

Swelling and Glass Transition Relations for Epoxy Matrix Material in Humid Environments

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Synopsis

An experimental investigation has established coherent data sets describing effects of moisture absorption upon swelling and glass transition of an epoxy resin. Equilibrium moisture absorption levels and resultant swelling can be represented by power law functions of relative humidity and quantity of absorbed moisture, respectively. Depression of glass transition temperature is shown to be described by a relationship derived from free-volume theory.

INTRODUCTION

It is an accepted fact that epoxy matrix composites absorb moisture and that this absorption can alter behavior of certain properties.¹ The absorption process has been defined in various ways but is reasonably well described by classical diffusion law.² Altered behavior due to this absorption has been predicted for both loaded and unloaded structures due to swelling of the matrix.³ Methods have been developed which incorporate this hygrothermal conditioning effect into thermal stress analysis.⁴ However, coherent data sets describing the swelling behavior have not been reported.

Altered mechanical behavior has been observed in matrix dominated properties such as compression strength and shear modulus.⁵ Behavior alteration is particularly apparent at elevated temperatures. This has been related to depression of glass transition temperature caused by the moisture absorption.⁶ It has also been shown that moderate temperature transients can alter the subsequent diffusion behavior of laminates containing certain amounts of moisture.⁷ The importance of these temperature effects requires a coherent data set and theory describing glass transition shifts due to moisture absorption.

This paper presents experimental findings of swelling behavior, thermal expansion behavior, and changes in glass transition of an epoxy matrix material resulting from moisture absorption. Theories describing these properties are discussed, and modifications to currently accepted views are proposed.

EXPERIMENTAL

Narmco 5208 epoxy resin was used for all of the investigations discussed in this report. Specimens for all tests were rectangles having a thickness of about 0.035 in. (0.89 mm) and were cut from a neat resin casting. The resin was cured using the cycle shown in Table I.

Special care was taken to assure that all specimens were completely dry at the start of testing. The resin casting was kept in a desiccator following cure until

TABLE I
Cure Cycle for Neat Narmco 5208 Resin

(1) Heat at 200°F (93°C) for 20 hr.
(2) Increase temperature to 250°F (121°C) and hold for 3 hr at 250°F (121°C).
(3) Increase temperature to 300°F (149°C) and hold for 2 hr at 300°F (149°C).
(4) Increase temperature to 350°F (177°C) and hold for 2 hr at 350°F (177°C).
(5) Turn oven off and allow to cool in oven.

individual specimens could be cut with a Micromatic Wafering Saw. The individual specimens were then postcured for 4 hr at 400°F (204°C) and placed immediately into a room-temperature desiccator.

One group of specimens was maintained in the reference dry condition. The remainder were placed in groups of three into each of several hygrothermal conditioning environments. The various stagnant-air, constant humidities were provided in laboratory jars containing appropriate saturated salt solutions. The constant temperatures resulted from placing the jars in ovens. Table II identifies the environmental conditioning matrix.

Specimens from each environment were removed periodically, weighed, and dimensionally measured. Measurements were made with four-place slip-ratchet micrometers which were permanently mounted on indexing fixtures. Specimens also were indexed so that measurements were always made at the same points.

After specimens reached moisture equilibrium as determined by weight and dimensional measurements, glass transition tests were conducted. Glass transition temperature can be determined by measuring the temperature dependence of many different properties, but measuring thermal expansion behavior is one of the more commonly accepted approaches.⁸ This technique was used for all glass transition tests discussed herein.

A loaded-columnar thermal expansion method was developed which involved the use of Perkin-Elmer TMS-1 thermomechanical analyzer (TMA). Neat resin samples (12.7 mm × 6.35 mm × 0.89 mm) were loaded with 60 psi (414 kN/m²) applied parallel to the 12.7-mm dimension. This loading is less than 1% of the resin's load capability. It is used to stabilize the specimen and to avoid spurious indications from surface irregularities. The loading resulted from placing a 100-g weight on the top of the vertical quartz probe which rested on the test specimen. Changes in specimen length were measured using a linearly variable differential transformer through which the probe moved. The probe used was a flat-bottomed quartz expansion probe with a diameter of approximately 0.10 in. (2.54

TABLE II
Environmental Conditioning Matrix

Exposure media	Relative humidity, %, at temperature				
	75°F (24°C)	120°F (49°C)	150°F (66°C)	180°F (82°C)	195°F (91°C)
Vapor above saturated solution of					
LiCl·H ₂ O	14.2	—	—	—	—
KF	—	—	21.1	—	—
CrO ₃	45.5	—	46.0	—	—
NaCl	75.5	—	74.0	—	—
Pb(NO ₃) ₂	97.5	94.5	93.0	91.0	90.0
Water immersion	100	100	100	100	100

mm). Figure 1 illustrates the probe, specimen, and general details of the TMA apparatus.

To minimize both moisture desorption and possible creep effects during test setup, each test specimen was chilled to -75°F (-59.5°C) immediately after placement in the TMA unit. After stabilization at -75°F and completion of calibration steps, heating of the specimen began and proceeded at a constant rate of $36^{\circ}\text{F}/\text{min}$ ($20^{\circ}\text{C}/\text{min}$). This rate roughly represents a lower boundary of heating rates applied during structural hardware tests and is realistic for certain aircraft missions. Certain other fighter missions could involve faster heating rates.

This rapid heating rate not only represents realistic service conditions but is also one key to successful use of the TMA test procedure. The small size of the TMA specimen, hence its high surface area-to-volume ratio, tends to promote faster drying than would occur in larger specimens. However, when heated at $36^{\circ}\text{F}/\text{min}$, a substantial portion of the specimen maintains its initial moisture content upon reaching temperatures of interest for measurements of T_g . Experimental measurements showed that a specimen at initial moisture equilibrium in 91% R.H. and containing 6.0% moisture by weight will retain 4.7% moisture upon reaching 300°F (149°C). A finite difference diffusion analysis conducted

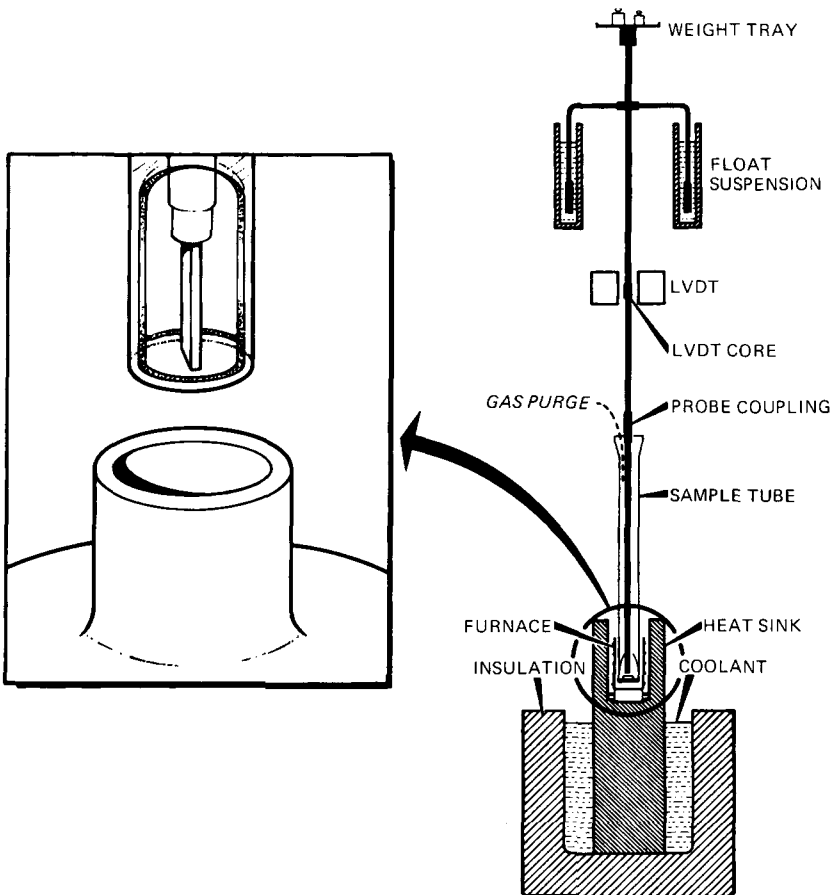


Fig. 1. TMA schematic for loaded-column thermal expansion tests.

for drying at any constant temperature will show the probable distribution of this 4.7% bulk moisture content. The distribution predicted for an average effective drying temperature of 230°F (110°C) is shown in Figure 2 and confirms that the center portion of the specimen maintains its initial moisture level.

It should be noted that a material with a diffusion rate larger than that of epoxy could dry at the center. For such a material the heating rate would have to be increased and/or the specimen thickness would have to be increased.

Because of shrinkage effects, the drying of the surface layers indicated by Figure 2 does not compromise the loaded column expansion test as it would in certain other test methods. As will be discussed subsequently, the resin swells because of moisture absorption, and desorption causes shrinkage toward the original dimensions. Consequently, the outer sheath of the specimen shortens slightly, leaving the dilation probe in contact only with the still-saturated core of the specimen. This behavior is illustrated by Figure 3.

Whether for wet or dry specimens, glass transition temperature was defined as that temperature coinciding with the first significant change in the rate of expansion. This is analogous to the use of first increase in deflection rate in heat distortion tests reported by Browning, Husman, and Whitney.⁶ Figure 4 compares typical expansion profiles for dry and moisture-conditioned specimens.

RESULTS

Absorption and Swelling

Weight and dimensional measurements were made periodically until equilibrium was indicated by constant successive values. Weight-versus-time data were analyzed for overall diffusion coefficient D , using a regression program based upon a finite difference solution of Fick's law of diffusion assuming concentration independence,

$$\partial c/\partial t = D\partial^2 c/\partial x^2 \quad (1)$$

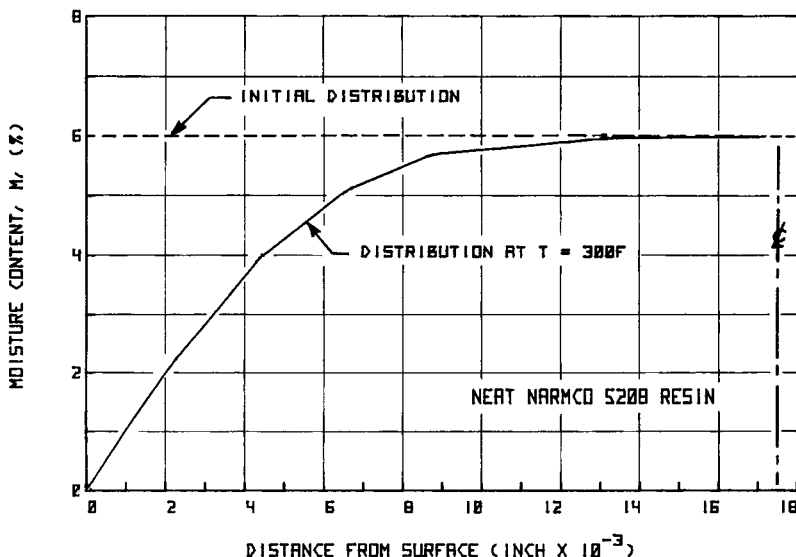


Fig. 2. Moisture distribution in T_g specimen after heating from -75°F to 300°F at $36^\circ\text{F}/\text{min}$, specimen initially saturated.

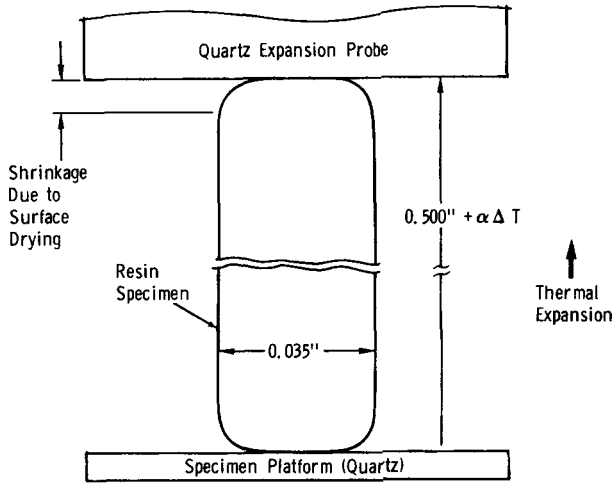


Fig. 3. Specimen configuration after heating to T_g .

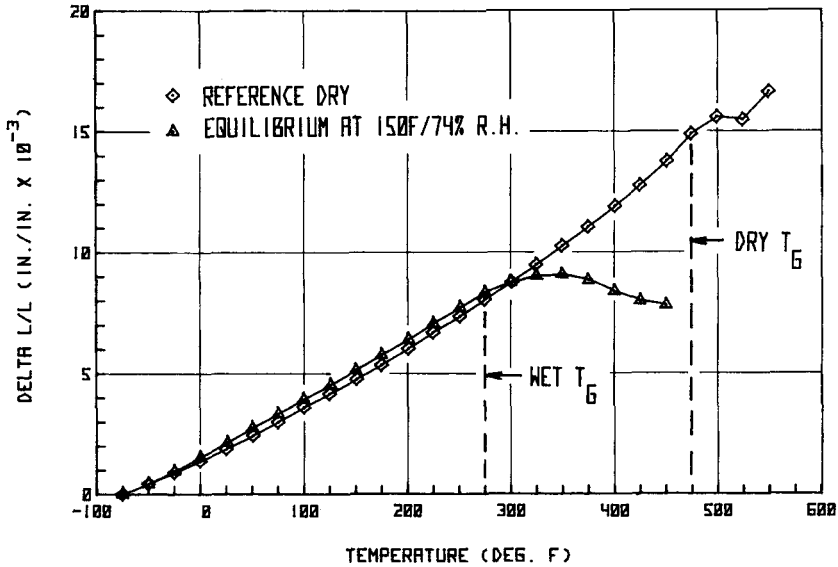


Fig. 4. Typical expansion profiles for dry and moisture conditioned specimens of neat Narmco 5208 resin.

where c = concentration, t = time, D = diffusion coefficient, and x = distance. Mean values of D are plotted against reciprocal conditioning temperature T in Figure 5. Using the Arrhenius relationship,

$$D = D_0 \exp(-E/RT) \tag{2}$$

where D_0 = permeability index, cm^2/sec , E = activation energy for diffusion, cal/g-mole , R = universal gas constant = $1.986 \text{ cal-mole}/^\circ\text{K}$, from which $E = 8063 \text{ cal/g-mole}$ and $D_0 = 5.14 \times 10^{-4} \text{ cm}^2/\text{sec}$.

Equilibrium moisture contents M_∞ , as percent of dry resin weight, are plotted in Figure 6 with respect to the relative humidities H in which the specimens were conditioned. Each plotted point represents the average of three specimens; the

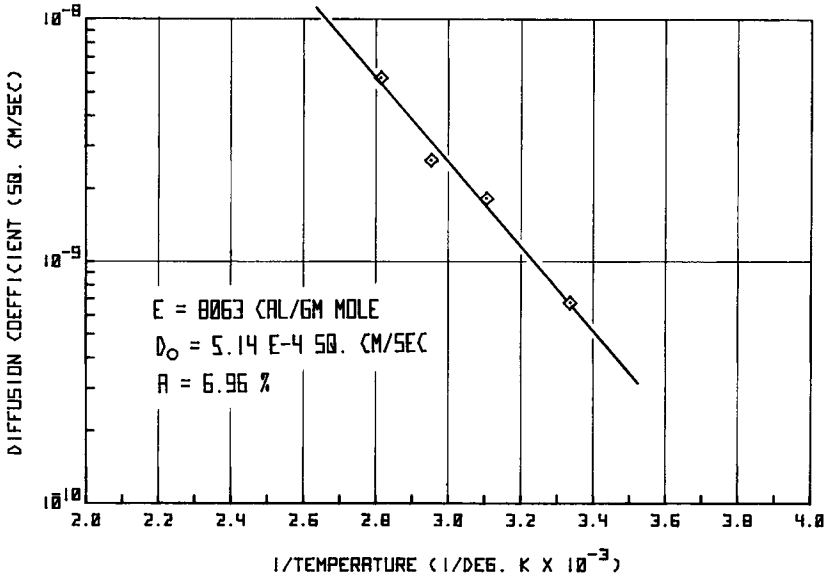


Fig. 5. Overall diffusion coefficient vs reciprocal exposure temperature for neat Narmco 5208 resin soaked in water.

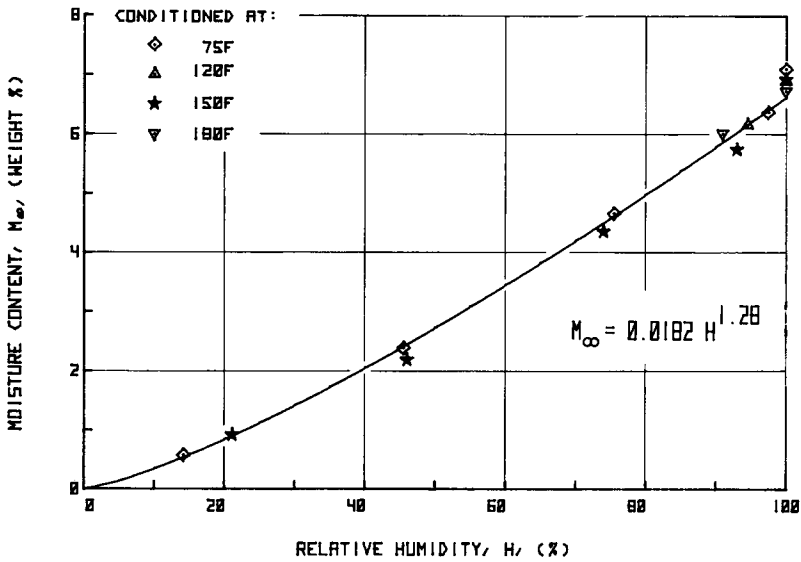


Fig. 6. Equilibrium moisture content vs relative humidity.

typical range of values was $\pm 0.06\%$, which falls within the data symbol. These data show the slightly nonlinear characteristics noted by Shen and Springer² for a graphite-epoxy laminate, and can be described by

$$M_{\infty} = aH^b \tag{3}$$

where $a = 0.0182$ and $b = 1.28$. These values were determined by regression analysis which showed the correlation coefficient to be 0.9982. Husman⁹ reported $b = 1.8$ for Narmco T300/5208 laminates; and McKague, Reynolds, and

Halkias¹⁰ found $b = 1$ for an earlier group of T300/5208 specimens. For uncured T300/5208 prepreg, the authors have found $b > 2$. For Fiberite T300/934 without postcure, Shen and Springer² reported $b = 2$, whereas Bergmann¹¹ found b substantially less than 2. These variations in values of b suggest some strong dependence upon resin molecular structure, perhaps determined by batch stoichiometry and/or degree of polymerization. (Current investigations by the authors now indicate that b diminishes as polymerization advances.)

Figure 7 shows change in length versus weight during the transition from dry to equilibrium absorption in high humidity. These data also have a slightly nonlinear character and, based upon regression analysis, can be described by

$$100 \cdot \Delta l/l = cM^d \quad (4)$$

where $c = 0.133$ and $d = 1.36$ and where the correlation coefficient is 0.9913. This value for d is similar to the value of b found from eq. (3) for equilibrium absorption levels in various humidities. Again, the data points represent the averages of three specimens each, and the range of values falls within the plotting symbols. The coherent behavior of the data shows that the investigated range of conditioning temperature does not influence the range of swelling values for a given moisture content.

The total volume change due to swelling from a dry state to a moisture-equilibrium state can be calculated based upon ideal mixing law. This would predict a volume increase equal to the volume of absorbed water; consequently,

$$\Delta V_\infty/V_0 = 0.01M_\infty\rho\dot{V} \quad (5)$$

where M_∞ = equilibrium absorbed moisture, %, ρ = resin density = 1.27 g/cc, and \dot{V} = specific volume of water = 1 cc/g.

Figure 8 shows the total volume changes ΔV_∞ that occurred due to swelling from the dry resin state to the various moisture equilibrium states M_∞ . The figure shows that the observed swelling is less than that which would be represented by ideal mixing. Regression analysis shows that change in volume also would be better represented by a power law relationship:

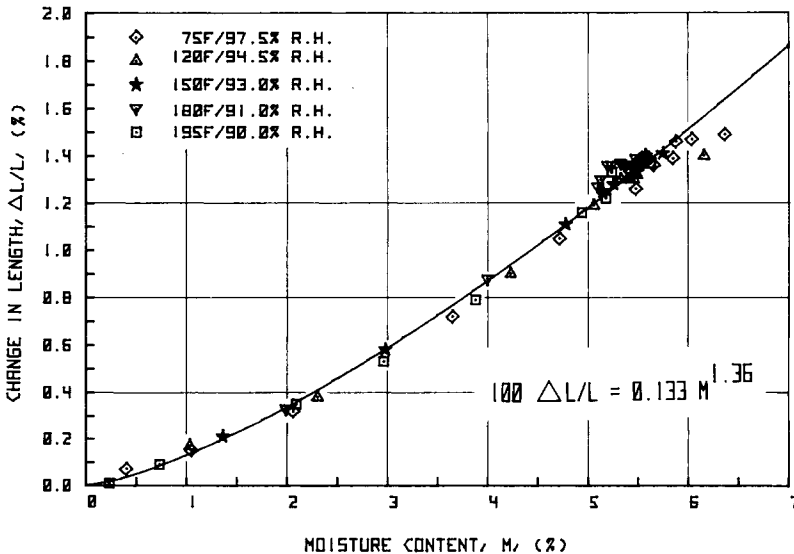


Fig. 7. Change in length during absorption.

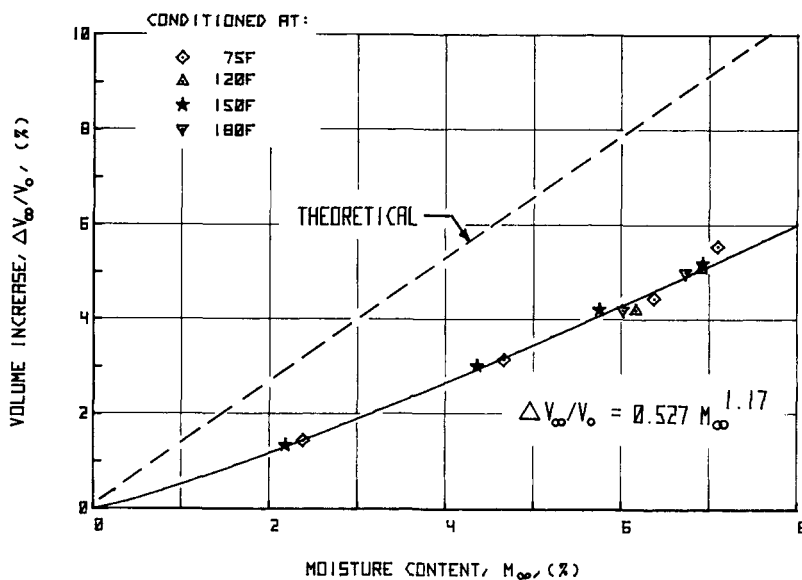


Fig. 8. Volumetric swelling of neat Narmco 5208 resin due to absorbed moisture.

$$\Delta V_{\infty}/V_0 = 0.01K\rho\dot{V}M_{\infty}^m \quad (6)$$

where $K = 41.49$ and $m = 1.173$. The correlation coefficient for these data is 0.9964. Finding a smaller amount of swelling should be expected since, thermodynamically, ideal mixing implies no effect of absorption upon the polymer, which is not consistent with reported mechanical effects. However, the power law behavior has not yet been interpreted.

Thermal Expansion and Glass Transitions

The loaded-column expansion (L.C.E.) tests produced a nominal value of $1.4 \times 10^{-4} \text{ cm}^3/\text{cm}^3 \text{ }^\circ\text{C}$ for the glassy volumetric expansion rate of the Narmco 5208 resin. This value resulted from tripling the average values of linear expansion coefficient calculated over the range from -60°C to $T_g - 14^\circ\text{C}$. Volumetric expansion rate varied within $\pm 9\%$ of the nominal value for all expansion tests, whether dry or conditioned at any humidity.

From the plots of unit specimen expansion versus temperature, the glass transition temperature of dry Narmco 5208 resin was found to be 475°F (246°C) for each of five specimens. Above the glass transition the "liquid" volumetric expansion rate was determined to be $6.0 \times 10^{-4} \text{ cm}^3/\text{cm}^3 \text{ }^\circ\text{C}$. This expansion rate continued until an apparent decomposition point was reached at $\sim 600^\circ\text{F}$ (316°C).

Average values of glass transition temperature varied with moisture content, but for a given condition the typical specimen-to-specimen variation was within $\pm 6^\circ\text{C}$. These values are plotted against the average equilibrium moisture contents for each three-specimen group in Figure 9.

The following relationship was derived by Kelley and Bueche¹² to describe such depression of glass transition temperature by a diluent:

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd}}{\alpha_p V_p + \alpha_d (1 - V_p)} \quad (7)$$

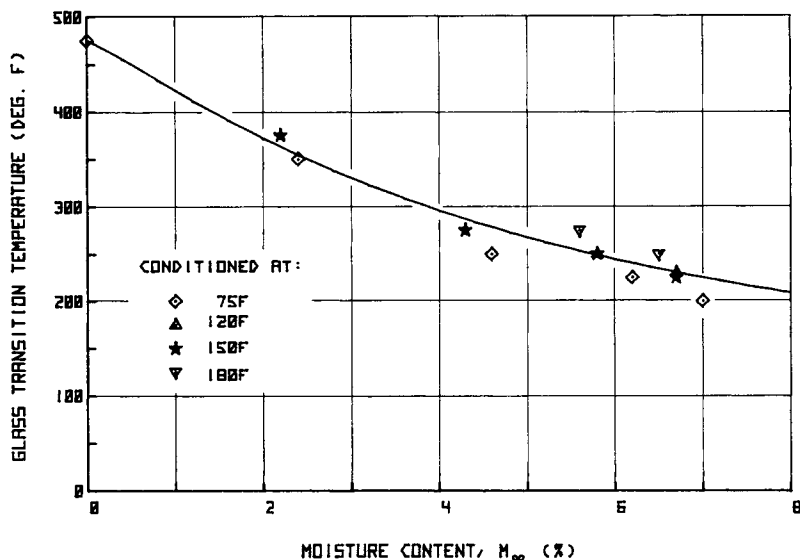


Fig. 9. Glass transition behavior.

where T_g , T_{gp} , and T_{gd} refer to the glass transition temperatures of the system, the polymer, and the diluent, respectively; V_p is the volume fraction of the polymer in the system; and α_p and α_d refer to volumetric expansion terms for the polymer and diluent, respectively. This relationship is based upon the semiempirical work of Williams, Landel, and Ferry.¹³ Consequently, each expansion term is taken to be the difference in liquid and glassy expansions, above and below the T_g , of the respective constituent; for example,

$$\alpha_p = \alpha_{lp} - \alpha_{gp} \quad (8)$$

and $\alpha = l dv/v dT$, where v is the specific volume.

This definition of α_p and α_d results from three assumptions. One is that at T_g some fraction of total volume is free volume f_g and that all volume increases above T_g are due to increases in free volume. Williams, Landel, and Ferry established the constant free volume fraction at T_g for a wide class of materials to be the same ($1/40$ th of total volume) so that the free volume fraction f is given by

$$f = f_g + (\alpha_l - \alpha_g)(T - T_g) \quad (9)$$

where $T \geq T_g$.

The second assumption, made by Kelley and Bueche, is that free volume of the diluent is added to the free volume of the polymer. This, too, is a well established principle which implies that T_g of a polymer can be lowered by mixing with it a liquid containing more free volume than the undiluted polymer.

Based upon these two assumptions, Kelley and Bueche¹² established the free-volume fraction of a polymer-diluent system to be

$$f = V_p[f_g + \alpha_p(T - T_{gp})] + (1 - V_p)[f_g + \alpha_d(T - T_{gd})] \quad (10)$$

where α_p and α_d are defined as in eq. (8).

The third assumption made by Kelley and Bueche is that T_g of the system can be substituted for T in eq. (10). However, this is not true because the limit for

T in this relationship is $T > T_{gp} > T_{gd}$. Instead, consider the polymer and diluent volumes for $T_{gd} < T_g = T < T_{gp}$. For the polymer,

$$f = f_g - (\alpha_g - \alpha_0)(T_{gp} - T) \quad T < T_{gp} \quad (11)$$

and for the diluent,

$$f = f_g + (\alpha_l - \alpha_0)(T - T_{gd}) \quad T > T_{gd} \quad (12)$$

where α_0 represents the expansion rate for the occupied volume. As summarized by Ferry,¹⁴ this occupied volume includes both the molecular volume, as determined by van der Waals radii, and volume determined by vibrational motions.

Among the various free-volume concepts which Ferry¹⁴ discusses, one concept assumes $\alpha_0 = 0$. Certainly for the case of a highly crosslinked, rigid polymer it is believable that α_0 might be negligible, if not actually zero.

Since moisture absorption by epoxy is a process of water vapor diffusion, the expansion coefficient α_l must be defined according to Charles' law. Consequently, α_0 for the diluent also is negligibly small, if not zero, since the occupied volume is a small part of the vapor volume.

With $\alpha_0 = 0$, adding the fractional free volumes of polymer and diluent, eqs. (11) and (12), and setting the combined fractional free volume = f_g for T_g , simplifies to

$$T_g = \frac{\alpha_{gp} V_p T_{gp} + \alpha_{ld}(1 - V_p) T_{gd}}{\alpha_{gp} V_p + \alpha_{ld}(1 - V_p)} \quad (13)$$

This is identical to the equation derived by Kelley and Bueche except that α_{gp} and α_{ld} are used instead of $(\alpha_{lp} - \alpha_{gp})$ and $(\alpha_{ld} - \alpha_{gd})$, respectively.

This redefinition of the Kelley-Bueche relationship is empirically justified by the expansion, swelling, and T_g data obtained in these investigations. Figure 10 shows the volume-temperature envelope established by the dry, swollen, and thermally expanded resin samples. Added to this envelope is the volume-temperature relationship established from the T_g -versus-moisture data. The

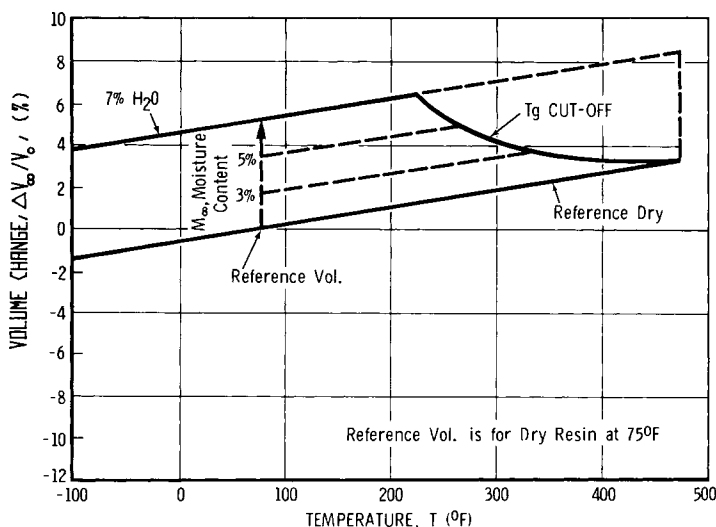


Fig. 10. Volume-temperature envelope established by swelling and expansion.

figure illustrates that the T_g of the swollen system is reduced from that of the T_{gp} by contracting along the slope established by the glassy expansion.

For T_{gd} , 0°C would seem to be a candidate choice, but the maximum density point of water, 3.98°C , might be a better choice. However, the 4°C difference between the two values would have a negligible effect on the prediction of T_g .

From Charles' law, $\alpha_{ld} = 3.66 \times 10^{-3} \text{ cm}^3/\text{cm}^3 \text{ }^\circ\text{C}$, and per above, $T_{gd} = 4^\circ\text{C}$. Using these values and using the experimental values $T_{gp} = 246^\circ\text{C}$ (475°F) and $\alpha_{gp} = 1.4 \times 10^{-4} \text{ cm}^3/\text{cm}^3 \text{ }^\circ\text{C}$, with V_p defined from eq. (6) to be

$$V_p = \frac{1}{1 + 0.01K\rho\dot{\nu}M^m} \quad (14)$$

where $\rho = 1.27 \text{ g/cc}$, $K = 41.49$, $\dot{\nu} = 1 \text{ cc/g}$, and $m = 1.173$, a prediction of T_g versus moisture content M_∞ was made. This prediction is represented by the solid curve in Figure 9, and it agrees very well with the measured values of T_g .

This result is somewhat different than that reported by Browning, Husman, and Whitney.⁶ They described heat distortion temperature versus moisture content using the larger value of volumetric expansion required by the original Kelley-Bueche equation. However, this apparent discrepancy might be rationalized on the basis that whatever drying occurred during the test would affect the outer plies. The outer plies would be most sensitive in a beam test, whereas they are not so sensitive in the L.C.E. test. As a result, the wet T_g values would be somewhat higher than they should be, and the data would require the larger value of $\alpha_{lp} - \alpha_{gp}$ for correlation.

CONCLUSIONS

Moisture absorption by epoxy resin results in dimensional swelling by an amount less than that predicted by ideal mixing. The absorption occurs through a diffusion-controlled process and proceeds until an equilibrium absorption level is reached which is determined by the characteristics of the resin and by the relative humidity in which absorption occurs. Absorption level and the resulting swelling are described well by power law functions of relative humidity and quantity of absorbed moisture, respectively. In addition to swelling, this absorption causes a reduction in glass transition temperature which is described by a relationship similar to that derived by Kelley and Bueche, wherein experimental values of volume fraction, dry glass transition temperature, and glassy volumetric expansion rate are used and where the reference dry condition is rigorously established.

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