THE CORRELATION BETWEEN ADHESIVE STRESS-RELAXATION AND JOINT PERFORMANCE

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ABSTRACT

Generally, a cured adhesive will absorb moisture from the ambient environment until it is in equilibrium with the environment at that temperature. When subjected to additional stress, it will absorb further moisture and establish a new equilibrium. Consequently, the long-term durability of any adhesively bonded joint is limited by the response of the adhesive to environmental factors, primarily moisture. Indeed, the combined environmental strains of temperature expansion and moisture swelling can exceed the elastic limit strain of an adhesive with low temperature and moisture resistance. These strains are further compounded by the effect of sustained (creep) loading. Under an Army program, we have evaluated the environmental and mechanical responses of several adhesive specimens concurrently by straining the specimens to failure at predetermined strain increments in an environmentally controlled chamber. The adhesives stress-relax under the quasi-fixed displacements. Correlation is excellent between the equilibrium stress-strain behavior of the adhesives and their strengths and, more important, their joint performance. The mechanism(s) of stress-relaxation are discussed.

INTRODUCTION

The performance and durability of an adhesively bonded structure is frequently measured in terms of the long-term loading capacity of the adhesive or composite material in adverse environments. Other important considerations are the material's resistance to brittle fracture and its ability to withstand high and low temperatures.

Cured adhesives contain little moisture. When subjected to environmental stress, they absorb moisture from the ambient environment until they are in equilibrium with it. Imposition of an additional stress causes further moisture absorption until a new equilibrium is established. Conversely, they lose water when the stress is reduced.

The environmental strains of thermal expansion and moisture swelling on an adhesive specimen are therefore additive with mechanical strains, and both must be considered in determining the strength limits of the adhesive. The environmental strains alone can exceed the elastic limit strain of an adhesive with poor temperature and moisture resistance.

EXPERIMENTAL PROCEDURES

We cast adhesive specimens for the stress-relaxation/tensile measurement by pouring the thoroughly mixed adhesive composition onto an aluminum block 30.5×12.7×2.5 cm^3 (12×5×1 in.) covered with a silicone release sheet, placing another sheet on top, and rolling the adhesive pool with a rolling pin to remove entrapped air. An aluminum block with four 2.5 micrometers (10-mil) shims glued to its corners is then placed on top of the sheet, the entire assembly is clamped, and the adhesive is allowed to cure for 18 h at ambient temperatures and to post-cure at 50°C (122°F) for 2 days.

For testing, a strip of adhesive, 10.2-12.7×0.5×0.025 cm^3 (4-5 in. long, 0.20 in. wide, and 0.010 in. thick), is placed under roughly 10% of its ultimate strain in a self-contained stress jig positioned inside a humidity chamber (1). The relaxation of the stress as the adhesive stretches causes a logarithmic decrease in the stress level until it reaches a new equilibrium after several hours. At that point, another increment of strain is applied. The result is a measure of the sustainable stress as a function of strain for an adhesive in equilibrium with its environment. Three strips of each adhesive are tested.

RESULTS AND DISCUSSION

Stress Relaxation

When a stress is applied to a viscous body, the body undergoes deformation so as to relieve the stress. The resulting decrease in stress with constant deformation is called stress relaxation. The deformation ceases when the stress level reaches a new equilibrium and the molecules or molecular segments return to their state of rest. At any time t, the stress, σ, in the deformed body is given by

$$\sigma=\sigma_0\exp(t/t_{\mathrm{rel}}) \qquad [1]$$

where σ_0 is the initial stress and t_{rel} is the relaxation time, i.e., the time required for the stress to fall to 1/e of the original value.

At high relative humidity (RH), bulk adhesives absorb moisture and stress-relax under quasi-fixed displacements, in addition to the viscoelastic relaxation (1). This effect is important because the long-term stability of any adhesively bonded joint is determined by the response of the adhesive to environmental factors, primarily moisture. The strength of an adhesive joint rapidly deteriorates when it is exposed to the high end of temperatures and relative humidities within the usual service environment of the structure; furthermore, the rate of such environmental attack is accelerated under sustained (creep) loading. This lack of durability in adverse environments has limited adhesives' use in primary load-bearing structures.

In our initial tests, using tensile strips of adhesives that had been equilibrated in a 90% RH, 49 °C (120 °F) environment, we rarely found significant changes in ultimate tensile strengths and elongations; in other words, moisture alone did not drastically affect the properties of most of the adhesives (2). Rather, it is the combination of stress and moisture that actually causes joint failure. Therefore, we now evaluate our formulations by the stress-relaxation test, which measures the strain sustained by adhesives exposed to a moist, warm environment while under stress.

The equilibrium stress-strain curves for our test adhesives 100 and 96 are shown in Fig. 1; Table I shows the results of relaxation testing on several of our adhesives. As described above, the strain was incremented in predetermined steps to failure in an environmentally controlled chamber, and stress relaxation was measured at each increment. The locus of the lowest points of all stress-relaxation segments represents the equilibrium tensile stress-strain curve, i.e., where the moisture content in the adhesive is in equilibrium with the RH of the environment. We have observed that the size of the strain increment has no effect on the equilibrium stress-strain curve in the linear elastic region.

Table I and Fig. 1 indicate that adhesives differ dramatically in their response to moisture. Some lose all load-carrying capacity as a result of moisture ingression, while

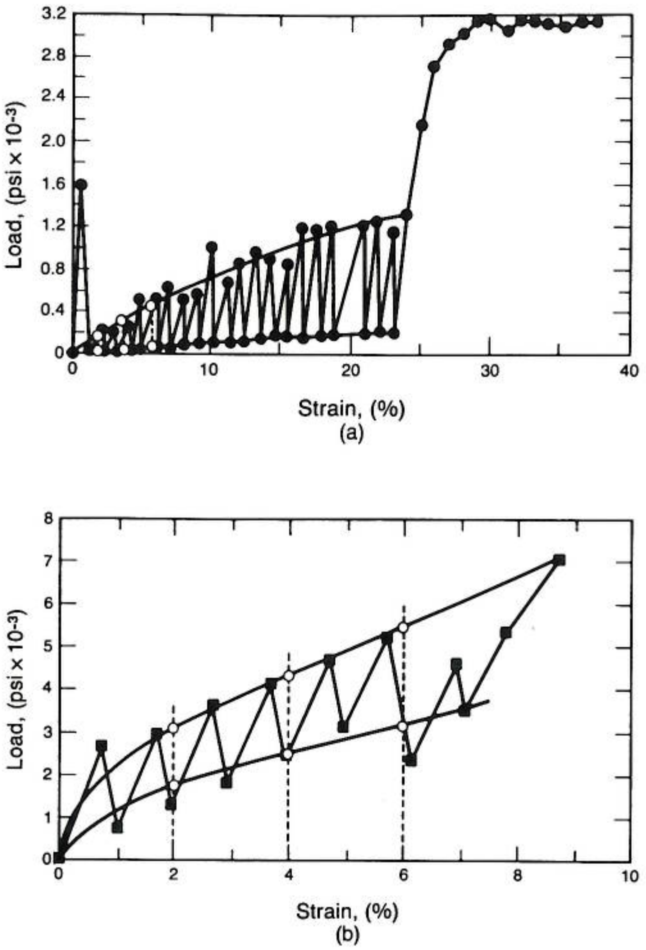

Figure 1. Stress-relaxation records of adhesives, (a) 100 and (b) 96. To convert psi to KPa multiply by 6.9.

Table I.
Stress-Relaxation Data.

Sample	2% Strain	4% Strain	6% Strain	UTS (psi)*
	Equalibrium Stress/Initial Stress (psi)*			
1	500/2500	1600/2900	2300/3800	3600
12	100/1200	200/1400	300/1500	2800
13	700/2200	1200/3000	–	2500
14	900/2500	1700/3300	2000/3700	4800
15	700/2500	1600/3700	2200/4100	10,000
17	600/2500	1400/3200	1700/3900	6200
29	800/2900	1500/3700	–	3700
30	100/1500	300/1900	800/2400	5000
55	1800/3700	2800/5000	3500/5500	6100
75	500/1300	1000/2000	1500/2600	2700
85	200/1200	500/1800	700/2100	1900
91	1600/3400	2300/4700	2700/5300	5000
96	1300/3000	2600/4200	3500/5500	7100
100	20/200	40/200	60/500	3200

*To convert psi to KPa multiply by 6.9.

others are able to sustain some load over a considerable length of time, even though their ultimate load-bearing capacity is reduced. Thus, some adhesives subjected to severe environments may still retain a potentially useful load-carrying capacity.

Relaxation Mechanisms

Three mechanisms appear to cause the bulk adhesive specimen to stress-relax above and beyond normal viscoelastic relaxation (1). The first is water absorption from the surrounding environment. A state of strain changes the volume of a unit cubic element by

$$\delta V=(1+\epsilon_x)(1+\epsilon_y)(1+\epsilon_z)-1, \qquad [2]$$

or, for small deformations

$$\delta V=\epsilon_x+\epsilon_y+\epsilon_z. \qquad [3]$$

A longitudinal strain increment $\Delta\epsilon_x$ produces lateral contractions, $\Delta\epsilon_y=\Delta\epsilon_z-\nu\Delta\epsilon_x$. Substituting these values and $\Delta\epsilon_x=\Delta\sigma_x/E$ into Eq. [3] gives

$$\delta V=\Delta\delta_x(1-2\nu)/E, \qquad [4]$$

where δV is unit change in volume or volumetric strain, $\Delta\sigma_x$ is the stress increment, E is the rapid-loading modulus, and ν is Poisson's ratio.

The increase in adhesive volume described by Eq. [4] also increases its water capacity, so that it absorbs additional water from the environment until it is again in equilibrium with the RH of the environment. As the additional moisture swells the adhesive, the stress relaxes under fixed displacement.

The second mechanism of stress relaxation is the reorganization of water molecules lodged between the polymer chains. The pressure exerted by lateral adhesive contraction, induced by Poisson's effect, could force the water molecules to rotate and displace into positions that would allow additional lateral contraction and, hence, stress relaxation under fixed displacement.

The third mechanism involves the breakage of physical crosslinks, which allows the polymer chains to slide past each other until new links form. The dominant mechanisms in the linear elastic region of the stress-strain diagram appear to be water absorption and internal reorganization. Breakage of crosslinks becomes pronounced as the "yield" point of the adhesives is approached.

The first two mechanisms are reversible while the third is not. Currently, there is no method of separating the contributions of each mechanism to the total stress relaxation.

CONCLUSIONS

Stress-relaxation measurements on thin strips of neat adhesive specimens can be used to predict the long-term load-bearing capacity of bonded joints subjected to adverse environments. The locus of the lowest points of all stress-relaxation segments represents the equilibrium tensile stress-strain curve, i.e., the strain at which the moisture content in the adhesive is in equilibrium with the RH of the environment.

Most adhesives lose all load-carrying capacity as a result of moisture ingression; a very few can sustain some load over a considerable length of time, even though their ultimate load-bearing capacity is reduced. This result suggests that there is a reduced (but potentially useful) upper bound of load-carrying capacity for some adhesives subjected to severe environments. This upper bound of load, i.e., the highest load a structure can sustain indefinitely, then, may provide the long-term design criterion for adhesives to be used in adverse environments. If that same adhesive also demonstrates sufficient toughness or fracture resistance, it might be suitable for the construction of a (correctly designed) severe weather structure.

Adhesives stress-relax under fixed displacement mostly due to swelling/water reorganization mechanisms during moisture absorption. A third mechanism involving the breakage of physical crosslinks becomes pronounced as the "yield" point of the adhesive is approached. Most of the adhesives tested lost a significant fraction (more than 90%) of their dry strength after loading in the 49 °C (120 °F) and 90% RH environment. In view of the nature of the test and the susceptibility of epoxy adhesives to moisture-induced degradation, adhesives retaining more than 30% of their dry strength under these conditions are considered satisfactory.

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Chike Arah is a scientist at Martin Marietta Laboratories and received his Ph.D. in Chemistry from the University of Tennessee. His interests lie in the areas of adhesion, polymeric coatings, and composite materials.

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THE COVER

The CFD Code developed for the NASP shows a simulation of airflow around the vehicle, highlighting flow uniformity and high drag areas. See Material News.

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