

THE RELATIONSHIP OF EXTERNALLY APPLIED STRESSES
TO ENVIRONMENTALLY INDUCED STRESSES

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Abstract: The stresses developed in composites due to changes in temperature (T) and relative humidity (RH) are due largely to mis-matches in the different moisture and thermal coefficients of expansion of the materials. The stresses and strains developed in the materials due to thermal or moisture changes can easily exceed the yielding and ultimate strength of the materials if the magnitude of the environmental change is sufficiently large. Predicting these stresses requires the accurate determination of the mechanical and dimensional properties of the materials involved. In this paper, a general model is developed in which the mechanical properties of materials can be directly related to the temperature and humidity related restrained response of materials. The basic measurements are force, length, temperature and relative humidity. The information developed is useful in developing predictive numerical models for the behavior of composite structures [1].

Keywords: Adhesives, Analysis, Environment, Equilibrium, Moisture Content, Polymers, Relative Humidity, Restraint, Stress, Strain, Swelling, Temperature.

Introduction

Any unrestrained material subjected to a temperature change will exhibit a change in volume. In one dimension, considering only the length, the change in length is calculated as:

$$\delta = \alpha \cdot L_0 \cdot \Delta t \quad \text{Eq. 1}$$

where: δ is the change in the length of the material
 α is the thermal coefficient of linear expansion
 L_0 is the original length of the specimen and,
 Δt is the change in temperature [2].

The stress free change in strain is calculated as:
$$\Delta \epsilon = \delta / L_0 = \alpha \cdot \Delta t. \quad \text{Eq. 2}$$

If the material were restrained and subjected to a change in temperature, then either tensile or compressive stresses would result depending on whether the materials were cooled or heated. The change in stress is calculated as:

where: $\Delta\sigma = E \cdot \Delta\epsilon = -E \cdot \alpha \cdot \Delta t$ Eq. 3
 $\Delta\sigma$ is the change in stress and
 E is the modulus of elasticity of the material.

The minus sign in the right side of equation 3 indicates that a positive (tensile) stress results from a negative change in temperature in a restrained specimen. For metals, the modulus is typically measured using a simple axial test either in tension or compression at a constant temperature. For polymers however, the question often arises as to how to determine the correct value of the modulus.

The mechanical properties of polymers are quite sensitive to the rate at which the load is applied and, to differing degrees, the amount of water they absorb from the environment. They have been considered to have time dependent or viscoelastic properties. This feature alone has generated considerable discussion with regard to determining meaningful mechanical properties. For adhesively bonded structures intended for outdoor environments, the question of adhesive performance and durability merits serious consideration. Having no way of characterizing the long term mechanical properties seriously lessens the ability to determine a reliable analytical approach to adhesive bonded joint analysis. An alternative approach to determining the modulus is presented.

It is simple enough to rearrange Equation 3 and determine what value of E has meaning. If one divides the left and right sides of Equation 3 by Δt then:

or $\Delta\sigma/\Delta t = -E \cdot \alpha \cdot \Delta t/\Delta t$
 then $\Delta\sigma/\Delta t = -E \cdot \alpha$
 where: $-(\Delta\sigma/\Delta t)/\alpha = E$ Eq. 4
 $\Delta\sigma/\Delta t$ is the change in stress with respect to the change in temperature for a fully restrained material,
 α is the thermal coefficient of linear expansion
 E is the modulus of the material as measured by a tensile test at a fixed temperature.

Equation 4 states that the modulus, E, of a material can be measured in the traditional method using a tensile test at a constant temperature or it can be measured by dividing the slope of the stress versus temperature test of a restrained specimen by the coefficient of linear expansion. If all of the properties of the materials are measured under equilibrium conditions, meaningful information can be extracted and used for analytical studies of bonded systems subjected to long term loading. Equation 4 was experimentally verified using different types of polymers. These materials included clear butyrate dope, used as an aircraft coating, an epoxy (adhesive II-3h) developed under a research program at the Martin Marietta Laboratories in Arbutus, Maryland, [3] and a 50 year-

old nitrocellulose photographic film base.

Experimental Methods

For all of these materials, three tests were conducted. One was the simple measurement of the thermal linear expansion. From this measurement the thermal coefficient of linear expansion could be calculated. A second test was the measurement of the stress in a material resulting from the cooling of a restrained specimen. In these tests the RH was held constant. The third test was the measurement of the stress-strain properties under near equilibrium conditions. Measuring the modulus of a material from a tensile test can require more time. If one were to truly determine the modulus at equilibrium, the time dependent properties have to be eliminated. One of the ways to satisfy this requirement was to incrementally load the specimen and allow it to stress-relax until nearly all stress reduction ceased. After little stress relaxation was noted, a further load was applied and the load/stress-relaxation cycle repeated. Some materials stress relax a considerable amount in a relatively short time and others very little, even over extended periods. Since the specimens were small, 8 inches (203mm) long, .2 inches (5mm) wide, and .01 inches (.25mm) or less thick, the experiments were conducted using what were effectively miniature screw driven tensile testers. Test methods and sample preparation are described in reference 5.

The butyrate dope used in the experiments was cast on a polyester sheet and allowed to dry for 7 months. The cast film was easily removed from the polyester and cut into strips. The epoxy was cast between sheets of polyester 6 years ago and the nitrate film base was Dupont 35 mm motion picture stock from 1945. The image emulsion layer was stripped using warm water and the film base allowed to dry. The reason for choosing many of these materials is that they are typically found in the objects of the collections of the Smithsonian Institution and research on the effects of the environment on the structural stability of museum objects is currently underway.

The chamber environments are maintained several different ways. Controlling the RH is done using conditioned silica gel, saturated salt solutions, or pans of water when high humidity is required. The temperature control is provided by using Cincinnati SubZero environmental chambers (ZH 16). The environments are monitored using dew point hygrometers. These are the General Eastern M2 controller with a D2 sensor head.

Experimental Results for the Temperature Studies

The experimental measurements were used to compare the modulus, E, as measured by the stress relaxed, stress-strain method to a modulus calculated from the restrained cooling test and the measured thermal coefficient of linear expansion.

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Figure 1 shows the experimental results for measuring the strain of specimens as a function of temperature of clear butyrate dope at three different RH levels.

The slope of these plots is the thermal coefficient of linear expansion and are labeled in Figure 1. The higher moisture content, at 80% RH, has increased the thermal coefficient of the clear butyrate dope when compared to the other values tested at lower RH levels. At 80% RH, the coefficient was determined to be .000082 in./in./C. Figure 2 shows the stress measured as a result of cooling a restrained sample of butyrate dope in an environment of 80% RH. The slope of this plot is $-(\Delta\sigma/\Delta t)$ and in figure 3 is labeled Phi which is equal to -8.925 psi/%RH (-61.5 KPa/%RH).

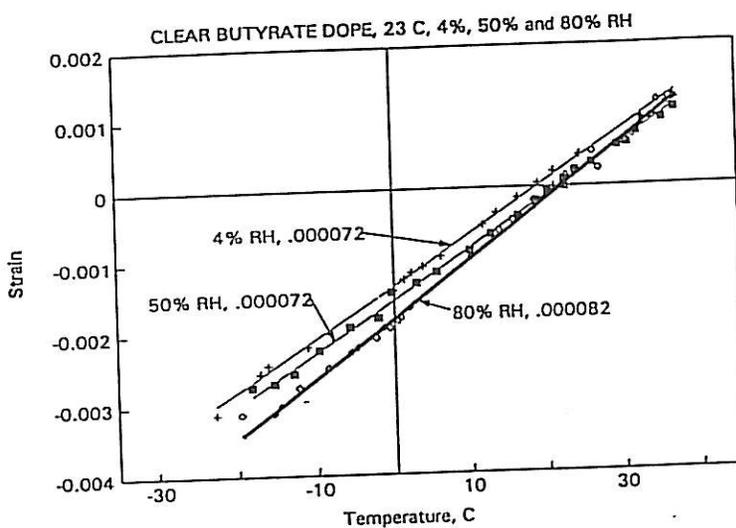


Figure 1. Free swelling strains induced by changes in temperature for specimens of cast clear butyrate dope. The films were allowed to dry 8 months prior to testing. The increased moisture content at 80% RH increases the thermal coefficient of linear expansion.

During the stress-strain tests, the butyrate dope relaxed little. However, depending on the environment, other materials such as room temperature cured epoxies can lose up to 70% or more of their initial stress over time [4,5,6]. In the case of the butyrate dope specimens the relaxation times for tests conducted at 80% RH were short, 30 seconds, and in this case not quite long enough.

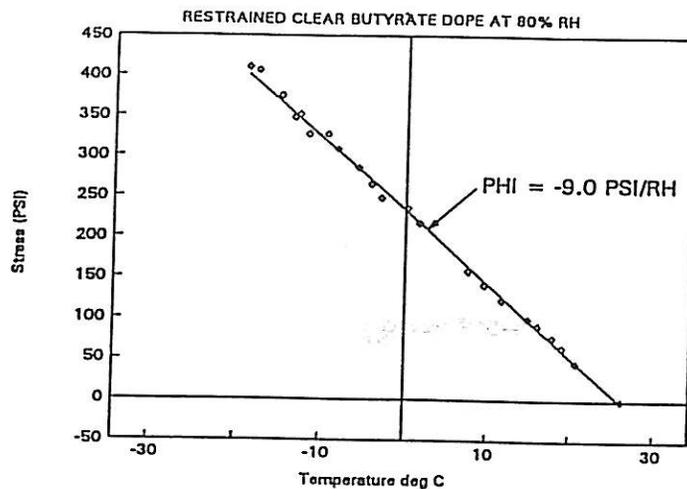


Figure 2. The results of a stress versus temperature test for restrained clear butyrate dope conducted at 80% RH. Phi is the slope of the line fit through the data.

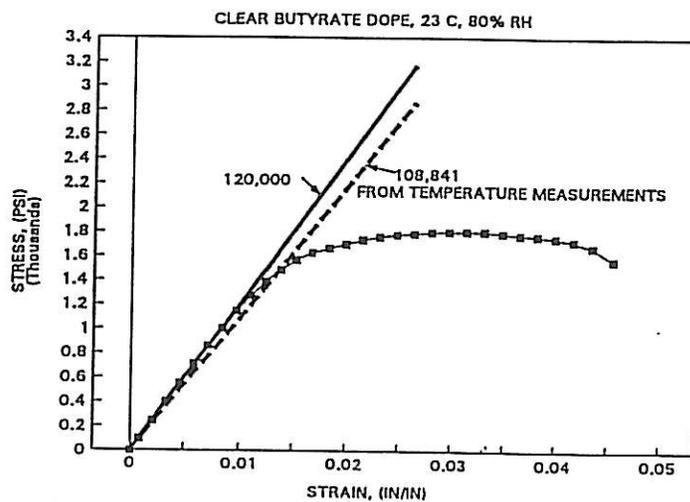


Figure 3. A comparison of the modulus of clear butyrate dope samples at 80% RH as measured from a stress-strain test and calculated using the results of the free swelling and restrained cooling tests. Figure 3 illustrates the results of the 80% RH incremented

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tensile test and compares the measured modulus of 120,000 psi (827 MPa) with the modulus as calculated from the results of the coefficient and restrained cooling tests 108,800 psi (751 MPa). Clearly the tensile test specimen should have been allowed to relax further, since the measured modulus is higher than the calculated modulus. This experiment was repeated at 50% RH and table 1 shows the results of this and other tests. Experimental measurements for a large variety of materials shows that yielding in previously untested materials seems to initiate at a strain of approximately .004 [7].

Table 1. The Comparison of the modulus (E) of selected materials as measured by the stress-strain test and as calculated from thermal measurements.

Modulus in PSI	E from stress strain tests	E from thermal measurements
Butyrate dope at 50% RH	130,000	131,950
Epoxy Adhesive II-3H, 50% RH	220,000	199,000
50 year-old Nitro-cellulose film at 50% RH	530,000	516,400

Relative Humidity Effects

While changes in temperature are important to the structural performance of polymers, moisture can have an equally dramatic effect. In a dry state, many organic materials retain a high modulus and in a wet state become extremely flexible. If too much moisture is available many structural adhesives lose all load carrying ability.

Most organic materials are hygroscopic to some extent, structural polymers are subject to swelling and shrinking with these moisture changes. These dimensional changes, coupled with the changes in the mechanical properties of the bonding materials can adversely affect structural performance. When considering the number of parameters such as rate of loading, viscoelastic behavior, moisture content, temperature and even chemical degradation, it is difficult to define the useful mechanical properties of polymers.

The experimental approach taken for the RH studies was identical to that of the temperature studies. Here RH replaced temperature as the independent variable. The cast test films were all unsupported when tested. The paints, oils and alkyds, were cast on polyester sheets in 1979 and 1980 respectively and allowed to dry in a normal interior environment. The

epoxies were all cast 6 years ago between polyester sheets and cured at either room temperature or at 50°C. The rabbit skin glue was cast in 1981 and conditioned by hanging the cut specimens in an 85% RH environment to relieve casting strains.

Alternate Paths To Stress Development

If a specimen of a hygroscopic material is allowed to swell from one RH to another; i.e., RH_0 to RH_1 , and then restrained, and desiccated back to RH_0 , it will develop a state of stress (σ_1) and an increase in length (L). A specimen subjected to an equilibrium tensile test at a constant RH, in this case RH_0 , will also attain the same state of stress, length and RH. This is illustrated in figure 4, where the separate paths from one state of stress (σ_0), to another state of stress (σ_1), are illustrated. In this diagram the coordinates are relative humidity (RH); length (L); and stress (σ).

The rationale for using length rather than strain will become clear later in this discussion. The two paths from σ_0 to σ_1 , can be defined as path 1, the equilibrium stress-length test (the equilibrium stress-strain test in terms of length); and, path 2, the two part paths of first, free swelling, and second, the restrained desiccation of the specimen.

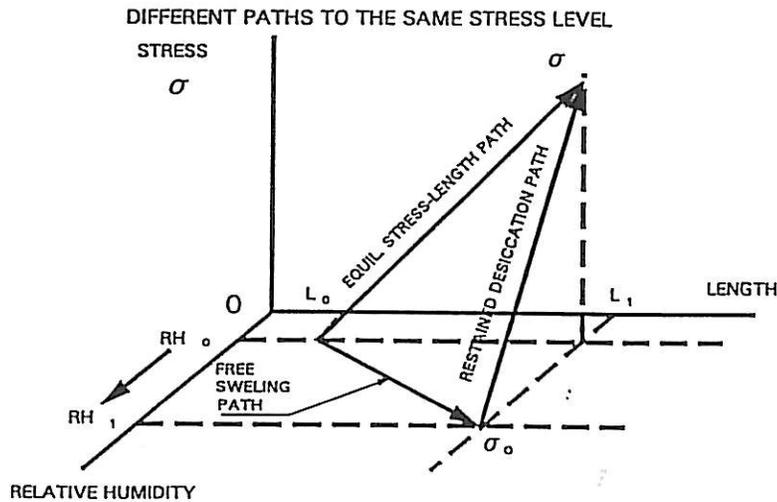


Figure 4. Diagram illustrating the different paths from one state of stress to another. One path is the equilibrium stress-length (strain) test and the other path consists of the free swelling test and the restrained desiccation test.

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Experiment

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Paths in planes parallel to the stress-length plane are equilibrium tensile tests at constant temperature and relative humidity. Paths in planes parallel to the stress-relative humidity plane are restrained desiccation tests. The paths in the length-relative humidity plane are swelling isotherm measurements which can be either stress free or under a constant stress.

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The illustration shown in figure 4 implies that there is a link between the environmentally induced stress and the externally applied loads of a simple tensile test. It also implies that fundamental mechanical and dimensional properties of the materials govern the ultimate state of stress and strain whether the forces are externally applied or environmentally induced in the materials.

Experimental Results of the RH Tests

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Several different types of materials were tested at ambient temperature (23°C) to determine if this test concept holds generally. Some of the data of this test program are illustrated in figures 5-10. The tensile test results shown are the locus of stress-relaxed data points. The stress-relaxation times for all of the materials shown were on the order of weeks. The total times to run such tests were often a year or more. For the free swelling tests and the restrained desiccation tests, equilibration time was in the order of a week to 10 days for the specimens used. The dimensions of the cross-sections of the specimens for all of the materials were approximately .25 inches (6.3mm) by .012 inches (.3mm). The specimen lengths were typically 5 inches (125mm).

Figure 5 illustrates experimental results of three the different tests conducted using a 16-year-old unsupported cadmium yellow alkyd paint film. The plot on the base of the figure is the stress-free RH related swelling of the paint. The plot running through points I₀₁, I₁, and I₂ is the locus of points of the equilibrium stress-length plot at 50% RH. The six plots in the stress-RH plane are the restrained desiccation data. The restrained desiccation plots intersect the stress/length plot at points I₁ and I₂. This plot shows that the separate paths can be used to go from stress level I₀₁ to stress levels I₁ or I₂ for this material.

In figure 6, four intersection points, I₁-I₄ were established in a 15-year-old paint, titanium dioxide in safflower oil. The curvature of the stress-length plots indicate that yielding is occurring and can be predicted from RH changes.

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Figures 7-9 are three different epoxy films. The first epoxy (figure 7) is a commercial product HYSOL™ EA 9394, which is highly modified with powdered aluminum and amorphous silica.

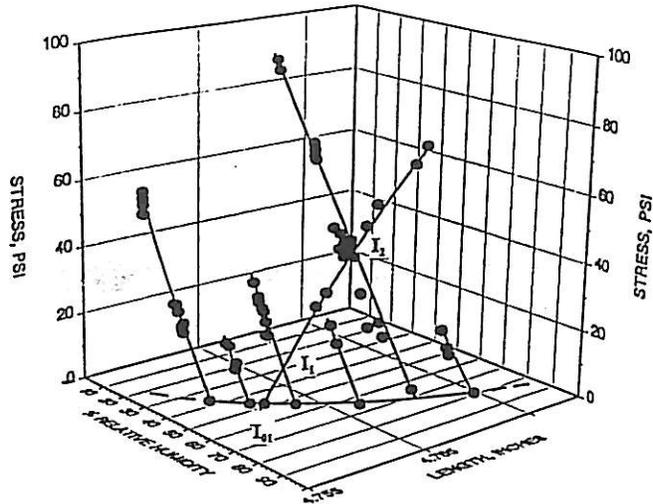


Figure 5. Stress-length-relative humidity plot for cadmium yellow alkyd paint showing mutual intersection points of stress starting at I_0 , and going to I_1 and I_2 .

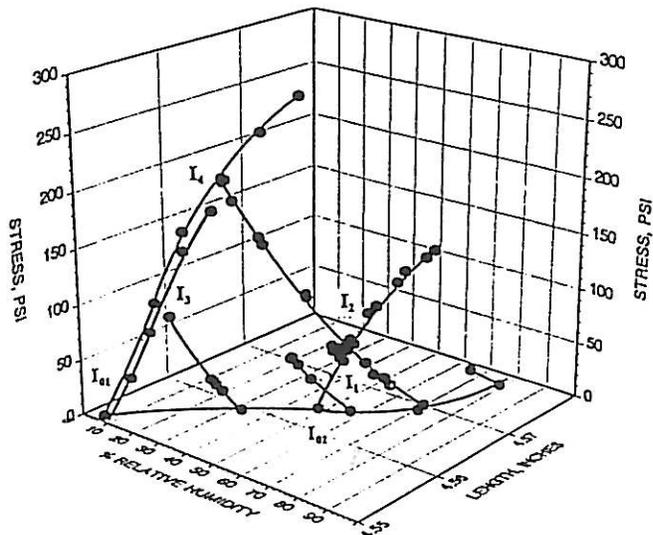


Figure 6. Stress-length-relative humidity plot for titanium dioxide oil paint showing mutual intersection points of stress starting at different points, I_{01} , I_{02} and going to four different stress states I_1 , I_2 , I_3 , and I_4 .

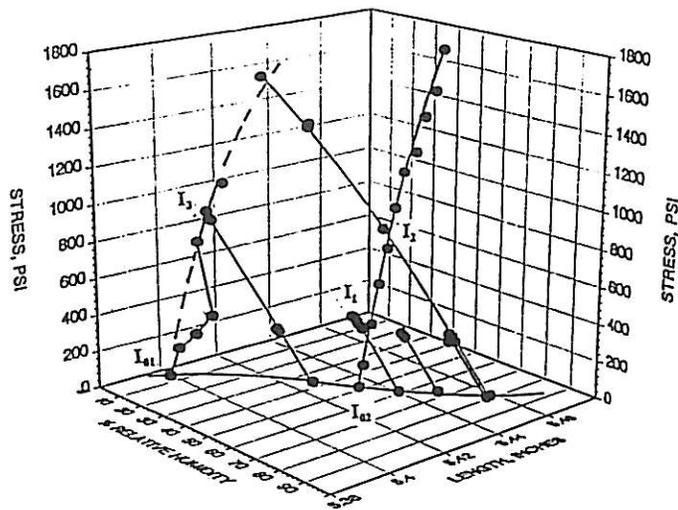


Figure 7. Stress-length-relative plot for epoxy adhesive HYSOL EA 9394 mutual intersection points of stress starting at different points, I_{o1} , I_{o2} and going to three different stress states I_1 , I_2 , and I_3 .

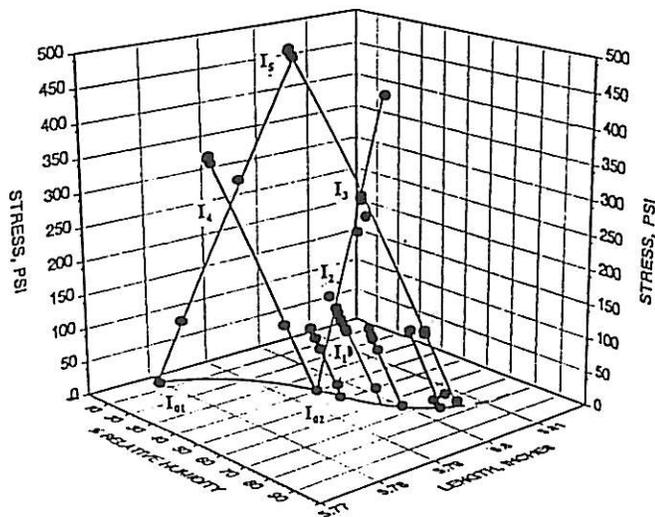


Figure 8. Stress-length-relative humidity plot for epoxy Adhesive 96 mutual intersection points of stress starting at different points, I_{o1} , I_{o2} and going to five different stress states I_1 , I_2 , I_3 , I_4 , and I_5 .

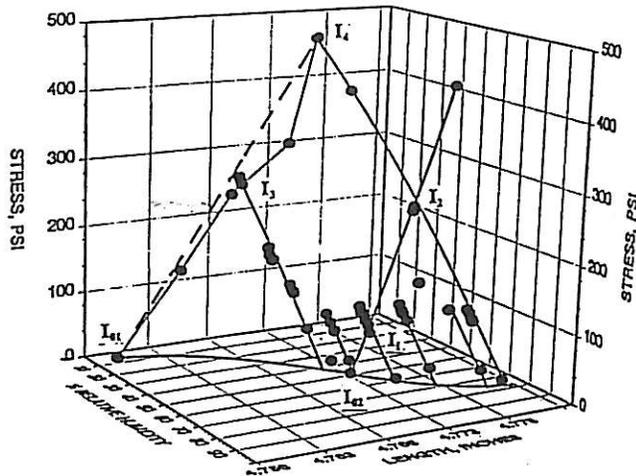


Figure 9. Stress-length-RH plot for epoxy Adhesive II 3H mutual intersection points of stress starting at different points, I_{01} , I_{02} and going to four different stress states I_1 , I_2 , I_3 , and I_4 .

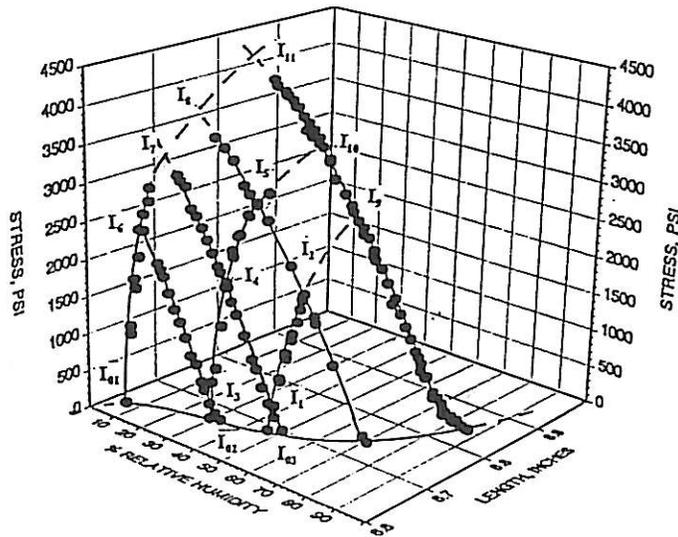


Figure 10. Stress-length-RH plot for rabbit skin glue mutual intersection points of stress starting at different points, I_{01} , I_{02} , and I_{03} and going to five different stress states I_1 , I_2 , I_3 , I_4 , and I_5 . Six additional projected mutual stress points are shown at I_6 , I_7 , I_8 , I_9 , I_{10} , and I_{11} .

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This equation relates the externally applied forces in a material to the environmentally induced forces. In addition, the stiffness, the equilibrium modulus, of a material as measured by externally loaded processes in a constant environment is the same stiffness that determines the forces developed by changes in relative humidity for a restrained material.

Engineering Application of the Case

It would be useful to apply these concepts to the engineering problems that confront the researcher. The immediate question that can be answered is, do environmental fluctuations induce plastic deformations? This can be approached by rewriting equation 5 into engineering terms. This conversion is accomplished by first dividing both sides of the equation by A, the cross-sectional area of the test sample:

$$(\partial F/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} (1/A) = -(\partial F/\partial RH)_{L,T} (1/A) \quad \text{Eq. 11}$$

the equation then becomes:

$$(\partial \sigma/\partial L)_{RH,T} (\partial L/\partial RH)_{F,T} = -(\partial \sigma/\partial RH)_{L,T} \quad \text{Eq. 12}$$

and if L_0 is the initial length of the specimen, and by multiplying the left side of the equation by (L_0/L_0) , the equation becomes:

$$(\partial \sigma/\partial \epsilon)_{RH,T} (\partial \epsilon/\partial RH)_{F,T} = -(\partial \sigma/\partial RH)_{L,T} \quad \text{Eq. 13}$$

For linear elastic behavior of a material the term, $(\partial \sigma/\partial \epsilon)_{RH,T}$, is in fact the modulus of elasticity (E) or Hooke's Law. The term $(\partial \epsilon/\partial RH)_{F,T}$ is γ , the moisture coefficient of expansion when $\sigma=0$ and the term, $-(\partial \sigma/\partial RH)_{L,T}$, is ϕ_{RH} , the change in stress with the change in relative humidity when the length is fixed. This last term describes the restrained specimen stress development. Looking at this specific relationship in symbolic form becomes:

$$(E)_{RH,T} (\gamma)_{\sigma=0,T} = -(\phi_{RH})_{L,T} \quad \text{Eq. 14}$$

This equation was found to be applicable to all classes of materials studied such as, hide glues, photographic gelatin, epoxy adhesives, oil and alkyd paints.

Thermal Analogy

There is a thermal analogy to Equation 14. At the beginning of this paper Equation 4 was derived by dividing both sides of Equation 3 by Δt . The result was

$$\begin{aligned} \Delta \sigma/\Delta T &= -E \cdot \alpha \cdot \Delta T/\Delta T \\ \text{and} \quad \Delta \sigma/\Delta T &= -E \cdot \alpha \end{aligned} \quad \text{Eq. 15}$$

Equation 15 can be rewritten to appear as:

$$E \cdot \alpha = -(\Delta\sigma/\Delta T), \quad \text{Eq. 16}$$

but this is actually:

$$(\partial\sigma/\partial\epsilon)_{T,RH} (\partial\epsilon/\partial T)_{F,RH} = -(\partial\sigma/\partial T)_{L,RH}, \quad \text{Eq. 17}$$

or:

$$(E)_{T,RH} (\alpha)_{\sigma=0,RH} = -(\phi_T)_{L,RH}, \quad \text{Eq. 14}$$

where: E is the slope of the stress-strain curve conducted under both constant temperature and RH,
 α is the thermal coefficient of linear expansion and,
 ϕ_T is the slope of the stress versus temperature results of a restrained and cooled specimen.

Conclusions

A series of experiments were performed on several classes of museum materials and structural epoxy adhesives. These experiments measured the dimensional response with respect to temperature and relative humidity, the stress-strain curve under rapid and equilibrium conditions, and stress development under restrained conditions with variation in temperature or relative humidity. From this data one unifying observation emerged. From the changes in force with respect to length, the changes in length with respect to RH (or temperature), and the changes in force with respect to RH (or temperature), a general equation for the behavior of materials under environmental changes was developed. A similar treatment relating temperature to force, dimensional change and temperature has also been developed.

Under equilibrium conditions it can be shown that the free swelling strains as determined from moisture or thermal swelling tests, can be directly related to strains developed from external loading. The analysis of a structure that responds to moisture can be conducted by determining the degree of moisture diffusion into the hygroscopic material, applying the proper material mechanical properties corresponding to the moisture content and, imposing the swelling response of the material to the moisture changes occurring.

The volume under the surface generated in the RH-L-F (T-L-F) coordinate system can be viewed as a region of plastic deformation of the material. The region above can be viewed as a region of mechanical instability of the materials.

Acknowledgements

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