameter in the gauge section. Again, the specimens were conditioned to moisture contents of 2, 4.5, 6.1, 8.5, and 8.9% using the relative humidity conditioning environments discussed in Stokes [11]. The specimens were heated to 177 and 260°C using a heating rate of 5.55°C/s, and the mechanical load was applied at a rate of 68.95 MPa/min (10 ksi/min). Multiple heating sources were used to minimize the thermal gradients and obtain a near-uniform temperature within the specimens.

The average ply-normal tensile stress-strain behavior at 177 and 260°C reported by Stokes [10] for the specimens preconditioned to 4.5, 6.1, and 8.9% moisture is shown in Fig. 3. The 177°C results are plotted as solid lines, and the 260°C results are plotted as dashed lines. Again, the transition from a glassy to a rubbery behavior is evident in the results in Fig. 3. For two specimens with the same moisture content, the specimen at 260°C has a lower initial modulus and a higher strain to failure than the specimen at 177°C. Moreover, it should be noted that the effect of moisture content is the same as the effect of temperature. That is, at a fixed temperature within this region of glass transition, a higher moisture content causes the material to behave more rubbery. Indeed, there is very little difference in the stress-strain behavior between a specimen at 177°C containing 8.9% moisture and a specimen at 260°C containing 4.5% moisture.

Figure 4 is a summary of the ply-normal initial modulus results obtained by Stokes [10]; the initial modulus at 177 and 260°C is plotted versus the initial moisture content. It will be more useful to plot the initial modulus using temperature as the abscissa. The average initial modulus was obtained at each temperature and moisture content from the results in Fig. 4. The average ply-normal initial modulus is plotted in Fig. 5 as a function of temperature for four initial moisture conditions.

#### B. Moisture Diffusion

In an attempt to determine the best approach for moisture conditioning CCP specimens, Stokes [12] conditioned FM5055 CCP specimens in various relative humidity environments and at a handful of different temperatures and measured the moisture uptake or weight loss versus time for each conditioning environment. A summary of the various moisture conditioning studies conducted by Stokes [12] is given in Table 2. The moisture conditioning studies were conducted at 22°C (72°F), 35°C (95°F), 71°C (160°F), and 163°C (325°F). The initial moisture content, the conditioning environment, and the specimen configuration for each case is listed in

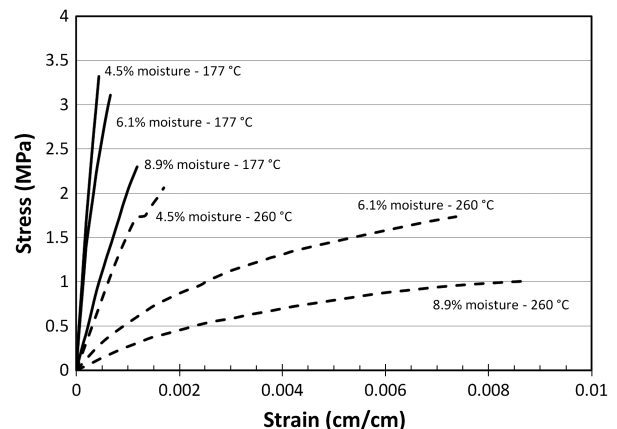


Fig. 3 Average ply-normal stress-strain behavior at 177 and 260°C for specimens preconditioned to 4.5, 6.1, and 8.9% moisture (from Stokes [10]).

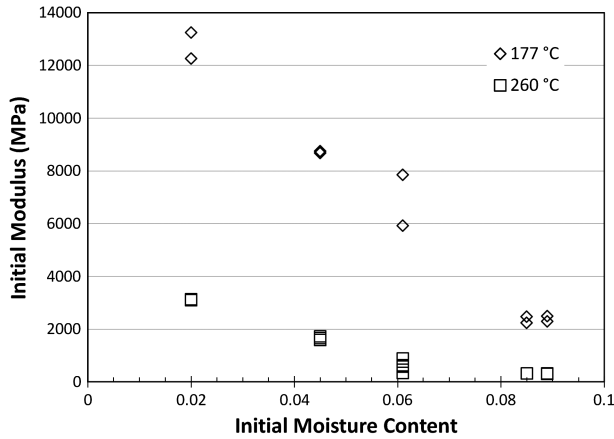


Fig. 4 Plot of initial ply-normal modulus versus initial moisture content measured at 177 and 260°C (from Stokes [10]).

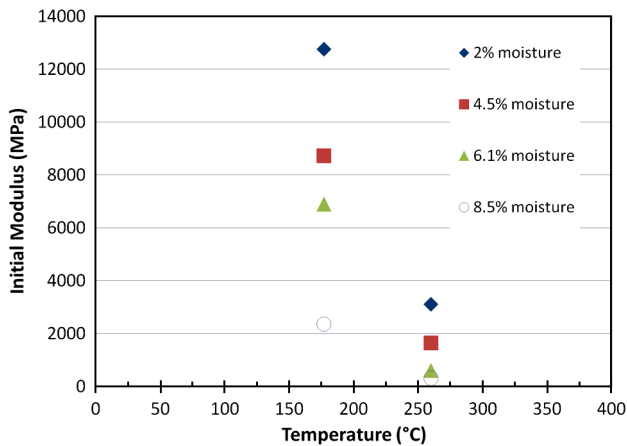


Fig. 5 Plot of average initial ply-normal modulus at 177 and 260°C for four initial moisture conditions.

Table 2. Notice that the table includes two case studies at 22°C. One specimen (A1) was dried before being conditioned at 65% relative humidity and 22°C, and the other specimen (A2) was preconditioned in a saturated atmosphere at 82°C (180°F) before being placed in the 65% RH/22°C conditioning environment. Thus, case A1 is a moisture absorption experiment and case A2 is a moisture loss experiment. It should also be noted that the conditioning experiment at 163°C (case D) was performed on six specimens.

The ratio  $(c_w - c_w^o)/(c_w^f - c_w^o)$ , where  $c_w$ ,  $c_w^o$ , and  $c_w^f$  are, respectively, the current, initial, and final moisture content, is plotted versus the square root of time in Fig. 6 for each of the moisture uptake/loss cases listed in Table 2. Figure 6a shows the diffusion results for the two cylindrical specimens, which were conditioned at 22°C (cases A1 and A2). Figure 6b shows the results for the 1.27 cm cubic specimens, which were conditioned at 35 and 71°C (cases B and C). The results for the six 2.54 cm cubic specimens, which were conditioned at 163°C (case D), are shown in Fig. 6c. It is obvious

from these results that the moisture diffusion rate increases with temperature.

The results of the moisture conditioning studies provide valuable information about the rate of moisture diffusion in carbon phenolic and the dependence of temperature on the diffusion rate. This information will be used in a later section to determine the value of the moisture transport property and its dependence on temperature.

#### IV. Model for Initial Ply-Normal Young's Modulus

The dependence of the initial ply-normal modulus on temperature and moisture content, which is illustrated by Fig. 5 and Table 1, can be simulated using the complementary error function:

$$E_n = A \operatorname{erfc}\left(\frac{T - T_m}{\Delta T}\right) + B \quad (1)$$

The complementary error function shown in Eq. (1) is a sigmoidal function centered at the midpoint temperature  $T_m$ . It has a maximum value of  $2A + B$  for all temperatures less than  $T_m - 2\Delta T$  and a minimum value of  $B$  for all temperatures greater than  $T_m + 2\Delta T$ . The function transitions from its maximum value to its minimum value in the temperature range  $T_m - 2\Delta T < T < T_m + 2\Delta T$ . Changing the value of  $T_m$  has the effect of shifting the error function curve along the temperature axis. Thus, the effect of moisture on the glass transition temperature can be simulated by determining the relationship between the midpoint temperature  $T_m$  and the moisture content.

A series of complementary error functions are plotted in Fig. 7. All the curves were generated using the values  $A = 6722$  MPa,  $\Delta T = 55.6^\circ\text{C}$ , and  $B = 345$  MPa. The curves are offset along the temperature axis according to their midpoint temperatures. Each curve represents the modulus versus temperature for a specific and constant moisture content.

The measured average ply-normal modulus for four initial moisture contents, which was shown previously in Fig. 5, is also plotted in Fig. 7. The relationship between the midpoint temperature and the initial moisture content was determined by adjusting the midpoint temperature until the error function curve lies close to its respective measured modulus data. The midpoint temperatures, which were obtained for each of the four initial moisture contents, are shown as the data points in Fig. 8. Fitting a linear function through these data yields the relation  $T_m = -1489.1c_w^o + 262.86$  and provides a very good fit to the data ( $R^2 = 0.999$ ).

The primary objective is to develop the ability to calculate the ply-normal initial modulus as the material is heated and moisture diffusion occurs simultaneously. Equation (1) can be used to calculate the ply-normal modulus as a function of temperature for a varying moisture content if the midpoint temperature can be determined as a function of the current moisture content  $c_w$ . Since moisture diffusion will occur as the specimens are heated to the test temperatures, the moisture content at 177 and 260°C will not be equal to the initial moisture content. However, it will be shown in a following section that, for a heating rate of 5.55°C/s, the average moisture content in the 1.02 cm dog bone specimen at 177 and 260°C is not significantly different than the initial moisture content. This is particularly true at 177°C, since very little diffusion occurs before 177°C. Therefore, a reasonable approximation of the midpoint temperature as a function of the current moisture content can be

Table 2 Summary of moisture conditioning experiments from Stokes [12]

Case	Temperature, °C	Conditioning type	Initial moisture condition	Conditioning environment	Specimen configuration	Source of data
A1	22	Uptake	$c_w^o = 1.4\%$	65% RH	Cylindrical 1.27 cm diam × 5.7 cm long	Fig. 1.5.2-1 from Stokes [12]
A2	22	Loss	$c_w^o = 7.1\%$	65% RH	Cylindrical 1.27 cm diam × 5.7 cm long	Fig. 1.5.2-1 from Stokes [12]
B	35	Uptake	Dry <sup>a</sup>	95% RH	1.27 cm cube	Fig. 1.5.3-1 from Stokes [12]
C	71	Uptake	Dry <sup>a</sup>	Immersed in distilled water	1.27 cm cube	Fig. 1.5.3-1 from Stokes [12]
D	163	Loss	As received	Convection oven at 163°C	2.54 cm cube	Fig. 1.7-3 from Stokes [12]

<sup>a</sup>Desiccated at room temperature for 16 days. Subsequently dried at 38°C for 4 h, 60°C for 4 h, and 104°C for four days at 0.1 torr.

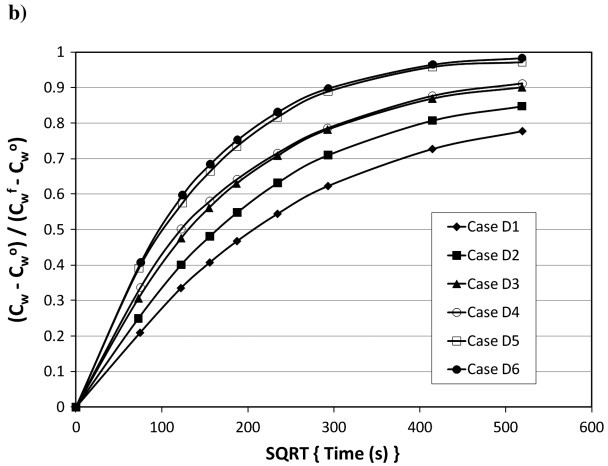
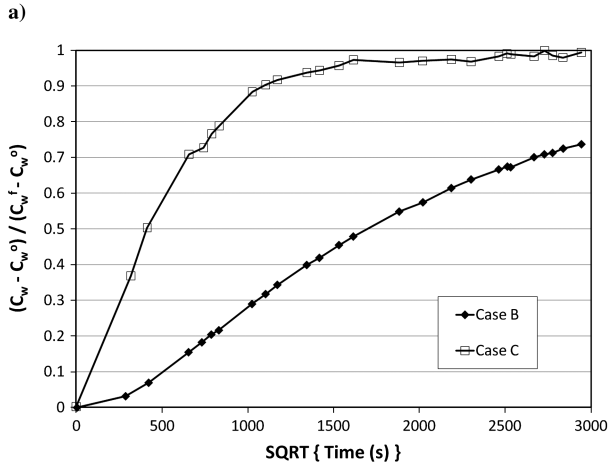
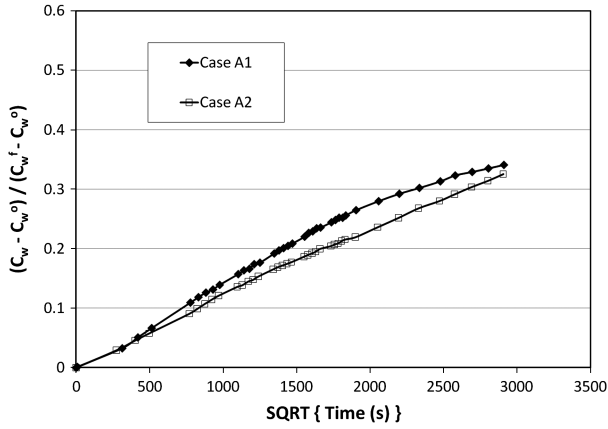


Fig. 6 Plot of ratio  $(c_w - c_w^0) / (c_w^f - c_w^0)$  versus square root (SQRT) of time for moisture conditioning cases listed in Table 2 (from Stokes [12]): a) 22°C; b) 35 and 71°C; and c) 163°C.

obtained by using the previous linear relation with the initial moisture content replaced by the current moisture content,  $T_m = -1489.1c_w + 262.86$ .

The linear relation between moisture content and midpoint temperature indicates that, for a dry specimen ( $c_w = 0$ ), the midpoint temperature would be 263°C. Using this value for the midpoint temperature, the modulus versus temperature for a theoretical dry specimen is plotted as the black dashed line in Fig. 7. The average modulus measured by McCurdy [2] for the specimens heated at 1.11°C/s and held at 260°C for 3 min before testing is also plotted in Fig. 7 using a solid black circle. Note that the black circle lies on the dry modulus curve. This would imply that the specimens that were held at 260°C were either completely dry or nearly dry after the 3 min hold.

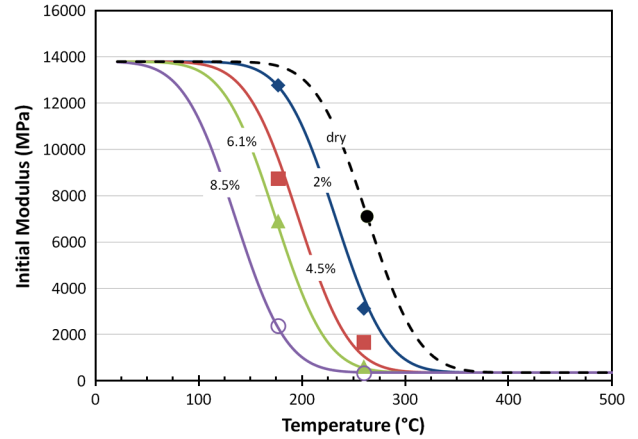


Fig. 7 Plot of initial modulus versus temperature for specific constant moisture contents using the complementary error function. Data points represent the measured average modulus from Fig. 5.

### V. Moisture Diffusion Model

The rate of effusion of water from the ply-normal tensile specimens is governed by the rate of transport of water from interior locations to the free surfaces of the specimen. When the water reaches the free surfaces of the specimen, it is then evaporated to the environment. There have been a variety of models proposed for simulating the diffusion of moisture in polymer composites. In this paper, moisture transport in carbon phenolic specimens will be modeled using Fick's first law:

$$J_{w_i} = -D_{ij} \frac{\partial \rho_w}{\partial x_j} \quad (2)$$

In Eq. (2),  $J_{w_i}$  are the components of the mass flux vector,  $D_{ij}$  is a second-order tensor of moisture diffusivity coefficients,  $\rho_w$  is the partial density of water in the phenolic polymer, and  $\partial/\partial x_i$  represents the partial derivative with respect to the spatial coordinates  $x_i$ . A differential equation for modeling the diffusion process is obtained by combining Fick's first law with a conservation of mass equation,  $\partial \rho_w / \partial t + \partial J_{w_i} / \partial x_i = 0$ . If the moisture content is small ( $c_w \leq 10\%$ ), the partial density of water may be approximated as  $\rho_w = c_w \rho_p$ , where  $\rho_p$  is the partial density of the phenolic polymer, and the mass conservation equation can be rewritten in terms of the moisture content as

$$\frac{\partial c_w}{\partial t} + \frac{\partial}{\partial x_i} \left( -D_{ij} \frac{\partial c_w}{\partial x_j} \right) = 0 \quad (3)$$

At temperatures above the boiling point, the water inside the specimens could be at high pressures, and there may be high pressure gradients within the specimens. The rate of moisture transport will be

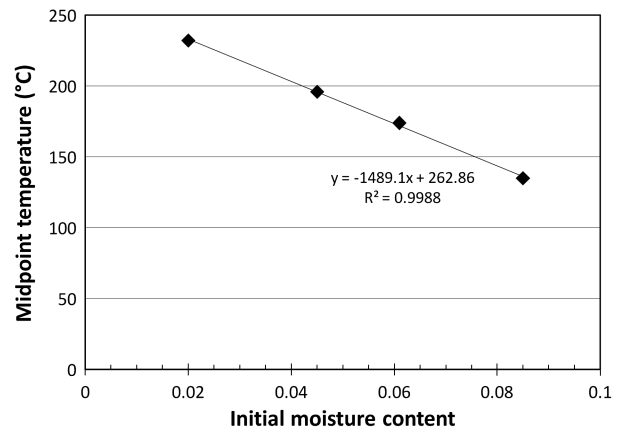


Fig. 8 Plot of midpoint temperature versus moisture content.

proportional to the magnitude of the pressure gradients. It could be argued that it may be more appropriate to simulate the moisture diffusion at the higher temperatures using a diffusion law of the form

$$J_{w_i} = -D_{ij}^p \frac{\partial p_w}{\partial x_j} \quad (4)$$

where  $p_w$  is the partial pressure of water in the material, and  $D_{ij}^p$  is the tensor of diffusion constants relating partial pressure gradients to mass flow. However, if the temperature is uniform within the specimens ( $\partial T/\partial x_i = 0$ ), it can be shown that Eqs. (2) and (4) are equivalent and that the use of either equation is a valid approach for modeling the moisture transport. In this case, the diffusion constants  $D_{ij}$  and  $D_{ij}^p$  are related by  $D_{ij} = D_{ij}^p (\partial p_w / \partial \rho_w)_T$ , where the subscript  $T$  indicates that the partial derivative is performed with temperature held constant. Using the approximation  $\rho_w = c_w \rho_p$ , the relation between the diffusion constants may also be written  $D_{ij} = (D_{ij}^p / \rho_p) (\partial p_w / \partial c_w)_T$ .

The value of the moisture diffusivity and its dependence on temperature was obtained by simulating the diffusion of moisture in the moisture conditioning experiments conducted by Stokes [12] and by comparing the simulation results to the measured moisture gain/loss versus time histories. The simulations were performed by solving Eq. (3) for each of the environmental conditions listed in Table 2. The solutions were performed numerically using the general-purpose finite element program ABAQUS [13]. For the cases involving cylindrical specimens (cases A1 and A2), two-dimensional axisymmetric diffusion solutions were performed using DCAX4 mass diffusion elements. For the cases involving the cubic specimens, three-dimensional diffusion solutions were performed using DC3D8 mass diffusion elements. The time transient numerical solution yields the distribution of moisture content within the specimen at each time step. The moisture content distributions were volume averaged, and the average moisture content in the specimen was determined as a function of time. The average moisture content versus time profiles were compared with the measured profiles shown in Fig. 6. The value of the diffusivity that provided the best match between the measured and predicted moisture versus time profiles was determined for each temperature. The optimum diffusivity was the value that maximized the coefficient of determination  $R^2$  in a comparison between the predicted and measured profiles.

In all of the moisture conditioning experiments listed in Table 2, moisture diffusion occurs (to some extent) in both the in-plane and ply-normal directions. Previous moisture diffusivity measurements on carbon phenolic specimens indicate that the ratio of the moisture diffusivity in the in-plane and normal directions can vary considerably (Stokes [14]). In some cases, the moisture diffusivity

in the ply-normal direction was approximately equal to the value in the in-plane direction, while in other cases, the in-plane diffusivity was several orders of magnitude greater than the ply-normal diffusivity. To address the potential effect of two-dimensional diffusion in the numerical simulation of diffusion in the moisture conditioning specimens, two solutions were performed for each of the cases listed in Table 2. In one solution, the moisture diffusivity in the ply-normal direction was set equal to zero ( $D_n = 0$ ), and in the other, the normal diffusivity was set equal to the in-plane diffusivity ( $D_n = D_f$ ). These two cases covered the two possible extremes.

The optimum in-plane moisture diffusivity at each conditioning temperature, and for each of the two conditions on the diffusivities, is listed in Table 3. The  $R^2$  values for each condition are also listed in Table 3. For the cylindrical specimens (cases A1 and A2), there was very little difference between the results obtained from the solutions with  $D_f = D_n$  and those obtained with  $D_n = 0$ . These results indicate that moisture diffusion in the ply-normal direction had a negligible effect on the moisture uptake/loss history. This is not surprising, since the cylindrical specimen has a large length-to-diameter ratio (5.72/1.27). The amount of moisture that flows across the end surfaces will be a small fraction of the total moisture mass flow. As a result, only one in-plane diffusivity is listed in Table 3 for cases A1 and A2. For the cases involving the cubic specimens (cases B, C, and D), there was a small but noticeable difference between the optimum in-plane diffusivities obtained from the solutions with  $D_n = D_f$  and those obtained from the solutions with  $D_n = 0$ . The best estimate of the in-plane diffusivity for cases B and C was obtained as the average of the two optimum diffusivity values listed. There are 12 diffusivity values listed in the table under case D, since diffusion solutions were performed to match each of the six moisture versus time profiles shown in Fig. 6c. For case D, the average of all 12 diffusivity values was obtained. The average diffusivity values for each temperature are listed in the last row in Table 3.

The results in Table 3 reveal that the moisture diffusivity  $D$  is an increasing function of temperature. Although  $D_{ij}^p$  is probably also an increasing function of temperature, the temperature dependence of  $D$  is, to a large extent, due to  $(\partial p_w / \partial c_w)_T$ . The value of  $(\partial p_w / \partial c_w)_T$  is an increasing function of temperature, since for two temperatures  $T_1$  and  $T_2$ , where  $T_2 > T_1$ , a unit mass of water within the carbon phenolic specimens will result in a higher partial pressure at temperature  $T_2$  than at  $T_1$ .

Likewise, the partial pressure gradients, under isothermal conditions, may be written as  $\partial p_w / \partial x_i = (\partial p_w / \partial c_w)_T \partial c_w / \partial x_i$ . As a consequence, given a constant concentration gradient, any increase in temperature will result in an increase in the pressure gradient and a subsequent increase in the mass flux by virtue of Eq. (4). This will be observed as an increase in the moisture diffusivity since the mass flux

**Table 3 Summary of in-plane diffusivity versus temperature determined from numerical simulations of moisture diffusion in the moisture conditioning experiments**

	Case/temperature, °C							
	A1/22	A2/22	B/35		C/71		D/163	
	—	—	$D_n = 0$	$D_n = D_f$	$D_n = 0$	$D_n = D_f$	$D_n = 0$	$D_n = D_f$
In-plane moisture diffusivity, cm <sup>2</sup> /h	4.65E-06	4.65E-06	3.25E-05	1.74E-05	5.11E-04	2.90E-04	6.97E-03	4.65E-03
							11.6E-03	6.97E-03
							18.6E-03	9.29E-03
							20.9E-03	11.6E-03
							32.5E-03	18.6E-03
Coefficient of determination $R^2$	0.9211	0.9904	0.9904	0.9867	0.9920	0.9940	0.9427	0.9609
							0.9556	0.9705
							0.9646	0.9755
							0.9578	0.9699
							0.9894	0.9934
						0.9877	0.9937	
Average in-plane moisture diffusivity, cm <sup>2</sup> /h	4.65E-06		2.50E-05		4.00E-04		16.5E-3	

increase occurs in the presence of a constant concentration gradient. Thus, the temperature dependence of the moisture diffusivity is indicative of the effect of temperature on the pressure gradients and the mass fluxes.

It is common practice to express the variation of the moisture diffusivity with temperature using an exponential function of the form

$$D(T) = D_o \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where  $D_o$  is the preexponential coefficient,  $E_a$  is the activation energy, and  $R$  is the universal gas constant. It follows from Eq. (5) that a plot of the natural log of the diffusivity versus the inverse of the absolute temperature is a straight line with a slope of  $-E_a/R$  and a  $y$  intercept of  $\ln D_o$ . The natural log of the average moisture diffusivities listed in Table 3 are plotted versus the inverse of the absolute temperature ( $^{\circ}\text{K}^{-1}$ ) as the individual data points in Fig. 9. A fairly good fit to the data, ( $R^2 = 0.960$ ) is obtained with the linear function using the values  $D_o = 11.426 \times 10^6 \text{ cm}^2/\text{h}$  and  $E_a = 16.64 \text{ kcal/mole}$ . This is shown as the solid line in Fig. 9. The value of  $E_a$  compares well with the value obtained by DeIasi and Whiteside [5], Zhou and Lucas [15], and Popineau et al. [16] for epoxy and epoxy composites.

## VI. Moisture Diffusion in Ply-Normal Tensile Specimen

Numerical solutions for moisture diffusion in the 1.02 cm dog bone specimen were performed using the general-purpose finite element program ABAQUS [13]. Numerical solutions were performed to simulate the moisture diffusion in the ply-normal tensile tests by McCurdy [2] and Dunkin [3], which were assumed to contain 4% initial moisture and heated at 1.11 and 0.55°C/s, respectively. Numerical solutions were also performed to simulate the moisture diffusion in the ply-normal tensile tests by Stokes [10], which contained 4.5% initial moisture and were heated at 5.55°C/s. Since the specimens were heated to minimize thermal gradients and obtain a uniform temperature in the tensile tests conducted by McCurdy [2], Dunkin [3], and Stokes [10], the moisture diffusion solutions were performed under the assumption that the temperature within the specimens is isothermal.

Moisture diffusion in the tensile dog bone specimens was assumed to be axisymmetric. The numerical solutions were performed using DCAX4 mass diffusion elements. Furthermore, only diffusion in the gauge section of the specimen was considered. It was assumed that there was no diffusion of water across the boundaries between the gauge and grip sections. The following boundary and initial conditions were imposed:

$$\begin{aligned} c_w &= 0 & \text{at } r = a; 0 \leq z \leq L; t > 0 \\ \frac{\partial c_w}{\partial z} &= 0 & \text{at } r \leq a; z = 0, L; t > 0 \\ c_w &= c_w^o & \text{at } r \leq a; 0 \leq z \leq L; t = 0 \end{aligned}$$

where  $a$  is the outer radius in the gauge section, and  $L$  is the length of the gauge section. For the ply-normal tensile specimens,  $a = 0.51 \text{ cm}$  and  $L = 3.35 \text{ cm}$ . Under these boundary conditions, the value of the ply-normal diffusivity had a negligible effect on the solution results.

Since the temperature changes with time in the tensile tests, the in-plane moisture diffusivity must be updated at each time step. The in-plane moisture diffusivity was calculated at each time step using Eq. (5) and the values of  $D_o = 11.426 \times 10^6 \text{ cm}^2/\text{h}$  and  $E_a = 16.64 \text{ kcal/mole}$ . At the end of each time step, the temperature was increased according to the time-step increment and the heating rate. The moisture diffusivity was then updated based on the new temperature, and the solution was performed for the next time step. This process was repeated until the conclusion of the simulation.

The time incremental numerical solution yields the spatial distribution of the moisture content at each time step, and thus at each temperature. The moisture content distributions were used to calculate the volume average moisture content in the specimen at each time and temperature. The results of these numerical solutions are shown in Fig. 10. Notice the effect of heating rate on the average moisture content. For two specimens that start with the same initial moisture content, the specimen heated at a higher heating rate will contain more moisture, at any given temperature, than the specimen that was heated at a slower rate. A numerical solution for a heating rate of 1.11°C/s with a 3 min hold at 260°C was also performed. These results are shown as a dashed line in Fig. 10. The diffusion solution results indicate that there is very little moisture remaining in the specimen after the 3 min hold.

Notice also that, for a heating rate of 5.55°C/s, the moisture content at 177°C is very close to the initial moisture content. Even at 260°C, the specimen has only lost about 20% of its initial value. This justifies the previous decision to replace the initial moisture content with the current moisture content in the expression for the midpoint temperature.

The initial ply-normal modulus was calculated as a function of temperature and heating rate using Eq. (1). The midpoint temperature was calculated using the relation  $T_m = -1489.1c_w + 262.86$  and the results shown in Fig. 10, which define  $c_w = f(T)$  for the three heating rates. The predicted ply-normal modulus results are shown in Fig. 11 for each of the three heating rates. The average measured initial ply-normal modulus from the experimental studies of McCurdy [2] and Dunkin [3] (circles and diamonds, respectively), and the average ply-normal modulus measured at 177 and 260°C by Stokes [10] (squares) are also included. The modulus predictions,

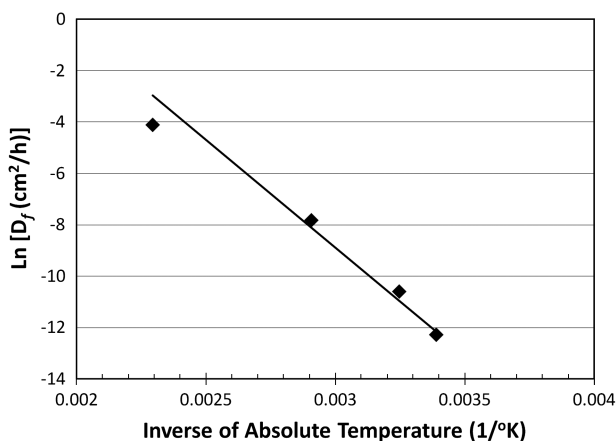


Fig. 9 Plot of the natural log of the in-plane moisture diffusivity versus inverse of the absolute temperature ( $^{\circ}\text{K}^{-1}$ ).

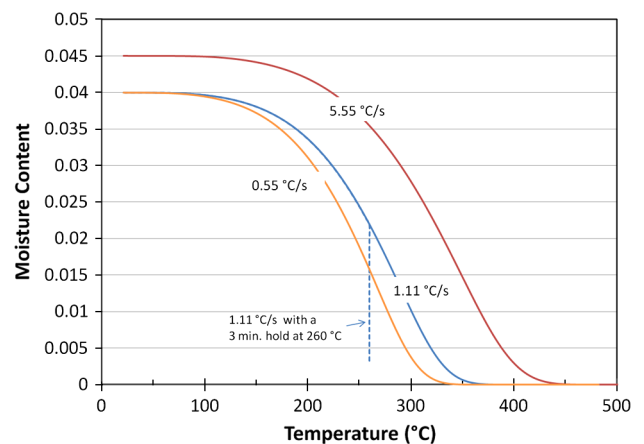
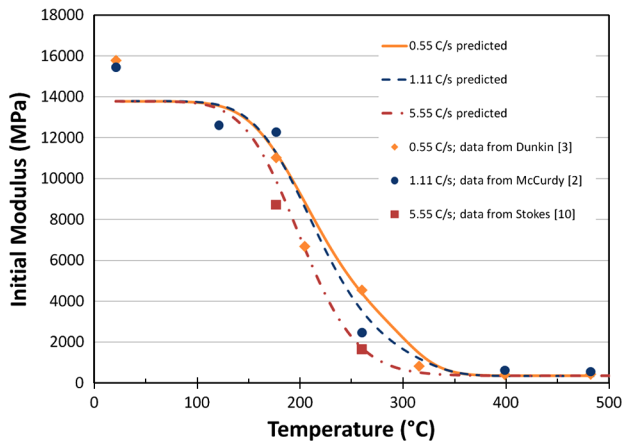


Fig. 10 Plot of average moisture content versus temperature for ply-normal tensile specimens heated at three heating rates: 0.55, 1.11, and 5.55°C/s.



**Fig. 11** Plot of modulus versus temperature for various heating rates using Eq. (1) and the results of moisture diffusion solutions. Data points represent experimental results from McCurdy [2], Dunkin [3], and Stokes [10].

which are obtained from Eq. (1), are in fairly close agreement with the measured ply-normal modulus at all temperatures.

The largest difference between the measured initial modulus and the predictions is at room temperature (21°C). The reason for this is that the modulus of the phenolic polymer exhibits a slight temperature dependence in the glassy state [17], whereas the complementary error function is constant at temperatures below 100°C. Regardless of this minor discrepancy, it appears that the use of Eq. (1) is fairly accurate at all other temperatures. In particular, the use of Eq. (1) appears to simulate the effect of heating rate on the measured ply-normal modulus in the temperature range where glass transition and moisture diffusion occur simultaneously.

It has been demonstrated that the effect of heating rate on the ply-normal modulus, which is evident by comparing the measurements from McCurdy [2], Dunkin [3], and Stokes [10] as well as the effect of time at temperature in the results from McCurdy [2], can be explained as the combined effect of moisture diffusion and plasticization of the phenolic polymer. A specimen that is heated at a higher rate will contain more moisture than a specimen heated at a slower rate, and the temperature at which the polymer becomes soft and rubbery is a decreasing function of the moisture content. Thus, higher heating rates will result in more moisture remaining and a lower value for the Young's modulus in the range of temperatures where glass transition and moisture diffusion occur simultaneously.

This combined effect is more than likely the cause of the time-at-temperature effect measured by Lander [1], where longer hold times resulted in an increase in the modulus. A tensile specimen, which is heated to a fixed temperature within the range of 200–300°C, will continuously lose moisture as time progresses. One can imagine a series of curves similar to that shown in Fig. 7, where each curve represents the modulus versus temperature for a fixed moisture content. The value of the modulus will be specified by a position along a constant temperature path, a path which traverses successive curves of constant moisture content. Since the modulus must necessarily increase as one travels in the direction of decreasing moisture content, the modulus must increase with the time at temperature.

## VII. Conclusions

A simple equation has been proposed that defines the value of the ply-normal modulus as a function of temperature and the moisture content. This equation simulates the drop in modulus at glass transition as well as the effect of moisture content in shifting the glass transition temperature. It can be easily incorporated into a thermostructural analysis solution to calculate the ply-normal modulus within each finite element based on the current temperature and moisture content. This can be achieved through the use of a user-supplied subroutine, which can be executed in concert with the

structural analysis solution and is available with most general-purpose finite element programs. Of course, a moisture diffusion solution will need to be performed in parallel with the structural analysis to determine the moisture content within each finite element and at each time step.

The measured effect of heating rate on the ply-normal modulus has been explained as the combined effect of moisture diffusion and plasticization of the phenolic polymer. Other properties of the phenolic polymer will be affected by temperature and heating rate in a similar manner. The polymer viscosity, for example, will also decrease at glass transition due to the increase in the mobility of the polymer segments. The viscosity should depend on temperature and moisture content in a similar manner. This is an important consideration in the analysis of the ply-normal thermal expansion behavior, since viscous and irreversible flow of the polymer is a significant part of the ply-normal thermal expansion signature.

## Acknowledgments

The first and third authors are grateful for funding from the Reusable Solid Rocket Motor V Project under NASA's Constellation Program. The first author is also grateful for funding from the Hypersonics Project under NASA's Fundamental Aeronautics Program. The second author acknowledges funding from the RSRM Project under NASA's Space Shuttle Program.

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M. Hyer  
Associate Editor