THE ROLE OF WATER ON THE STRENGTH OF POLYMERS AND ADHESIVES

by

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ABSTRACT

Title of Dissertation: The Role of Water on the Strength of Polymers and Adhesives

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This study presents methods and equipment developed which allow rapid determination of the suitability of structural adhesives for adverse environments. Previous test methods have provided test results which seriously overestimate performance capabilities or require multi-year test programs. Information provided in the study illustrates the severe effects of moisture penetration on adhesives as well as the effects of temperature. Such information is determined within a period of three weeks using described test procedures.

Further, the study reevaluates existing thermodynamics relationships of elasticity and proposes alternative interpretations of mechanisms which appear to govern mechanical properties of polymers.

CHAPTER I

INTRODUCTION

In the past ten years, several research projects investigated the feasibility and developed the technology of using adhesives to replace welding, bolting and riveting in metal-to-metal connections. (2 through 9)* The parameters that were examined included type of adherend, adhesive, surface preparation, loading and environment. The adherends consisted mainly of aluminum, and to a lesser degree steel and titanium. The most common adhesives were of the epoxy type. Statically loaded specimens were usually pulled apart at moderate to rapid rates or placed in test frames under fixed load until they failed. Cyclically loaded specimens were fatigued at rates faster than those encountered in service. The effect of the environment on the mechanical properties of bulk (neat) specimens and bonded specimens was determined mainly in terms of changes in temperature. Although the detrimental effect of water on the strength of adhesives was generally recognized, few studies attempted to quantify its effect and no study allowed the water content in the adhesive to equilibrate with the relative humidity (RH) of the ambient environment.

The projects usually lasted two to three years. As a consequence, the creep tests that were performed were necessarily of short length, with few exceptions. (26)

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*Numbers in parentheses refer to publications listed in the referenced bibliography.

The most encouraging aspect of bonded joints is their fatigue performance. Under cyclic loading they greatly outlast the equivalent welded, bolted or riveted joints. Yet all investigators reported low creep strength under long-term static loading, particularly in severe environments, such as high temperature and RH. (4 through 6) Despite the many studies performed to date, the long-term durability of bonded joints in adverse environments remains a problem that must be resolved before adhesives can be applied safely to primary structures. Although the detrimental effects of temperature and RH under sustained loading have been widely observed, there is no satisfactory explanation of the fundamental mechanism that governs these behaviors.

A second troubling observation is the lack of correlation between the properties of an adhesive tested as a bulk (neat) specimen and in a bonded joint. In fact, in the opinion of one researcher, "no correlation has been found with either neat adhesive coupon data or with quality-control tests like the single-lap or wedge crack tests." (3)

The lack of correlation in the properties of an adhesive in bulk and bonded specimens is attributed to the following widely different causes: (1) uniaxial stress state in bulk specimens versus triaxial stress state in bonded specimens; (2) initial curing stresses in bonded specimens; and (3) differences in the chemistry of the adhesive in bulk and bonded specimens. However, no conclusive data were presented in support of the aforementioned explanations.

It is likely that the reported lack of correlation in the long-term properties of bulk and bonded specimens comes, to a large degree, from having allowed insufficient time for the moisture content and the temperature of the adhesive to equilibrate with the RH and temperature of the environment surrounding the specimen. The effects of the RH and temperature on what will here be called the equilibrium stress-strain curve is presented in Chapter 2 of this study. Experience from the test program described herein showed that a 0.010 in (0.25 mm) thick bulk specimen equilibrates in about four to eight days, depending on material and environment. Others reported that the rate of moisture diffusion through the edges of a thin bond line is so slow that it takes a 1 in. (25 mm) wide bonded specimen one year to equilibrate. (2) Yet, with few exceptions, the data reported in the literature were obtained with bonded specimens that were exposed to the environment for at most two months prior to testing.

Current Approaches to Durability

The current approaches to solving the problems of long-term durability of bonded joints involve: creep testing, viscoelasticity and creep compliance. The durability can be determined experimentally by long-term creep testing of bonded specimens in various indoor and outdoor environments, and at various magnitudes of load. This technique is reliable if the investigator is willing to wait out the results of the test. The 3M Company, for example, reported data from 8-year creep tests. (26)

The concept of viscoelasticity implies a continuing breakdown of cross-linked entangled chains under stress and the formation of new chains in unstressed situations. (25) It presumes a gradual but relentless deterioration, even at low load levels, until the adhesive eventually fails. The advent of failure is believed to be only a matter of time. The literature contains data on the effect of temperature on creep strength, but the author has found only one reliable source of data on the effect of RH. (26) Furthermore, there will never be enough long-term data to fully characterize the viscoelastic creep behavior of the important adhesives in the environments of interest. Current extrapolations of results from creep tests typically lasting a few days to prediction of durability after decades of service are risky and inadmissible for primary structures. By the time reliable long-term data are obtained, a new generation of adhesives will make the data obsolete.

The creep compliance method is basically a modified version of the viscoelastic viewpoint, with the intent of including the effects of adverse environments and observing the changes in specimen deformation under loading. (9) As in viscoelasticity, the short-term observations of creep compliance are extrapolated to project long-term durability.

Another Viewpoint

The previously mentioned approaches to solving the problem of adhesive durability are costly and time-consuming, and the conclusions are based largely on somewhat inconsistent observations. In addition, these methods provide little insight into the fundamental mechanisms that govern the mechanical behavior of polymers in general and adhesively bonded joints in particular.

A review of the published data suggests that the specimens tested by previous investigators were routinely overloaded. The applied stresses were lower than the rapid-loading ultimate stress, but higher than the equilibrium ultimate stress. Under these conditions, atypical of those found in bonded structures in service designed with high safety factors, the high stresses damage the molecules and induce creep failure. As will be shown in Chapter 3, polymers creep to equilibrium, and not to failure, at sustained stresses lower than the ultimate equilibrium stress for a given environment. These observations suggest that additional mechanisms other than damage to molecules govern the equilibrium behavior and long-term durability.

To safely adhesive bond primary structures, the following design criteria must hold:

1. For a worst-case environment, an equilibrium ultimate stress exists below which the adhesive equilibrates without further creep, under fixed stress, or without further stress relaxation, under fixed strain. Hence, the adhesive does not fail at such loads.
2. Stresses and strains are recoverable. If they were not recoverable, the adhesive could not sustain impact loads without "ratcheting" to failure.
3. Occasional excursions above the equilibrium ultimate stress are admissible, provided that the loading rate is rapid and the maximum load not so high that the molecules are damaged.

Equilibrium stress-strain curves and the regions of recoverable stress or strain can be determined experimentally. With this information, reliable quantitative design criteria for primary structures can be formulated. The equilibrium strength of an adhesive in an adverse environment is, in part, a function of its resistance to heat and water vapor under applied stress. The difference between the rapid loading (nonequilibrium) stress-strain curve and the equilibrium stress-strain curve suggests a change in free energy that might be analyzed with concepts of thermodynamics. While a full analysis of this is beyond the scope of this paper, some basic observations are made.

Bond failure in an adhesively bonded joint generally occurs at the adhesive-adherend interface (adhesive failure) or within the adhesive layer itself (cohesive failure). Previous investigators generally desired that failure be cohesive, since it tends to be a more stable or ductile type of failure. In most cases, investigators attempted to test both adhesion and cohesion simultaneously. In testing bonded joints, they usually try to estimate the kind of failure that occurs by examining the failed specimen and observing the amount of bare metal exposed on the adherend. Manufacturers seldom give the form of failure when presenting their performance specifications.

In any event, if moisture and temperature adversely affect an adhesive, there is little doubt that both cohesion and adhesion will be affected. The difficulty is that information supplied by the manufacturers with certain adhesives suggests that outdoor environments should not present a problem. Nevertheless, some evidence from multi-year creep tests in outdoor or adverse environments indicates that caution should be exercised in using adhesives exposed to such environments. There is no clear evidence that some adhesives can be used safely for some adverse environments.

The range of environments, that is, combinations of temperature and RH, considered in this study corresponds to the outdoor climate of the continental United States. Meteorological data supplied by the National Oceanic and Atmospheric Administration (31) are graphically presented in figure 1, a plot of mean annual RH versus high and low temperatures on record. The mean annual RH was used because vapor penetration into a glue bond line is so slow that daily or monthly variations in RH have no significant effect on the moisture content of the adhesive. The moisture content in the adhesive eventually equilibrates with the annual mean RH after several years of exposure. The mean RH ranges from about 30% to 90%. On the other hand, materials respond rapidly to temperature, so that hourly changes are significant. The temperatures range from -70°F to 120°F. It should be noted that these air temperatures were measured in the shade. The temperature of a steel member boldly exposed to sunshine can reach 140°F. Based on the data shown in figure 1, it was decided to screen the adhesives at a combination of high temperature and high RH, in this case 120°F and 90% RH. This screening test became a first step in evaluation of adhesives. Additional environments were used in the pilot tests to explore the general behavior of adhesives.

To evaluate a wide spectrum of commercially available adhesives over a short period of time, current procedures of testing bonded specimens or relatively thick bulk specimens are inadequate, for they simply take too long. Moisture diffuses very slowly into a bonded specimen through the thin line of exposed adhesive between the metal adherends. Equilibrium times increase with the thickness of bulk specimens. The best way to shorten equilibrium times is to test thin bulk specimens.

While it is important to evaluate an adhesive's ability to bond to a metal adherend, the bond can be only as good as the cohesive properties of the adhesive. It therefore becomes reasonable to test the cohesive properties of the material in adverse environments. So-called "bulk" or "neat" specimen testing has the advantage of exposing all surfaces of the specimen to the environment and rapidly decreasing equilibrium time. If the specimen is small, moisture diffusion to equilibrium will be fairly rapid. Furthermore, in a complete testing program, any bulk specimen of adhesive that loses all mechanical capacity for a given environment within the range being studied can be eliminated from further consideration. On the other hand, if an adhesive demonstrates a significant capacity to develop strength in adverse conditions, then it becomes a candidate for further testing, specifically in cold, dessicated environments and subsequently for adhesive testing. This testing procedure, though seemingly more complex than the traditional creep testing of bonded specimens, is in fact quite straightforward and provides reliable, consistent results in known, specified environments in remarkably short periods of time.

CHAPTER II

TEST METHODS AND PROCEDURES

Equipment

The fundamental purpose of the experimental procedure was to determine the effect of a variety of controlled environmental conditions on an applied tensile force or displacement on a specimen of polymeric material. Any number of devices can be used to perform such tests on a wide range of materials. However, the unique requirement for this specific testing program is that the equipment must be dedicated to a single specimen for several weeks, since specimens must equilibrate to the specified environment prior to loading and then reequilibrate to the same environment after each load increment. Each equilibration requires between 4 and 8 days, and several tests are needed to obtain reliable information. This, then, demands a large number of testing devices if the program is to be conducted in a reasonable length of time. Additionally, since the diffusion of moisture into a polymer is a relatively slow process, the specimen should be as small as possible to hasten equilibrium time, and yet large enough to give reliable results. Consequently, the testing equipment must accomodate fairly small samples. Because the cost of purchasing such equipment is prohibitive, it was designed and fabricated by the investigator.

The following minimum equipment performance requirements were established. First, the equipment must measure accurately very small loads and displacements applied to a specimen. Second, the equipment must be relatively inert to variations in temperature and RH. Finally, the output signal from the devices must be compatible with standard reliable bridge circuits. At the same time, some compromises were made. Displacements of materials subjected to tensile tests are normally measured with some type of extensometer. Since the specimens used are small, this is impractical. Instead, deformation is measured over the full length of the specimen up to the clamping jaws. This initially presented a concern of premature failure at the jaws; however, only about one in three hundred specimens actually failed at the jaws over the wide range of materials tested.

The tensile testing device is illustrated in figure 2. The specimen is elongated by rotating a dial on a calibrated stainless steel threaded rod with 20 threads to the inch. This rotation produces a "near end" displacement of δ_1 and a "far end" displacement of δ_2. Since the specimen is stretched during the elongation process, δ_1 is always larger than δ_2. The value of δ_2 is, in effect, a result of the "load cell" deflection. This load cell consists of a cantilevered bar fitted with a full bridge resistance circuit and linked to the far end clamp jaws. Clearly the deflection of δ_2 will represent a force applied to the specimen and is calibrated to do so. It is equally clear that even though δ_2 is small in comparison to δ_1, it must be included in the strain calculations. The maximum value of δ_2 under normal operations is about 0.0110, whereas δ_1 can be as much as 0.510, depending on the length and stiffness of the specimen measured. Output from the bridge circuit is calibrated to give δ_2 and P, the force required to deflect the bar. This is also the force applied to the specimen. From the output data, it is then possible to compute the stress σ

$$\sigma = \frac{P}{A}$$

where A is the specimen's cross-sectional area, and the strain ε

$$\varepsilon = \frac{\delta_1 - \delta_2}{L_o}$$

where L_o is the gage length of the specimen.

The measured strains of polymers are usually large in comparison with those of metals, and the specimen gage lengths are anywhere from 4.5 in. to 7.0 in. This usually produces a displacement for δ_1 that is considerably greater than that for δ_2 during an increment of loading. True measurements of "stress relaxation" require a specimen to be of fixed length, so that stress reduction can be measured under these conditions. Since the load on the specimen is a function of δ_2, stress relaxation is a result of some elongation of the specimen, thereby reducing δ_2 and the load P. Since δ_2 is very small, but included in all calculations, the plots of stress relaxation reflect the increase in strain during stress relaxation and consequently do not plot vertically, but rather sloping down and to the right. For relatively stiff materials such as copper wire or a thick specimen of adhesive, δ_1 is not so large relative to δ_2, and even small changes in δ_2 during stress relaxation reflect a greater strain in the specimen during the relaxation process. Consequently, the plots of the stress decreases become even less vertical.

The displacement calibration of the cantilevered bar is performed by mounting a rigid steel specimen, turning the dial and measuring the displacement of the bar. Since the relative stiffness, a function of both specimen cross-sectional area and modulus of the steel bar, is 3 x E, or about 90×10^6 psi, it is about 3.6×10^3 stiffer than the average polymer specimen measured. In the results reported here, any error in measuring the bar deflection was small and had a negligible effect on the elongation of the specimen.

The load calibration is performed using a spring with a carefully measured spring constant. The equipment was found to respond linearly over a range of loading, temperature and RH that exceeded values used in the experimental program. Finally, the equipment was checked for stability against creep and drift by mounting a large steel specimen and loading it for the period of time expected with the longest tests. It was found that the test equipment drifted less than 0.5% of the stress relaxation found in the polymers.

Environmental Control

Controlling the environment was accomplished by enclosing groups of three tensile gages in closed chambers (fig. 3). These chambers were constructed so that the environments of the specimens could be controlled over long periods of time. The temperature was controlled in a simple manner by using 150-watt light bulbs as heaters and a thermocouple set point device. This way temperatures of 120°F ± 1°F could be easily reached. Cooling the chambers was most effectively accomplished by cooling the space occupied by the chambers. However, very cold temperatures can be obtained by refrigerant expansion in cooling coils within the chambers. This is done either by mechanical (compressor) devices or by bottled gas. Controlling the RH is somewhat more complex. Various methods can be used, such as dilute acid solutions, saturated salt solutions, buffered (conditioned) silica gel, or water evaporation. For high RH, pans of water with specific surface areas were used. For all other values of RH, silica gel was conditioned to the desired RH and spread over pans in the chambers. Circulating fans were running continuously within the chambers, agitating and mixing the air to provide an even environment. The fans also accelerated equilibrium times by scrubbing the surfaces of the specimen with a gentle flow of air. The RH could be maintained quite evenly over periods of several weeks using these methods.

Specimens

Fabrication of test specimens was accomplished by various methods depending on the type of polymer involved. Collagen specimens were cast on a sheet of carefully leveled plexiglass by pouring the warm gel solution onto the plexiglass and allowing it to dry. Films of 0.002 to 0.003 in. thick could be cast using this method. More viscous materials such as adhesives were cast between 1 in. thick polished aluminum blocks. The thickness of the specimens was controlled by using pieces of stainless steel foil as shims, and mylar release sheets were used to prevent the adhesive from adhering to the aluminum. The entire assembly of aluminum, mylar and adhesives was firmly clamped and cured either at room temperature (80°F) for 4 to 5 days or at elevated temperatures in ovens, as directed by manufacturers specifications. The thickness of the adhesive specimens was from 0.009 in. to 0.011 in. Cutting the 0.2 in. wide specimens from the castings was done by carefully milling the adhesive with a heated knife. Since the large castings could provide a considerable number of specimens, it was possible to select only the most uniform specimens for cutting. Even so, on one or two occasions, it was difficult to obtain near perfect specimens since the most brittle adhesives tended to have extremely small fractures at the edges due to milling. It was felt that this was the single most important source of early failure in those brittle specimens, and consequently replicate tests were performed on these specimens until some confidence of strength values was achieved. Replication of results was remarkable in that the slopes of the stress-strain plots were nearly identical; the variation was the breaking strength. In the rapid loading tests, the strengths of the adhesives compared favorably with those reported by the adhesive manufacturers.

CHAPTER III

PILOT STUDIES

During the final phase of equipment fabrication it became necessary to run pilot tests to determine the effect of moisture on the mechanical properties of polymers. Initially collagen was chosen as a test material. Collagen is a protein structure consisting of long-chained, water-bridged molecules which serves as the chief tensile stress-bearing material for all mammals and fishes. (21) When refined to gelatin it has significant commercial value, for it is found in photographic emulsions, medicine capsules and many foodstuffs. Since it is known to react to water, is very easily cast into thin film and there is extensive literature on the material, it became an obvious candidate for a pilot study. Additionally, adhesives recommended by manufacturers for structural applications in adverse environments were also tested.

Equilibrium Stress-Strain Curves

The various polymers were pilot tested in carefully controlled environments. In these tests, bulk specimens of collagen, epoxy adhesives and acrylic adhesives were rapidly loaded in tension and allowed to stress relax to equilibrium at a fixed strain. This cycle of incremental loading and stress relaxation was repeated until the specimen's strain reached about 1%. The loading time was about 1 second and the relaxation time varied from 24 to 96 hours, depending on specimen thickness and type of polymer. It took 2 to 3 weeks to measure each curve.

Figure 4 shows the stress-strain curves for collagen measured at 82°F and 5%, 30%, and 50% RH. All rapid loading paths were found to be nearly parallel and always slightly steeper than the initial slope, irrespective of the ambient RH and where on the curves the loading was incremented. The relaxation points for a given RH fell on a well-defined curve. This strongly suggests that such curves represent "equilibrium stress-strain curves" in tension at extremely slow strain rates. The curves level off at what appears to be an ultimate stress under sustained loading at a particular RH. The rapid loading paths are characteristic of behavior under cyclic loading.

The equilibrium stress-strain curves of the following three specimens of bulk adhesive were measured with the same test procedure: (1) a two-part epoxy adhesive (No. 1) cured at 160°F for two hours, although the manufacturer had stated that the adhesive would alternately cure at room temperature in 24 hours; (2) a two-part acrylic adhesive (No. 61) cured at room temperature; and (3) a one-part film epoxy (No. 11) cured at 246°F for 65 minutes. The time to equilibrium after each increment of loading was 96 hours for specimens 0.008 to 0.011 in. (0.020 to 0.27 mm) thick and 0.2 in. (5 mm) wide. The equilibrium stress-strain curves for the three adhesives are plotted in figs. 5 through 7. Clearly, increasing the RH had an adverse effect on the strength of all three adhesives. This was particularly evident for 91% RH, at which the two-part epoxy lost all strength and the two-part acrylic nearly all strength. There was some concern that the supporting scrim in the one-part film epoxy was contributing to its higher performance. However, subsequent tests of this epoxy, both with and without the scrim, indicated that the scrim only slightly increased the strength.

Rapid Loading Stress-Strain Curves

The three previously mentioned adhesives were also tested at relatively rapid strain rates of 1.2% to 1.5% per minute. These rates were comparable to those used by adhesive manufacturers and in most tests reported in the literature. For example, the highest strain rate in a General Dynamics study was 1.25% per minute. (9) The bulk specimens were made from the same castings as the specimens tested under equilibrium. They were equilibrated at 72°F and 46% RH prior to testing. The rapid loading stress-strain curves for these adhesives are plotted in figs. 8 through 10. The rapid loading ultimate strengths, ranging from 3,000 to 5,000 psi (21-35 MPa), were significantly higher than the equilibrium ultimate strengths in the comparable environment of 72°F and 50-51% RH, shown in figs. 5 through 7. Clearly, testing procedures used in previous studies overestimated the bulk adhesive strength. In light of this observation it is not surprising that previous investigators reported creep failures of bonded specimens subjected to sustained loads higher than the equilibrium ultimate strength.

The collagen specimens, tested at a strain rate of 0.1% per minute, also exhibited greater strength under rapid loading (fig. 11) than under equilibrium loading (fig. 4). Though not shown in fig. 11, collagen ultimate strengths routinely attained about 9,000 psi.

Effect of Strain Rate on Strength

Polymers seem to lose strength at extremely slow strain rates for the following reasons. First, the capacity of adhesives to absorb water increases with stress. Secondly, water molecules located between side chains move into the free volume when the specimen is stressed. Both phenomena take time and become, therefore, only evident in tests done at extremely slow strain rates. These conclusions were reached based on measurements of weight of water uptake versus RH, hereafter termed equilibrium moisture isotherm (EMI), and change in length versus RH, termed equilibrium swelling isotherm (ESI).

The measured EMI and ESI for collagen are shown in figs. 12 and 13, respectively. Both curves have similar shapes. In fact, the plot of water uptake versus swelling is approximately linear. The measured EMI for collagen is similar to that reported by Bull for the same material. (13)

Approximate ESIs for the three previously described adhesives were constructed from the measured length changes at 10%, 50% and 90% RH. The curves are plotted in fig. 14. The slopes of the curves represent the swelling rates. Matching the swelling rates for each adhesive and RH with the corresponding stress-strain curves plotted in figs. 5 through 7 indicates a correlation between the swelling rate and the loss in strength with increasing RH. For example, the two-part epoxy has the highest swelling rate at 90% RH. It also lost all strength. The one-part film epoxy had the lowest swelling rate and, accordingly, the smallest loss in strength at all three values of RH. Evidently, the more an adhesive absorbs water, the more strength it loses. The change in the EMI between an unstressed and a stressed specimen provides additional insight into the reasons for the strain rate effect. The upper curve in fig. 12 represents the EMI for a collagen specimen, whose length was fixed at 84% RH, and the environment dessicated slowly over a period of three weeks. At all values of RH below 84%, the restrained (stressed) specimen retained more water than did the unrestrained (unstressed) specimen, meaning that straining increased the free volume, and hence, the moisture absorption capacity.

Bull has reported a similar test with nylon in which he stretched a dessicated specimen and increased the RH. (13) It appears that the length was fixed in that test. The EMI for the stretched nylon specimen is plotted as a dashed curve in fig. 15. As was observed with the collagen, the EMI for stretched nylon had a smaller slope than the EMI for unstretched nylon, suggesting that water sites are altered.

The effect of straining on water content was also observed by Treloar. (19, 20) He reported that both a protein (hair) and cellulose gained weight with tensile elongation. In other words,

> . . . in contrast to sorption of simple gasses in glassy polymers, sorption of water is often accompanied by significant swelling of the polymer network. Therefore, the concentration of the available sites is not fixed, but changes with the degree of sorption. (27)

and in this case straining.

Clearly, the data for collagen, nylon, hair and cellulose show that both absorption and straining alter the number and location of water vapor sites. Since water diffuses very slowly during changes in RH and stress, the strain rate has a much greater effect on the strength of polymers than has previously been recognized.

Effect of RH on Strength

The observed swelling of polymers with water uptake and, conversely, shrinkage with water loss suggest that changes in RH cause changes in stress at fixed length and constant temperature. This was verified by restraining the specimens at different initial RHs (and therefore different lengths) and then dessicating them. The results are plotted in terms of stress increase versus RH at equilibrium.

Fig. 16 shows the results for collagen. The stress increased substantially with dessication to values comparable to those measured in tensile tests at equilibrium (fig. 4). All curves have similar slopes over the intermediate range. The response of nylon to dessication, shown in fig. 17, was similar to that of collagen. However, the stresses increased less with dessication because, for equal RH, nylon (fig. 15) holds less water than collagen (fig. 12).

Finally, the same test was performed on three adhesives: two-part acrylic (No. 61), film epoxy (No. 11) and two-part epoxy (No. 31). The first two are the same as those shown in figs 6 and 9 and 7 and 10 respectively. The third, not previously mentioned, was cured for 4 days at room temperature. The tests were conducted at 72-73°F. The specimens were equilibrated at 90% RH, and a low stress was applied to ensure initial restraint. The results are plotted in fig. 18. For the two-part acrylic and the film epoxy, the increases in stress with decreasing RH were the same as those observed in the equilibrium stress-strain curves (figs. 6 and 7). This is one more way of showing that the changes in the equilibrium stress-strain curves are directly related to the water content of the adhesive.

Apparent Path Independence

The recent work has related the following quantities, all measured at equilibrium: (1) stress versus strain, at constant RH; (2) water uptake versus RH, for unrestrained and restrained specimens; (3) length and volume change versus RH; and (4) stress versus RH, for restrained specimens. Since each pair of parameters is related to all others it would seem that tensile stressing and environmental stressing of polymers in equilibrium should also be equivalent. To show this the stress must be plotted versus the elongation, not the strain, as is commonly done when the conditions of comparability of displacements are written in problems of stress analysis.

Such a comparison was made for collagen tested in equilibrium at 82°F. The stress-elongation plots, figs. 19 through 21, are constructed from the equilibrium stress-strain curves (fig. 4), equilibrium moisture isotherm (fig. 12), equilibrium swelling isotherm (fig. 13) and RH versus stress curves at fixed length (fig. 16). All elongations, ΔL, due to tensile loading or changes in RH, are referenced to the length of the unrestrained specimen at 5% RH. An additional abscissa is plotted in terms of RH to identify, for convenience, the elongations (swelling) corresponding to increases in RH above 5%.

Fig. 19 shows the equilibrium stress-elongation curves for three collagen specimens subjected to tensile loading. The various curves begin at elongations corresponding to the free swelling of unrestrained collagen specimens of the same length due to increases in RH from 5% to 30% and 50%.

Fig. 20 shows the equilibrium stress-elongation curves for two collagen specimens subjected to environmental loading. Both were dessicated initially to 5% RH. Thereafter one specimen was swelled to 50% RH, restrained and dessicated first to 30% and then to 5% RH. The other was swelled to 70% RH, restrained and dessicated to 50%, 30% and 5% RH. The horizontal free swelling and vertical restrained dessication paths are labeled in fig. 20. The dashed vertical segments represent short extrapolations of the fig. 16 curves to 5% RH.

Fig. 21 shows the superposition of the equilibrium stress-elongation curves for the tensile loaded (fig. 19) and environmentally loaded (fig. 20) collagen specimens. The solid circles for specimens swelled and then dessicated at fixed length fall near the curves for specimens tensile loaded at the same RHs. The agreement is remarkable considering that the data were obtained with different specimens and types of tests. The apparent path independence strongly suggests that state functions govern the observed behavior of collagen and, quite likely, polymers in general. Furthermore, it reinforces the belief that equilibrium is reached, and cross-linked systems do not creep indefinitely if stressed below the equilibrium strength.

Other incidental evidence of equilibrium and path independence were observed. For example, referring to fig. 4, rapid loading followed by stress relaxation at fixed length (due to increased moisture capacity) leads back to the equilibrium curve regardless of both the point at which the load is increased and the size of the increment.

Application to Design

The following examples illustrate how the equilibrium stress-elongation curves and the path independence can help in understanding and determining the long-term performance of polymers in adverse environments. The equilibrium stress-elongation curves of fig. 19 are replotted in fig. 22. The specimen was initially equilibrated at 30% RH and rapidly loaded to σ_A = 1,500 psi (10 MPa). If the length is then fixed, the stress σ_A either relaxes to points 1 and 2, or it increases to point 3 on the equilibrium curves, respectively, depending on whether the RH remains unchanged, increases to 50% or decreases to 5%. On the path to point 2, swelling fully stress relieves the specimen. If instead the stress is held constant at σ_A = 1,500 psi (10 MPa), the specimen creeps to equilibrium at points 4 and 5 or shortens to point 6. However, if the stress is held constant at σ_B = 2,000 psi (13.8 MPa), the specimen creeps to equilibrium at point 7, but it creeps to failure at 50% RH because σ_B exceeds the ultimate strength at 50% RH.

Dynamically loaded bonded structures can sustain brief load excursions above the equilibrium ultimate stress. This is evident from fig. 4, for example, by noting the last rapid loading increment at 30% RH.

Referring again to fig. 22, one can speculate on how an adhesive would behave under cyclic loading. At σ_B mean stress and 30% RH, a specimen would creep to equilibrium at point 7 and eventually fail in fatigue. Displacements are known to drift in fatigue tests. On the other hand, at σ_B mean stress and 50% RH, the specimen would fail in creep. Load cycling would shorten this time, depending on the stress range. In both cases, the stresses would cycle about the mean stress, σ_B = constant, at the slope (modulus of elasticity) for rapid loading.

The equilibrium behavior, reported herein for bulk adhesive specimens, also applies to bonded joints. This was confirmed by 81 creep tests performed previously. (5) The double-strap A588 HSLA steel specimens had 1 x 1 in. (25 x 25 mm) or 1 x 1/2 in (25 x 12 mm) contact surfaces that were bonded with the two-part acrylic adhesive No. 61 (figs. 6 and 9). The ultimate shear stress at rapid loading was 3,970 psi (27.3 MPa). The creep tests were performed at various shear stress levels. All but two specimens failed within one year. The two specimens that failed after two years of outdoor exposure were stressed to 860 psi (5.9 MPa). The moisture in the adhesive bond equilibrated during the first year with the average annual RH of about 60% in College Park, Maryland. In the second year, the specimens recovered some creep displacements during the cold winter months and creeped again during the hot summer months. This behavior is similar to that shown in fig. 22, with temperature replacing RH as the driving mechanism, and the elongation going from point 4 to 6 and back towards 4. The equilibrium bulk tensile strength of this acrylic adhesive, No. 61,

$\sigma_u = 650$ psi (4.5 MPa) at 50% RH and 70-72°F, is close to the equilibrium bond shear strength cited previously, $\sigma_u = 860$ psi (5.9 MPa).

CHAPTER IV

RESULTS OF ADHESIVE SCREENING TESTS

Testing to this point had occurred primarily in room temperature environments, from approximately 70°F to 80°F. The pilot test program had revealed, among other things, the generally adverse effect of water on the polymers. It next became necessary to test polymers under the worst-case condition of 120°F and 90% RH. Initially, moisture condensing on the surface of the environmental chambers reduced the amount of water that could be dissolved in the air. Subsequent insulation of all outside surfaces of the chambers permitted an RH value of 88%.

The selection of adhesives for the test program was governed by several factors. The single most important was ease of application and cure. If steel structures were to be bonded in the field, two-part room temperature cure epoxy or acrylic adhesive systems would be ideal. On the other hand, communication with several manufacturers and users suggested that higher cure temperature adhesives would perform better in the specified environment of 90% RH and 120°F. Consequently adhesives with cure temperatures up to 350°F were included in the screening program. A list of the adhesives tested is presented in Table 1. A second factor used in adhesive selection was availability of previous test information. Multi-year projects by the various military research programs provided extensive test data on a limited number of adhesives. But this information provided not only insight into adhesive bond behavior in general but also information about manufacturers that were actively participating in adhesive development and production. During various communications with adhesive manufacturers, it became clear that while some manufacturers formulated their own resins, a large majority of companies make adhesives from resins supplied by relatively few large chemical companies. In fact, two of these chemical companies volunteered lists of adhesive manufacturers using their resins. This, then, suggested that although adhesives are identified by different brand names, they are probably, in fact, very similar in chemistry. None of the companies contacted was prepared to release specific chemical information about their adhesives. Companies were then selected on the basis of activity of development, range of adhesives provided, and amount of information about their adhesives from independent research programs. A given company was then asked to supply an adhesive that would survive the specific environment of 120°F and 90% RH. Therefore, the samples received came with manufacturers' recommendations that they would survive the environment specified. Only one major company declined to supply an epoxy adhesive, since it formulated no epoxy adhesive suitable for use in the screening environment.

The adhesives were screened by measuring an equilibrium stress-strain curve in tension as described previously. The load was incremented until sufficient information was obtained to evaluate the adhesive. Usually three increments were sufficient.

In addition to the equilibrium stress-strain curve performed at the screening environment, specimens of the adhesives were tested rapidly at a room environment of about 46% RH and 75°F. These specimens were obtained from the same processed batch as the screening specimens. The strain rate varied from 1.2% to 1.5% per minute. The results of the screening and rapid loading tests are presented in figs. 23 through 44. Of the 22 adhesives tested, only three, No. 3, No. 11 and No. 21 (figs. 25, 28 and 32, respectively) showed any promise. Further testing of these three adhesives indicated that equilibrium times might be longer than four days, so additional testing was done which will be discussed below. For the other 19 adhesives the strength left after several four-day relaxations was either zero or so small that the adhesives were not further considered. It should be recalled that these adhesives were supplied by the manufacturers as suitable for the screening environment. For the three adhesives mentioned above, a special test of long duration was devised. These specimens were stressed to levels of approximately 600 to 800 psi and allowed to stress relax for 42 days at an environment of 90% RH and 80°F. The results are shown in figs. 45, 46 and 47. After 36 days, No. 3 lost all strength; No. 11 showed some continued decay; and No. 21 appeared to be stable after some decay.

If a material has no stress at all after a period of time then it has no mechanical strain energy stored in the system at that environment. Adhesive No. 3 lost all strength. It must be concluded, then, that the combination of strain energy applied after one loading increment (initial strain of 0.0014) and the thermodynamic energy supplied by the environment during 42 days was sufficient to damage the molecule. If the time to equilibrate on reversible processes is from 4 to 8 days for these specimens, any decay after that reflects viscoelastic behavior. In other words, the material was overloaded. An extremely slow decay process suggests a near balance between the applied energy and the energy required to initiate damage. This seems to be the case with adhesive No. 11. Adhesive No. 21 appears to have stabilized after a period of 27 days and was still level after 42 days.

Adhesive No. 3 had lost all strength in only 4 days after the first load increment at the screening environment of 120°F and 82% RH (fig. 25). Increasing the energy of the material clearly had its effect. These comments on viscoelasticity are not meant to imply that thermodynamic effects are not occurring, but that the energy supplied by water vapor and heat have a very large effect on the polymers. It must also be stated that although the polymer has suffered some molecular damage, it still responds to the environment. For example, after 42 days in the 91% RH and 82°F environment, the RH was changed from 91% to 53% and the temperature maintained at 82°F. In all three adhesives the stress rose dramatically and stabilized. Specimen No. 11 went from 107 psi to 537 psi, No. 3 from zero to 775 psi, and No. 21 from 272 psi to 938 psi. This partial dessication increased the stresses to values higher than the stresses obtained initially by rapidly loading the specimens at 91% RH. Conversely, had the adhesives No. 3 and No. 11 been loaded at 50% RH to some stress levels comparable to the levels induced by the change from 91% to 53% RH, then a rise of RH to 91% would have ensured failure. Such loading and environmental conditions are likely to occur in bonded structures subjected to outdoor environments and must be guarded against.

The brittle behavior of adhesives No. 21, 11 and 3, particularly under rapid loading, suggests that these three adhesives are more cross-linked than the others tested herein. The higher degree of cross-linking appears to slow down the diffusion of moisture, thus accounting in part for the longer equilibrium time. Also noteworthy is the apparent lack of equilibrium in adhesives No. 11 and 3 after 42 days exposure to 91% RH and 80°F, despite being tested at a 40°F lower temperature and only slightly higher RH than in the screening program. This indicates that water vapor, and not temperature, is the dominant factor degrading the strength.

All of the adhesives, with the exception of one acrylic, were epoxies. It is felt that while these adhesives do not represent all epoxy or acrylic adhesives manufactured in the United States, they constitute a sufficiently broad sampling that certain general observations can be made. Environments of 90% RH and temperatures from at least 80°F to 120°F will so adversely affect these materials that they have either none or minimal cohesive strength. It can be said, then, that bonded structures using these materials and equilibrated to such environments, though the equilibration may take several years, will fail at least in cohesion. If moisture penetration in the bond line affects the adherend surface adversely as well, then adhesion failure will certainly occur.

Of the adhesives that retain some strength in adverse environments, such as adhesive No. 21, the brittle quality of the material suggests that it might be prone to fatigue failure. This, of course, will have to be checked.

With one exception, the equilibrium strengths of the adhesives ranged from 0 to 500 psi (including long-term test at 80°F). Nine developed no strength at all for all load increments observed, nine developed between 100 and 500 psi, and the three that were tested in 80°F and 90% RH showed ultimate strengths from 0 to 270 psi after at least one load increment. It should be noted that the strain of one load increment averaged from 0.2% to 0.25% or 0.002 to 0.0025. These strains are near yield for steels (approximately 0.0017). If a coverplate on a wide flange section used as a girder is expected to increase beam stiffness and strength, the coverplate must be in intimate contact with the lower flange of the section. Any relative displacement between the coverplate and the lower flange decreases the effectiveness of the coverplate. If shear deformations of an adhesive are sufficiently large, then the coverplate will provide no assistance to the beam at all. In a previous test program (5) displacements were measured in double lap shear specimens. These were tested under sustained constant loads. It was found that for a bond line (adhesive thickness) of 0.01 in. the relative adherend displacement was routinely about 0.005 in. or higher. In elastic theory shear strains are taken to be the angle γ formed by the vertical, dL, of an element and the horizontal distortional displacement, $d\delta$, of that element. In fact, since elastic theory requires that strain be small it is assumed that the angles formed in shear strain are so small that the $\tan \gamma = \gamma$. In the case of the adhesive layer in the bonded specimens discussed above, dL = 0.01,

$d\delta = 0.005$, therefore the shear strain

$$\tan \gamma = \frac{0.005}{0.01} = 0.5 \quad \text{and} \quad \gamma = 26.5^{\circ}$$

With shear strains of this magnitude the concept of a shear stress as described in elastic theory is difficult to conceive. What is easily envisioned is a transfer of tensile stress from one adherend through the bond line and into the other adherend. This idea is recognized in deep web plate girders where the web buckles and a tension field mimics a truss system. If a tension stress is the primary load path from adherend to adherend in a bonded joint, then there must be a correlation between the ultimate strength of tension tested bulk specimens and bonded specimens loaded in "shear." For rapid loading, a comparison of test data in tension with test data in bonded specimens provided by the manufacturers showed that six adhesives differed in ultimate strength by only 6% or less. These were presumably cohesive failures. Four tensile specimens failed at higher strength than the bonded specimens. Here one expects adhesive failure occurred, and three tensile specimens failed at lower loads than their bonded counterparts. Specimen preparation, difference in formulation of adhesives, even though they are supposed to be the same, or difference in cure processes could account for these unexpected results. This data is presented in Table 2.

Most interesting was data supplied by Pocius, Wangsness, Almer and McKown (26), which included bonded specimens tested at 100°F, 100% RH (this is questionable for it is extremely difficult to maintain an RH level above 95%). These authors also showed that after eight years, one epoxy bonded specimen survived a 1,200 psi load, but the vast majority of specimens could sustain loads between only 100 and 400 psi. Presuming the typical 1 in. wide specimen, eight years would certainly be sufficient time for environmental equilibration. The screening program of the tension tested specimens revealed that load levels of 0 to 400 psi in tension would be typical for nearly all of the specimens with an occasional higher ultimate strength for one specimen. The screening program was marginally different from the eight year test program in that the test environment was 120^oF, 82-88% RH. The large shear strains and the apparent correlation between tension testing of bulk specimens and shear testing of bonded specimens strongly suggests that elastic theory may not prove useful if one is to do a detailed analysis of a bonded connection. The suitability of existing epoxy and acrylic adhesives for application in adverse environments is questionable. The pilot studies showed that for 75^oF, 10% RH environments ultimate development may be as high as 2,000 psi, but the problem of large strain must still be resolved. Large deflection may not be suitable for certain steel structures.

CHAPTER V

THERMODYNAMICS OF ELASTICITY

While observing the effect of water vapor on the mechanical properties of collagen and the tested adhesives, several other facts became apparent. Water vapor and heat have similar effects on these polymers. Increasing either the temperature or RH swells, lowers the strength and tends to plasticize polymers. Decreasing either the temperature or RH shrinks, increases the strength, stiffens and embrittles the polymers. Dessicating at constant temperature or cooling at constant RH will induce a stress rise in a restrained polymer specimen. While metals are not affected by RH, temperature affects them in a manner similar to many polymers. In the pilot studies it was observed that establishing a stress in a collagen specimen could be achieved in more than one way and that an apparent path independence was evident. One method was to stretch the polymer to a point and let it equilibrate, all being done at constant temperature and RH. Another method would be to free swell the specimen by increasing the RH, then restraining the specimen, dessicate the environment to the original RH. It is certainly possible that the same apparent path independence could be achieved by stretching the materials and letting changes in temperature rather than RH provide an alternative path.

These observations suggest that thermodynamics concepts might be of value in understanding the observed behavior of polymers undergoing stretching. While this study has been primarily concerned with the effect of RH on the materials, most of the work involving the thermodynamics of elasticity has been done with regard to changes in temperature. It is worth reviewing current concepts of thermodynamics of elasticity.

Current Thermodynamics of Elasticity

Thermodynamics of elasticity has been widely explored, particularly with respect to rubber and rubber-like materials. Derivations of the thermodynamic relationships that govern this development of stresses and strains in materials were presented by Flory (15), Meares (25), Bull (12) and Treloar (18). The following derivation follows mainly Flory's text and starts by reviewing the accepted definitions of internal energy, work and entropy.

The change in internal energy, dU (Flory uses the symbol E), as an elastic body is stretched, may be written as

$$dU = dQ - dW \tag{1}$$

where dQ is the heat absorbed by the system (elastic body) and dW is the change in work done by the system on its surroundings. The change in work of a system subjected to an external pressure, P, and external force of extension, f, is given by

$$dW = PdV - fdL \tag{2}$$

where V and L are the volume and length, respectively. For a reversible process, the heat absorbed by the system is

$$dQ = TdS \tag{3}$$

where S is the entropy and T is the temperature. To substitute dQ from Eq. 3 into Eq. 1 requires that dW must also be reversible. Hence, the terms P and f in Eq. 2 must be assigned their equilibrium values. In particular, f represents the equilibrium tension for a given state of the system, which may be specified variously by S, V and L; T, V and L; or T, P and L. For reversible processes then

$$dU = TdS - PdV + fdL \tag{4}$$

Introducing the Gibbs free energy (17), defined by

$$G = H - TS = U + PV - TS \tag{5}$$

where H = U + PV is the heat content (enthalpy), its change can be expressed as

$$dG = dU + PdV + VdP - TdS - SdT \tag{6}$$

Substituting for dU from Eq. 4 gives

$$dG = VdP - SdT + fdL \tag{7}$$

This equation expresses the differential of the free energy in terms of the differentials of the variables P, T and L which are the easiest to measure in experiments. It follows from Eq. 7 that, for constant temperature and pressure,

$$\left(\frac{\partial G}{\partial L}\right)_{T,P} = f \tag{8}$$

and assuming dG = fdL (Eq. 7) and taking the derivative of Eq. 5 with respect to dL at constant temperature and pressure

$$f = \left(\frac{\partial H}{\partial L}\right)_{T,P} - T\left(\frac{\partial S}{\partial L}\right)_{T,P} \tag{9}$$

Similarly, for constant pressure and length it follows from Eq. 7

$$\left(\frac{\partial G}{\partial T}\right)_{P,L} = -S \tag{10}$$

According to the chain rule, the derivative of $(\partial G/\partial L)_{T,P}$ with respect to T at constant P and L is identical to the derivative of $(\partial G/\partial T)_{P,L}$ with respect to L at constant T and P. Taking these derivatives of the right hand side of Eq. 8 and Eq. 10 and equating them gives

$$\left(\frac{\partial f}{\partial T}\right)_{P,L} = -\left(\frac{\partial S}{\partial L}\right)_{T,P} \tag{11}$$

Substituting Eq. 11 in to Eq. 9 yields the Wiegand-Snyder equation

$$f = \left(\frac{\partial H}{\partial L}\right)_{T,P} + T\left(\frac{\partial f}{\partial T}\right)_{P,L} \tag{12}$$

which may be regarded as the thermodynamic equation of state for elasticity.

Anthony, Caston and Guth (30), and others found experimentally that for rubber

$$f - T\left(\frac{\partial f}{\partial T}\right)_{P,L} \cong 0 \tag{13}$$

From this experimental observation and Eq. 12, previous investigators concluded that

$$\left(\frac{\partial U}{\partial L}\right)_{T,P} = 0 \tag{14}$$

and, in Flory's case

$$\left(\frac{\partial H}{\partial L}\right)_{T,P} = 0 \tag{15}$$

If the enthalpy does not change with length, all work done by the applied force should evolve in heat because, from Eq. 9:

$$fdL = TdS \tag{16}$$

In fact, Treloar (18, p. 37) concluded that "putting $dU = 0$ we obtain $dW = dQ$ (constant T). The work done by the stretching force being necessarily positive, it follows that dQ, the heat absorbed, is negative, i.e., that heat is evolved on extension. The amount of the heat of evolution is exactly equal to the work done on the rubber by the applied force."

In Meares's words (25, p. 179), "This leads to the concept of an ideal elastomer in which f_U (the force component attributed to internal energy) is exactly zero, and all the work of isothermal stretching is dissipated as heat."

Generalized Thermodynamics of Elasticity

It is troublesome to conclude, as Treloar (18) did, that stretching does not increase the internal energy of rubber. Internal energy is in part defined as the internal elastic potential energy. When a stretched rubber is released, it returns to its original length. Additionally, rubber has a non-zero stress after stretching. This is the result of internal elastic potential energy or simply internal energy. Therefore, a reexamination of the derivation leading to the Wiegand-Snyder equation (Eq. 12) is in order.

In Flory's derivation Eq. 1 through Eq. 3 are accepted concepts from the First and Second laws of thermydynamics. Equation 4 presents the first difficulty. For the most general case the derivative of the internal energy U should be

$$dU = TdS + SdT - PdV - VdP + fdL + Ldf \tag{17}$$

Note that the last two terms are included since stretching a polymer changes both the force and length in the elastic or reversible region. Substituting dU from Eq. 17 into Eq. 6 gives

$$dG = TdS + SdT - PdV - VdP + fdL + Ldf + PdV + VdP - TdS - SdT$$

or

$$dG = fdL + Ldf \tag{18}$$

It should be noted that Flory assumes dG = fdL. From Eq. 17, it then can be written in general that

$$dG = fdL + Ldf = dU - TdS - SdT + PdV + VdP \quad (19)$$

If at this point constant temperature and pressure are assumed, then

$$dG = fdL + Ldf = dU - TdS + PdV \quad (20)$$

and if the derivative of G is taken with respect to L,

$$\left(\frac{\partial G}{\partial L}\right)_{T,P} = f + L\left(\frac{\partial f}{\partial L}\right)_{T,P} = \left(\frac{\partial U}{\partial L}\right)_{T,P} + P\left(\frac{\partial V}{\partial L}\right)_{T,P} - T\left(\frac{\partial S}{\partial L}\right)_{T,P} \quad (21)$$

or

$$f = \left(\frac{\partial H}{\partial L}\right)_{T,P} - T\left(\frac{\partial S}{\partial L}\right)_{T,P} - L\left(\frac{\partial f}{\partial L}\right)_{T,P} \quad (22)$$

which is not the same as Eq. 9 in Flory's derivation.

Similarly, for constant pressure and length the derivative of G with respect to T from Eq. 19 is

$$\left(\frac{\partial G}{\partial T}\right)_{L,P} = L\left(\frac{\partial f}{\partial T}\right)_{L,P} = \left(\frac{\partial U}{\partial T}\right)_{L,P} + P\left(\frac{\partial V}{\partial T}\right)_{L,P} - T\left(\frac{\partial S}{\partial T}\right)_{L,P} - S \quad (23)$$

or

$$\left(\frac{\partial G}{\partial T}\right)_{L,P} = L\left(\frac{\partial f}{\partial T}\right)_{L,P} = \left(\frac{\partial H}{\partial T}\right)_{L,P} - T\left(\frac{\partial S}{\partial T}\right)_{L,P} - S \quad (24)$$

which again is not the same as Eq. 10, derived by Flory.

After Eq. 10 Flory takes the derivative of $(\partial G/\partial L)_{T,P}$ with respect to T and the derivative of $(\partial G/\partial T)_{L,P}$ with respect to L and equates them. It is worth commenting that because of the conditions of constant temperature and pressure imposed on $(\partial G/\partial L)_{T,P}$ terms were removed from the equation. The same is true for $(\partial G/\partial T)_{L,P}$. These equations are no longer general, and it is difficult to understand how it is possible to impose conditions on an equation, alter the equation due to those conditions, and then remove the conditions and proceed with a derivation in general terms.

The goal of this exercise is to determine the value of $(\partial f/\partial T)$, Flory's Eq. 11, to see if it leads to the Wiegand-Snyder equation. This may be achieved from Eq. 19 which is completely general.

Taking the derivative of G with respect to L and assuming only constant pressure gives

$$\left(\frac{\partial G}{\partial L}\right)_P = f\left(\frac{\partial L}{\partial L}\right)_P + L\left(\frac{\partial f}{\partial L}\right)_P = \left(\frac{\partial U}{\partial L}\right)_P - T\left(\frac{\partial S}{\partial L}\right)_P - S\left(\frac{\partial T}{\partial L}\right)_P + P\left(\frac{\partial V}{\partial L}\right)_P \quad (25)$$

then

$$f = \left(\frac{\partial U}{\partial L}\right)_P - T\left(\frac{\partial S}{\partial L}\right)_P - S\left(\frac{\partial T}{\partial L}\right)_P + P\left(\frac{\partial V}{\partial L}\right)_P - L\left(\frac{\partial f}{\partial L}\right)_P \quad (26)$$

If the derivative is now taken with respect to T, the result is

$$\left(\frac{\partial f}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)\left(\frac{\partial U}{\partial L}\right)_P - \left(\frac{\partial}{\partial T}\right)\left(T\left(\frac{\partial S}{\partial T}\right)\right)_P - \left(\frac{\partial}{\partial T}\right)\left(S\left(\frac{\partial T}{\partial L}\right)\right)_P$$

$$+\left(\frac{\partial}{\partial T}\right)\left(P\left(\frac{\partial V}{\partial L}\right)\right)_P - \left(\frac{\partial}{\partial T}\right)\left(L\left(\frac{\partial f}{\partial L}\right)\right)_P \qquad (27)$$

Upon expanding Eq. 27:

$$\left(\frac{\partial f}{\partial T}\right)_P = \left(\frac{\partial^2 U}{\partial T\partial L}\right)_P - \left(\frac{\partial T}{\partial T}\right)\left(\frac{\partial S}{\partial L}\right)_P - T\left(\frac{\partial^2 S}{\partial T\partial L}\right)_P - \left(\frac{\partial S}{\partial T}\right)\left(\frac{\partial T}{\partial L}\right)_P - S\left(\frac{\partial^2 T}{\partial T\partial L}\right)_P$$

$$+\left(\frac{\partial P}{\partial T}\right)\left(\frac{\partial V}{\partial L}\right)_P + P\left(\frac{\partial^2 V}{\partial T\partial L}\right)_P - \left(\frac{\partial L}{\partial T}\right)\left(\frac{\partial f}{\partial L}\right)_P - L\left(\frac{\partial^2 f}{\partial T\partial L}\right)_P \qquad (28)$$

In Eq. 28 some of the terms on the right hand side either simplify or vanish, as shown below:

$$\left(\frac{\partial S}{\partial T}\right)\left(\frac{\partial T}{\partial L}\right)_P = \left(\frac{\partial S}{\partial L}\right)\left(\frac{\partial T}{\partial T}\right) = \left(\frac{\partial S}{\partial L}\right)_P \quad \text{(chain rule)}$$

$$S\left(\frac{\partial^2 T}{\partial T\partial L}\right)_P = S\left(\frac{\partial}{\partial L}\right)\left(\frac{\partial T}{\partial T}\right) = S\left(\frac{\partial}{\partial L}\right)\text{(constant)} = 0$$

$$\left(\frac{\partial P}{\partial T}\right)\left(\frac{\partial V}{\partial L}\right) = 0$$

Since the pressure is assumed to be constant. (This would not be true for a closed system.)

$$\left(\frac{\partial L}{\partial T}\right)\left(\frac{\partial f}{\partial L}\right) = \left(\frac{\partial f}{\partial T}\right)\left(\frac{\partial L}{\partial L}\right) = \left(\frac{\partial f}{\partial T}\right)$$

Eq. 28 then simplifies to

$$\left(\frac{\partial f}{\partial T}\right)_P = \frac{1}{2}\left(\frac{\partial^2 U}{\partial T \partial L}\right)_P - \left(\frac{\partial S}{\partial L}\right)_P - \left(\frac{T}{2}\right)\left(\frac{\partial^2 S}{\partial T \partial L}\right)_P + \left(\frac{P}{2}\right)\left(\frac{\partial^2 V}{\partial T \partial L}\right)_P - \left(\frac{L}{2}\right)\left(\frac{\partial^2 f}{\partial T \partial L}\right)_P \quad (29)$$

In order for

$$\left(\frac{\partial f}{\partial T}\right)_{P,L} = -\left(\frac{\partial S}{\partial L}\right)_{P,T} \quad (30)$$

it must be assumed:

First $$\left(\frac{\partial^2 U}{\partial T \partial L}\right)_P = \left(\frac{\partial}{\partial T}\right)\left(\frac{\partial U}{\partial L}\right)_P = 0$$

The change in internal energy with respect to the change in length is independent of temperature. From current understanding, stretching a metal is largely a change in the internal elastic potential energy where cohesive forces between bonds are affected. (29) However, since cohesive bond distances are involved in stretching, and those bond distances are affected by changes in temperature, it is difficult to make this first assumption.

Second $$T\left(\frac{\partial^2 S}{\partial T \partial L}\right)_P = T\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial S}{\partial L}\right)_P = 0$$

The change in entropy with respect to the change in length is independent of changes in temperature. Based on current kinetic theory, the change in entropy with respect to the change in length ($\partial S/\partial L$) is due to reorganization or altering the molecular configuration. If a specimen is stretched isothermally and the length is fixed, then ($\partial S/\partial L$) is also fixed. However, heating this fixed length specimen will cause swelling in the transverse direction which further alters the molecular configuration. Additionally, the above term can be rewritten as:

$$\frac{T}{2}\left(\frac{\partial}{\partial L}\right)\left(\frac{\partial S}{\partial T}\right)$$

and is the only term that represents a change in entropy with respect to a change in temperature in Eq. 29.

In attempting to draw an analogy between the effects of water and the effects of temperature, this term is particularly important. When a polymer is rapidly stretched and its length is then fixed, stress relaxation is observed which could be caused by a molecular reorganization of the polymer. This reorganization might be the result of further absorption of water vapor from the atmosphere and a reorganization of the water vapor existing within the polymer itself. Furthermore, since the length has been fixed, the only reorganization possible results from changes in the transverse dimensions. This relates longitudinal energy to the transverse direction. Bull (12, p. 435) notes explicitly that the above two assumptions must be made in order to arrive at the Wiegand-Snyder equation.

Third $$\frac{P}{2}\left(\frac{\partial^2 V}{\partial T \partial L}\right)_P = \frac{P}{2}\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial V}{\partial L}\right)_P = 0$$

The change in volume with respect to the change in length is independent of temperature. In many of the derivations of the thermodynamics of elasticity and particularly with respect to rubber, it was assumed that $(\partial V/\partial L)$, the change in volume with respect to the change in length, is zero. This, then, required that Poisson's Ratio be 0.5. Measurements of the Poisson's ration of pure gum rubber in this study found that the ratio is not 0.5 nor is it constant. It increased during the early stages of deformation to about 0.35 and then decreased, approaching 0.1 as the elongation approached 400%. In general the volume of a material is affected both by stretching and by changes in temperature. If one assumes

$$\frac{P}{2}\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial V}{\partial L}\right) = 0$$

one must also assume

$$\frac{P}{2}\left(\frac{\partial}{\partial L}\right)\left(\frac{\partial V}{\partial T}\right) = 0$$

This is the same as saying that a specimen whose volume is changed by a change in temperature will experience no further volume change with stretching. No evidence can be found to confirm this. It should be noted that the value of this term is small because the volume change is small and the pressure is low. However, both heating and stretching alter the molecular configuration of a polymer.

Fourth $$\frac{L}{2}\left(\frac{\partial^2 f}{\partial T \partial L}\right)_P = \frac{L}{2}\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial f}{\partial L}\right)_P = 0$$

The change in force with respect to the change in length is independent of changes in temperature. This term does not appear in Flory's derivation, for he assumes dG = fdL and can be stated in another way if the term stress is assigned instead of force and strain instead of change in length. The assumption is then that the modulus of the stress-strain plot at a given point is independent of changes in temperature. This does not seem to be the case. If the term is rearranged such that

$$\frac{L}{2}\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial f}{\partial L}\right)_P = \frac{L}{2}\left(\frac{\partial}{\partial L}\right)\left(\frac{\partial f}{\partial T}\right) = 0$$

the assumption becomes, the slope of the force-temperature plot is independent of changes in length. What is most interesting here is that the force-temperature plots of rubber provided by Anthony, Caston and Guth (30) are shown to be quite sensitive to changes in length. For rubber, increasing the length dramatically increases the slope of the force-temperature plot.

If all of the four assumptions listed above cannot be made, then the Wiegand-Snyder equation cannot be reached. All five terms on the right hand side of Eq. 21 seem to have some relationship to the physical properties of the material. If this equation is in fact valid with respect to temperature and if the analogy between temperature and RH is valid, then additional terms must be added to Eq. 21 to account for changes in RH.

If the force in a specimen f is a function of U, S, T, L, V and P, then f can also be a function of RH. Terms involving RH seem to be quite influential. For example, in a completely closed humid environment if a piece of wood is stressed at equilibrium to a fixed length, changing the temperature will increase the stress in the wood. This is because the increase in temperature decreases the RH of the environment even though the number of water molecules remains unchanged in this confined system. The specimen of wood wants to dessicate and shrink due to the decrease in RH. If, however, the same experiment were conducted in a perfectly dessicated environment, heating would cause the specimen to stress relax. In this case the temperature rise attempts to swell the specimen and reduce the stress. In both cases, however, changes in the transverse geometry of the specimen are involved.

Molecular reorganization is occurring. In the humid environment increases in temperature have the reverse effect of raising the temperature in a dessicated environment. The humid environment process will probably require a longer time to equilibrate since water vapor must diffuse through the wood. In both cases the increase in temperature attempts to swell the wood. In the humid environment process this temperature-induced swelling is overridden by RH-induced shrinkage. These observations suggest that if terms involving RH are included in Eq. 21, those terms, with changes in temperature, will reflect a greater material response than the equation would now indicate for those materials sensitive to water vapor. Since the equation would be general, terms involving RH would be associated only with those materials affected by RH.

CHAPTER VI

SUMMARY AND CONCLUSIONS

This research program was prompted by the single question: Can commercially available adhesives be used to replace bolted and welded steel to steel connections exposed to outdoor environments? Previous studies in the laboratory environment using full scale bonded steel beams have shown that fatigue life for bonded connections improved dramatically over welded structures. However, the question of durability of the adhesive for the most part went largely unanswered.

Information provided in the literature indicated that moisture penetration into an adhesive bond line had a detrimental effect on the structural capacity of the adhesive. The literature also provided estimates of the rates of moisture diffusion, indicating that a 1 in. wide bonded specimen would require at least one year to equilibrate to a new environment. Additionally, it was found that a stressed polymer would absorb more water than an unstressed polymer.

In order to reduce the diffusion time and therefore the time to equilibrate the adhesive to the environment, thin bulk specimens would be tested in tension in carefully controlled environments. Since a large number of specimens would have to be evaluated and since a single specimen would be dedicated to testing equipment for at least a month, several testing devices would be required. Nine such devices were fabricated and divided into three groups. Each of these groups was assigned to environmental chambers capable of maintaining a fixed environment for long periods of time. The environment chosen for the adhesive screening program was 120°F and 90% RH and was based on United States climatic data provided by the National Oceanic and Atmospheric Administration. Adhesives selected for the program were provided by those adhesive manufacturers who demonstrated current development programs and who were reasonably active in other research studies. This provided some information from which comparisons could be made once data were accumulated in this testing program. Polymers other than adhesives were also tested and used for further comparative information.

It can be concluded from this study that:

1. The equipment used greatly accelerated the testing program. Data which would have required months or years to develop were generated in weeks.

2. The mechanical behavior, specifically the stress-strain curve, of adhesives and other polymers is sensitive to rate of loading. Rapidly loaded specimens develop considerably more strength than do slowly loaded specimens. It was typical for many of the adhesives to have a high loading rate strength ten times greater than the slow loading rate strength.

3. There appear to be both upper and lower bounds on the stress-strain

curves of the polymers. The upper bound limit is possibly established by extremely rapid loading. The lower bound is established by the equilibrium stress-strain curve. The existence of this curve depends heavily on the test environment.

4. The mechanical behavior, specifically, the stress-strain curve, of adhesives is greatly affected by the ambient environment. The strength decreases with increasing RH.

5. Increasing the ambient temperature at constant RH decreases the strength of the polymer.

6. Within the range of service environments (-30°F to 120°F temperature, 30% to 90% RH) increases in RH have a greater adverse effect on long-term mechanical properties than increases in temperature.

7. The adverse effect of the environment is less pronounced for rapidly loaded specimens than slowly loaded specimens. This can lead to misleading data regarding the long-term performance of polymers in adverse environments.

8. A specimen subjected to a constant load and environment will creep to equilibrium if the applied load is less than the equilibrium ultimate strength of the specimen in that environment, otherwise it will creep to failure.

9. A specimen subjected to a constant displacement and environment will stress relax to equilibrium if an equilibrium stress-strain curve exists for that environment.

10. If a specimen subject to a constant displacement stress relaxes to zero stress at a given environment, then it must be assumed that this specimen has no internal elastic potential energy at that environment.

11. Polymers that stress relax to zero stress in high humidity environments still retain considerable structural integrity since dessicating the specimen without changing the length will cause a large stress rise in the specimen. This stress rise can apparently be maintained for extended periods of time in the lower RH environments.

12. Of the twenty-one epoxy adhesives and one acrylic adhesive screened for use in the worst-case environment of 120°F and between 82% and 88% RH, only one had any potential as a candidate for use as a structural adhesive.

13. The strength of an adhesive in an adverse environment appears to increase with an increase of cross-linking. However, the increase in cross-linking tends to make the adhesive quite brittle.

14. Contrary to expected results, high temperature cure adhesives do not exhibit better mechanical performance in the most severe

environments of 120°F and between 82% and 88% RH than room temperature cure adhesives.

15. While this test program did not examine every possible adhesive manufactured, the sample represented in general the state of the art in structural adhesives. Considering the results obtained in the program, it is possible that some adhesives could be used in fairly dry climates. However, none could be recommended for use in environments of high RH, even at moderate temperatures.

Further Observations

Applying concepts of thermodynamics was prompted by parallel observations concerning the effects of temperature and RH on the mechanical properties of polymers. Generally, increases in either temperature or RH resulted in the swelling of the adhesives, reduced the ultimate strength of the adhesive and tended to "plasticize" the adhesive. Conversely, reducing either temperature or RH increased the strength of the polymer but tended to make it become brittle. Dessicating or cooling a restrained polymer caused considerable stress to develop in the specimen.

Of equal interest was the stress relaxation process. If a material can be rapidly loaded, then allowed to stress relax at a fixed strain to a stress considerably lower than that originally applied and still return to its original length upon removal of the load, it prompts the question as to whether the stress relaxation is due to molecular damage or is a result of some thermodynamic process.

A more detailed exploration into the thermodynamic behavior of solids is recommended as a means of understanding this problem.

The apparent correlation between the ultimate strength developed by specimens in the bulk testing program and data found on the shear strength of bonded specimens is yet to be explained. It must be assumed that both bulk tensile specimens and bonded specimens are failing in shear.

Finally, with regards to steel-to-steel bonding, the information found in the literature and that supplied during correspondence with researchers in the field of adherend surface preparation indicates that to date there is no satisfactory surface preparation for steel. Moisture penetration into the bond line in high RH environments tends to corrode the steel surface and degrade the steel-adhesive interface leading to bond failure. This further suggests that the use of adhesives in steel bridges in outdoor environments is premature.

TABLES AND FIGURES

TABLE 1

LIST OF ADHESIVES

No.	Type	Curing Method
1	Epoxy, 2-part	2 hrs. - 160° F
2	Epoxy, film	80 min. - 250° F
3	Epoxy, film	75 min. - 350° F
4	Epoxy, 2-part	60 min. - 200° F
5	Epoxy, without scrim	80 min. - 250° F
6	Epoxy, without scrim	80 min. - 250° F
11	Epoxy, film	65 min. - 250° F
12	Epoxy, 1-part	60 min. - 300° F
13	Epoxy, 1-part	40 min. - 250° F
14	Epoxy, 1-part	80 min. - 250° F
21	Epoxy, 2-part	4 days - 80° F
22	Epoxy, 2-part	2 hrs. - 260° F
31	Epoxy, 2-part	4 days - 80° F
32	Epoxy, 2-part	4 days - 80° F
33	Epoxy, 2-part	38 min. - 250° F
41	Epoxy, film	60 min. - 350° F
42	Epoxy, film	75 min. - 350° F
43	Epoxy, 2-part	60 min. - 200° F
44	Epoxy, 2-part	60 min. - 200° F
51	Epoxy, 2-part	48 hrs. - 78° F
52	Epoxy, 2-part	48 hrs. - 78° F
61	Acrylic, 2-part	24 hrs. - 78° F
71	Epoxy, 2-part	4 days - R.T.

TABLE 2

COMPARISON OF ADHESIVE STRENGTH UNDER RAPID LOADING AT ROOM TEMPERATURE

Adhesive No.	Bulk Tensile[a] Strength (psi)	Bond Shear[b] Strength (psi)	Adherend
1	4980	5300	Al
2	5380	5400	Al
3	4020	3200	Al
11	3020	4000	Al
12	6550	4500	Al
13	3510	4000	Al
14	6140	4000	Al
21	3460	3550	Al
22	3780	3700	Al
31	4260	3100	Al
32	4860	4680	Al
33	5720		
42	2330	4010,3450[c]	Al
43	4440	3100	Al
61	3970	5500,4600,4000[d]	Steel,Al,A588[d]

Notes:
a. FHWA study; 46% RH; strain rate about 0.001/minute
b. Manufacturer's literature
c. Different clamping pressure
d. Previous FHWA study

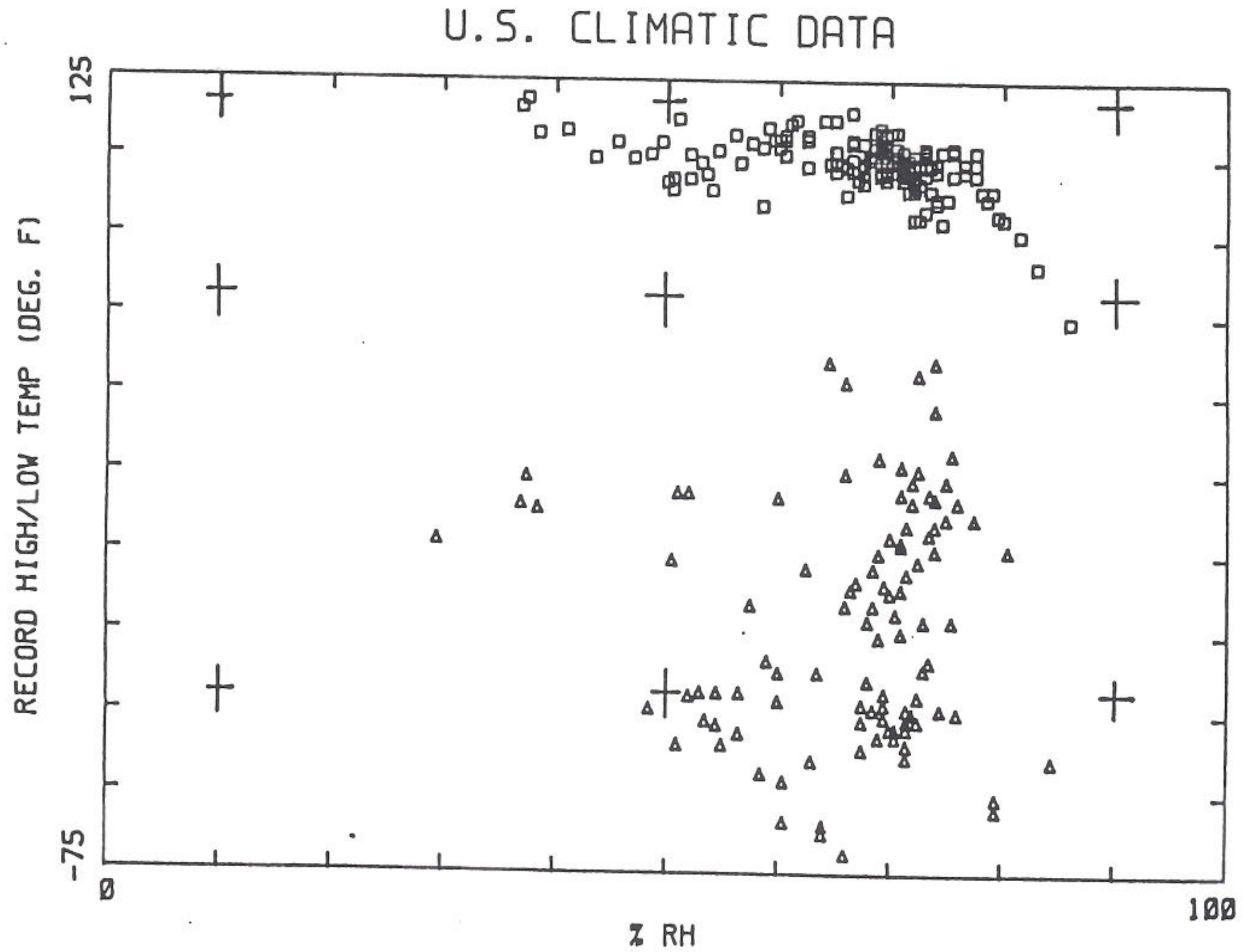

Fig. 1 Highest/lowest temperature of record vs. average relative humidity for weather observing stations in all 50 states, Puerto Rico, and Pacific Islands

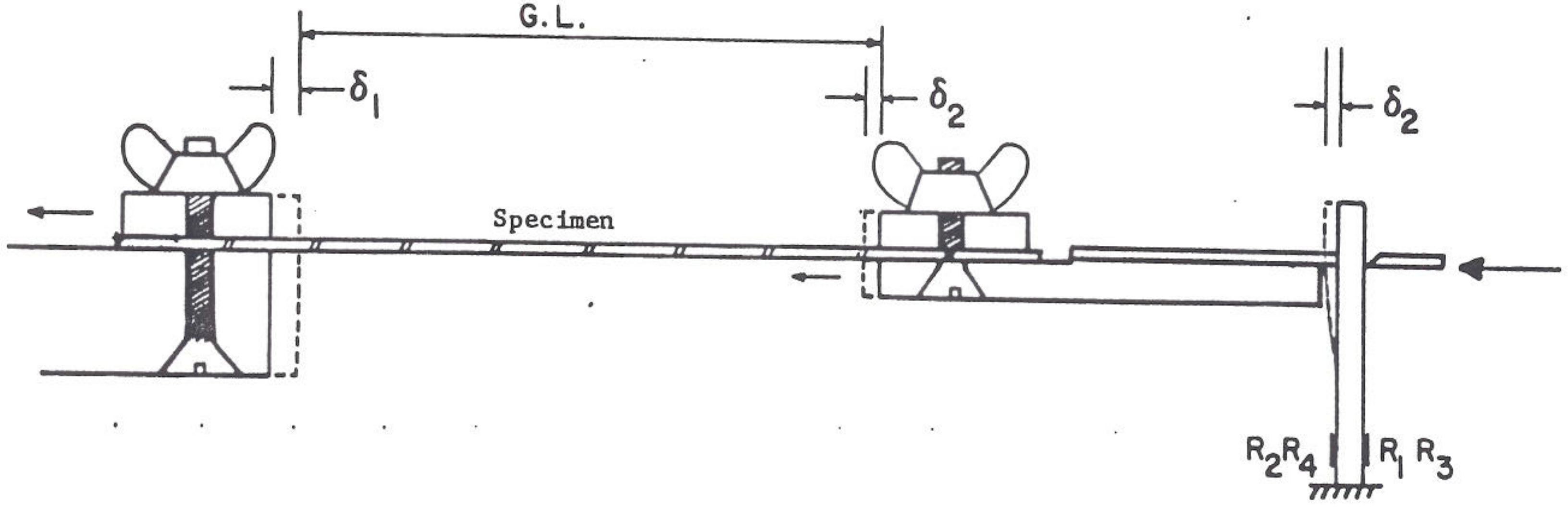

Fig. 2 Diagram of tensile testing equipment with specimen in place

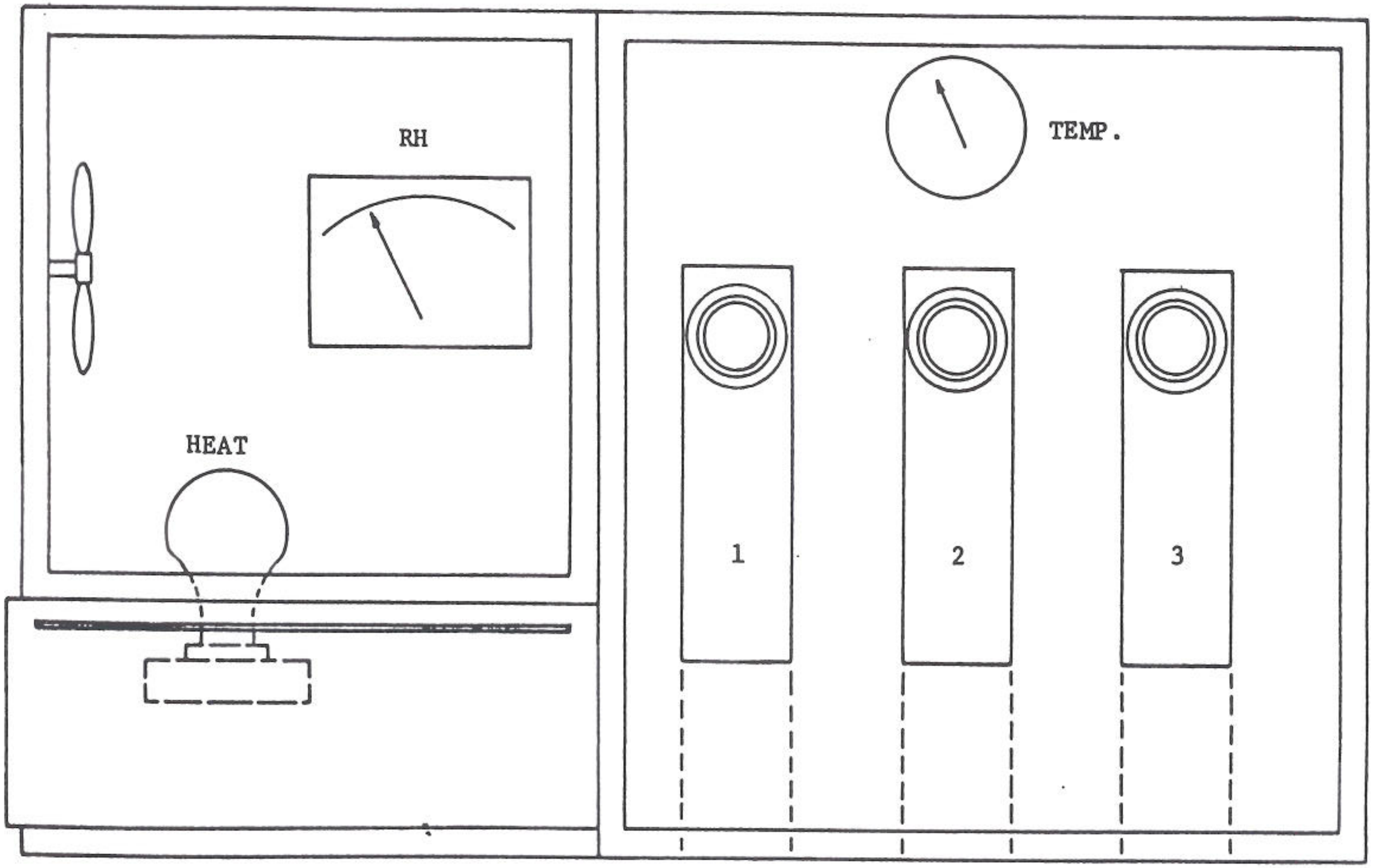

Fig. 3 Schematic Diagram of Environmental Chamber with Tension Gages 1, 2, 3 in place

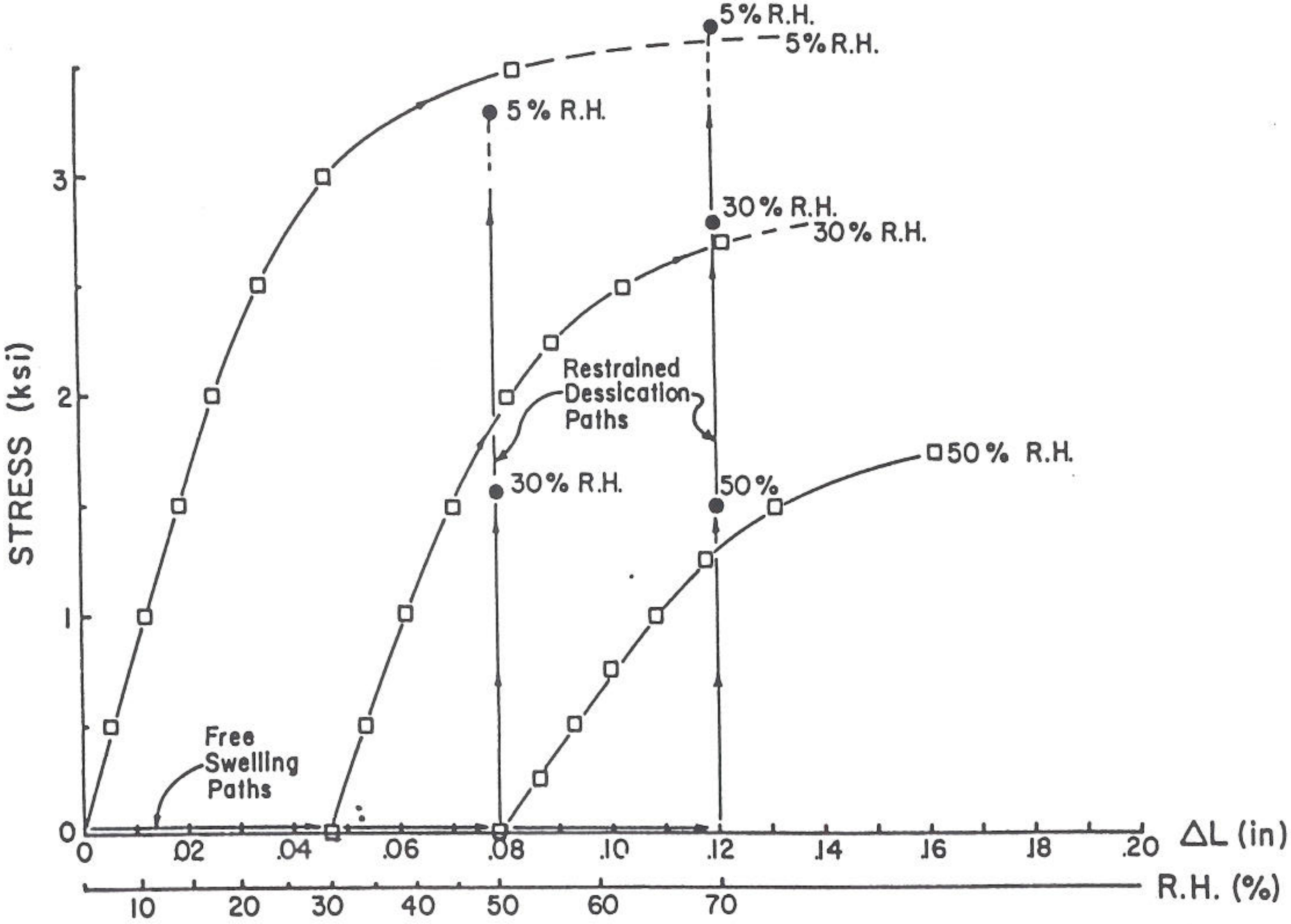

Fig. 21 Comparison of tensile stressing and environmental stressing of collagen

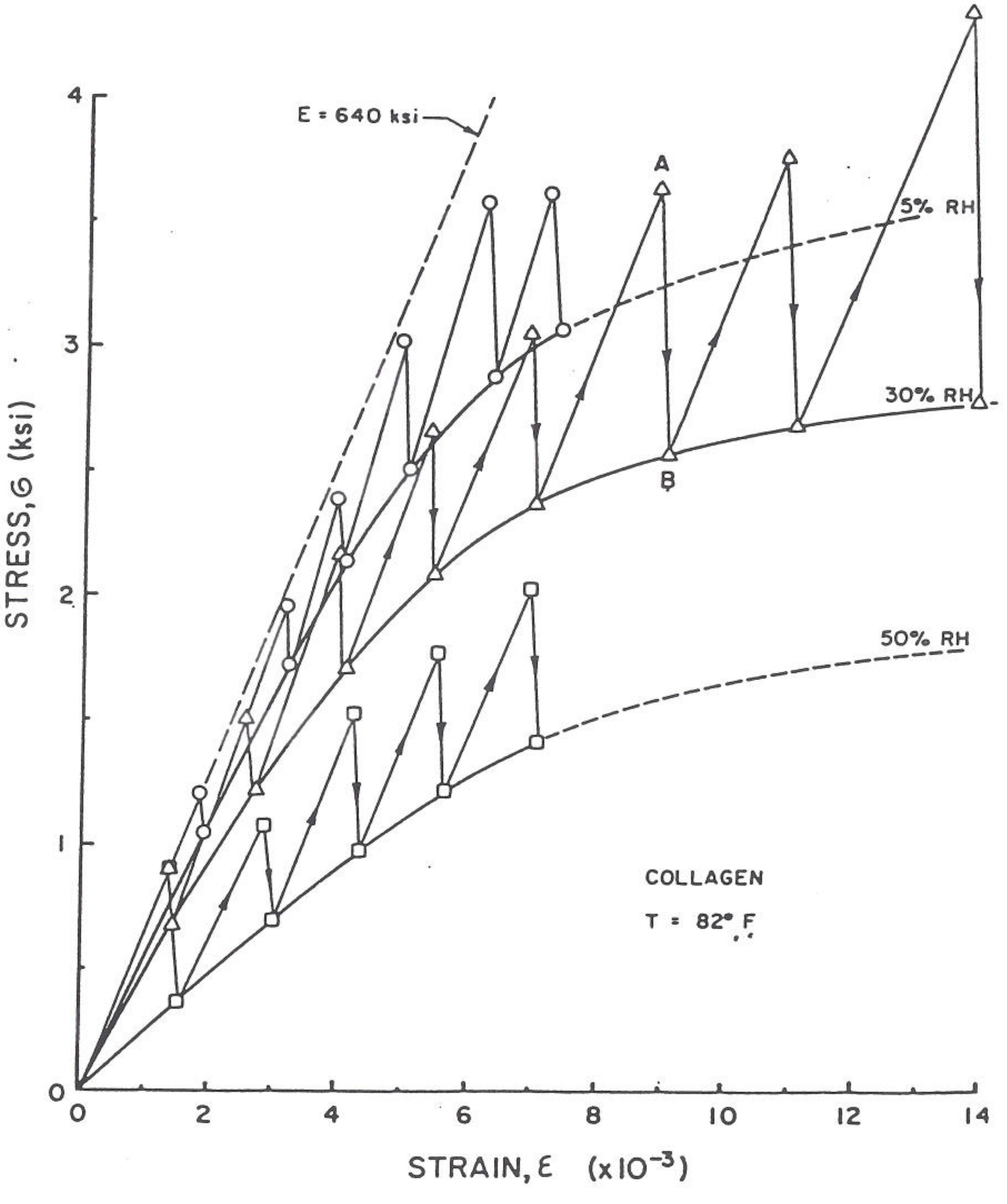

Fig. 4 Equilibrium stress-strain curves for collagen

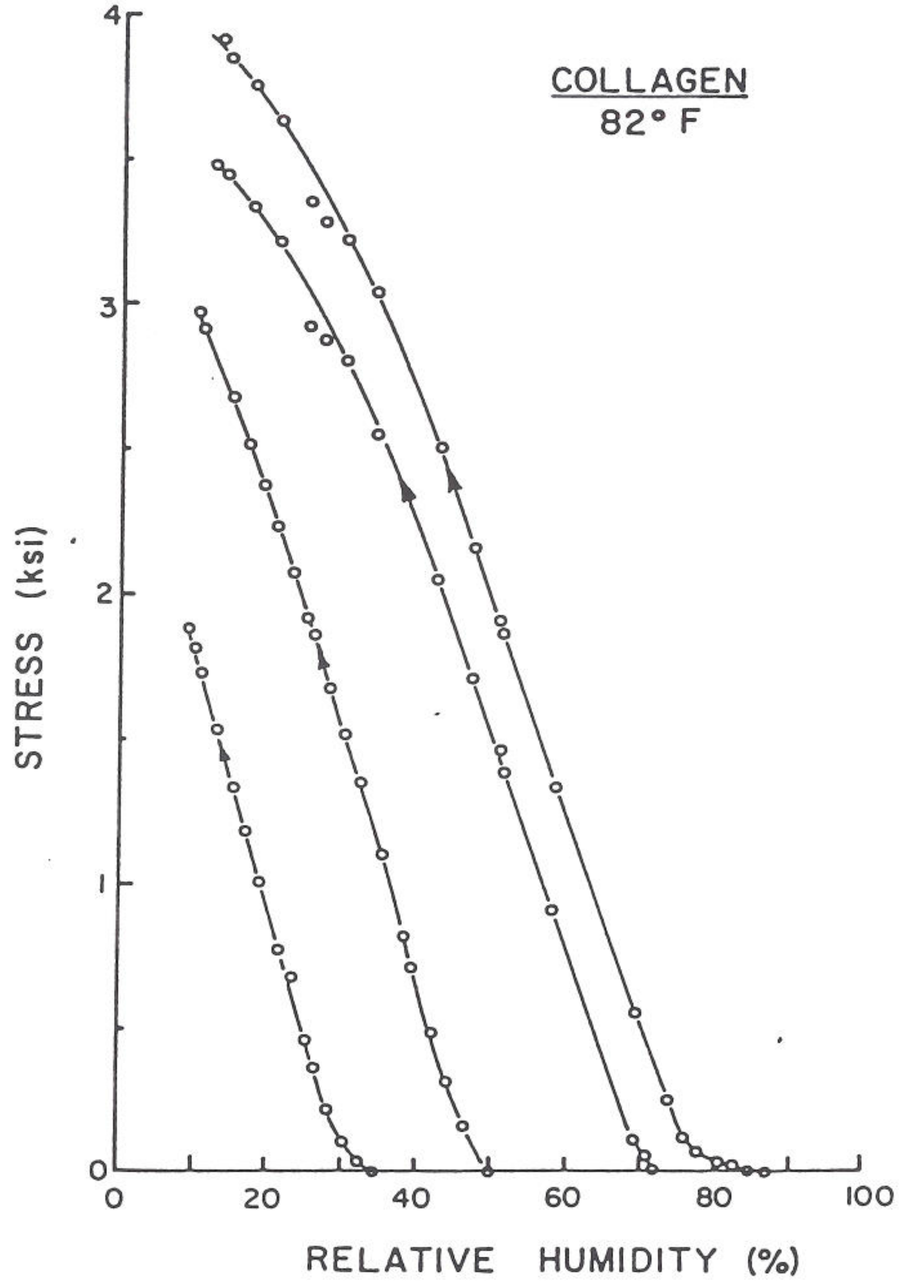

Fig. 16 Effect of changes in RH on stress of restrained collagen specimens

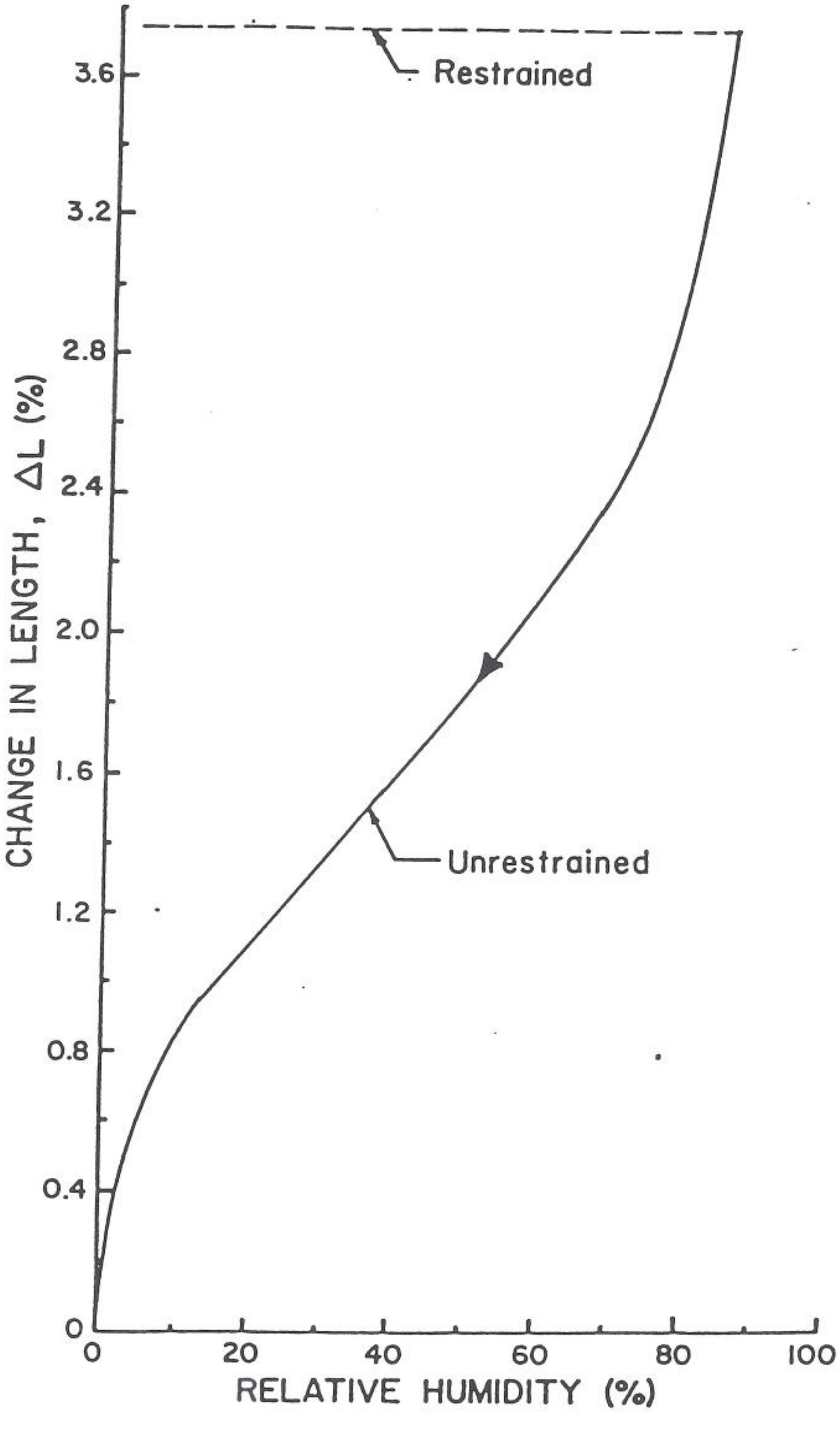

Fig. 13 Equilibrium swelling isotherm for collagen

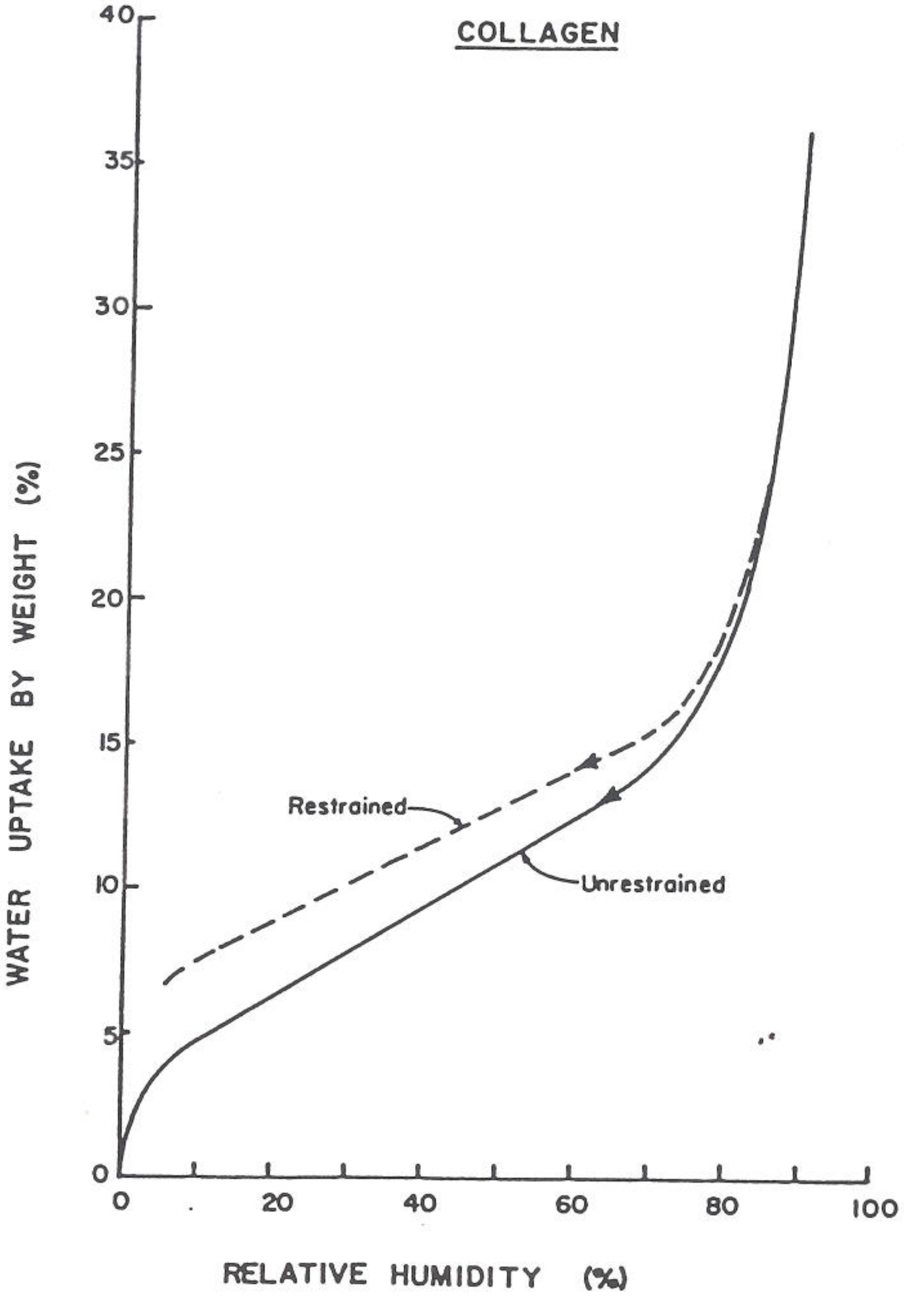

Fig. 12 Equilibrium moisture isotherm for collagen

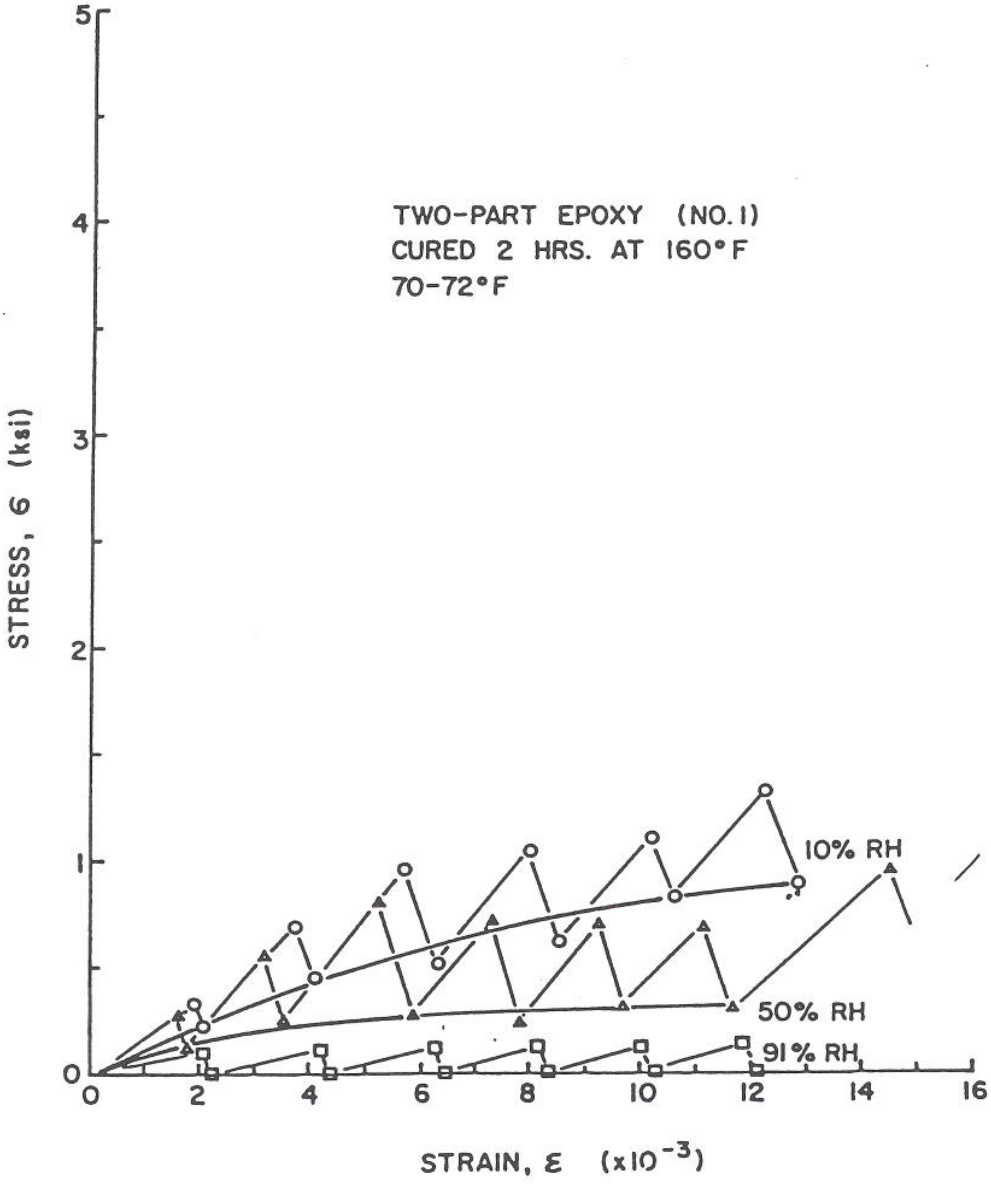

Fig. 5 Equilibrium stress-strain curves for two-part epoxy adhesive (no. 1)

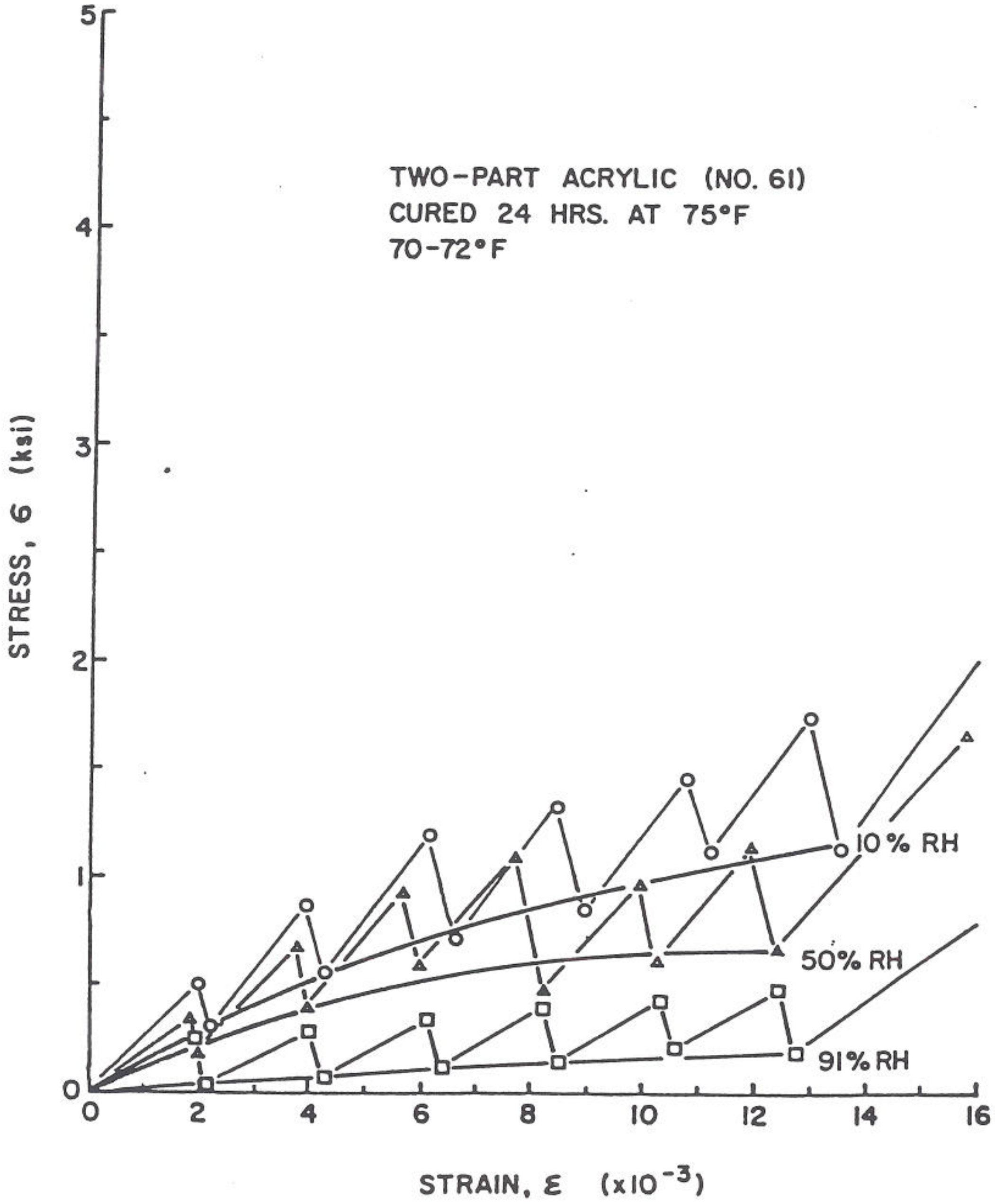

Fig. 6 Equilibrium stress-strain curves for two-part acrylic adhesive (no. 61)

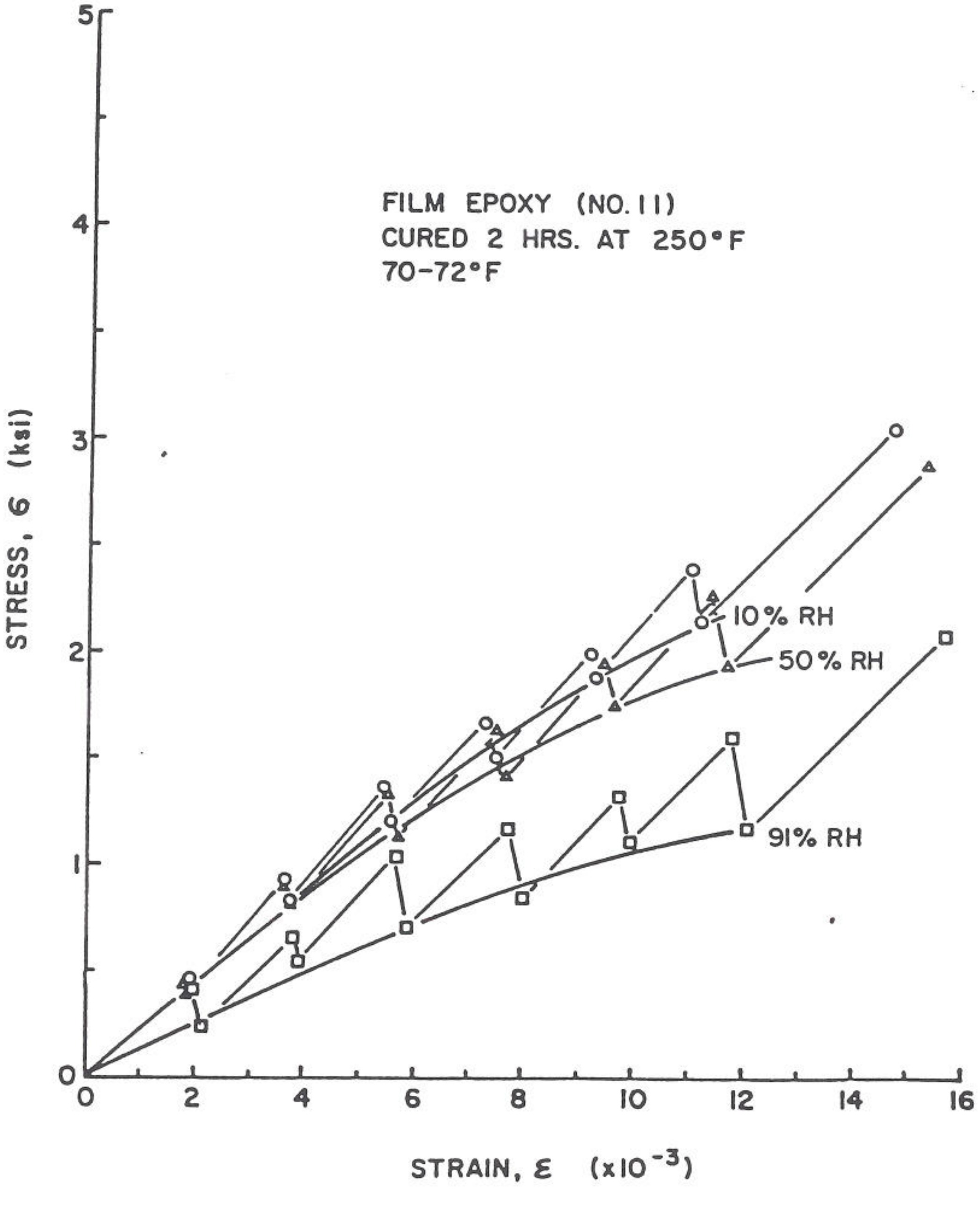

Fig. 7 Equilibrium stress-strain curve for one-part film epoxy (no. 11)

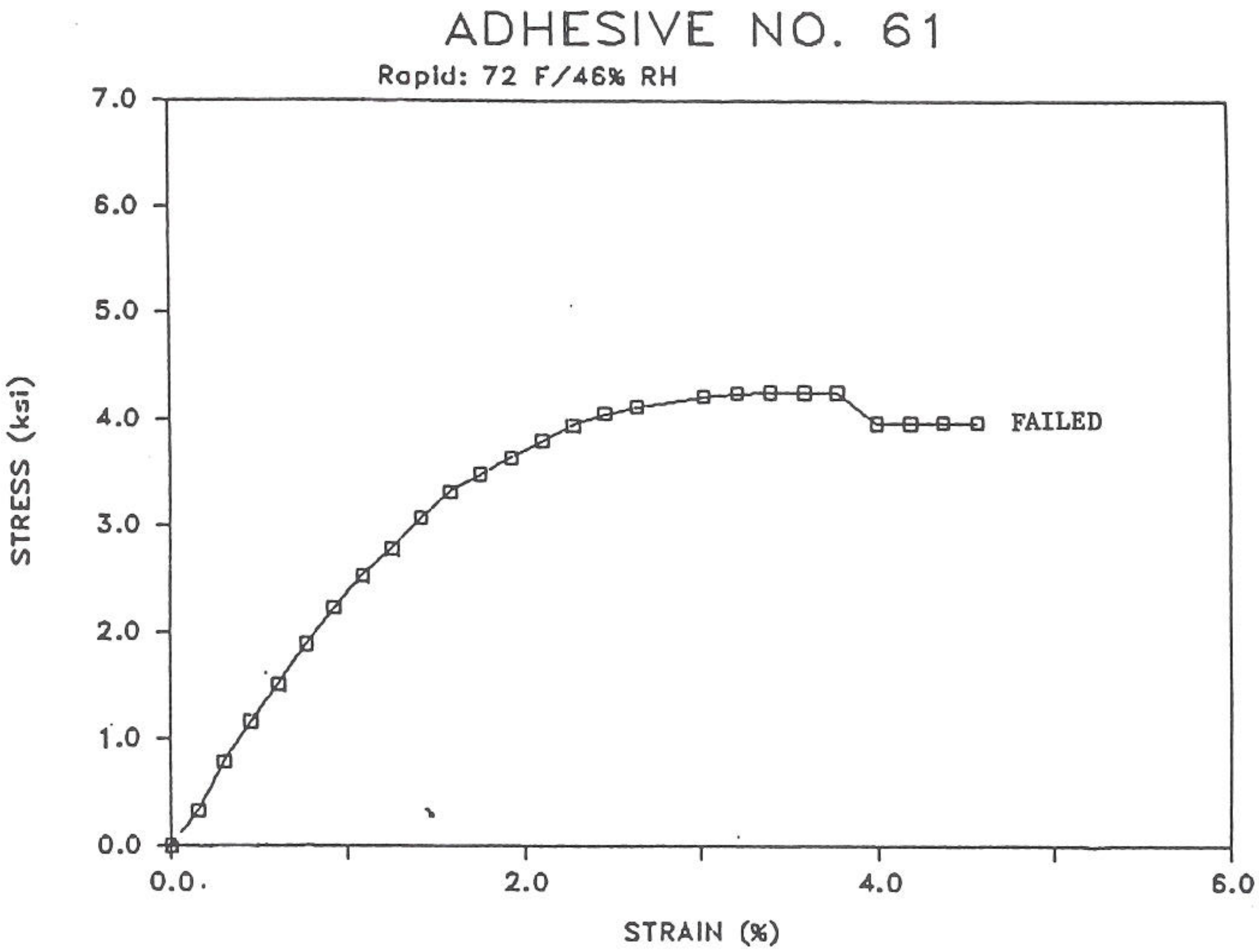

Fig. 8 Rapid test of two-part acrylic adhesive

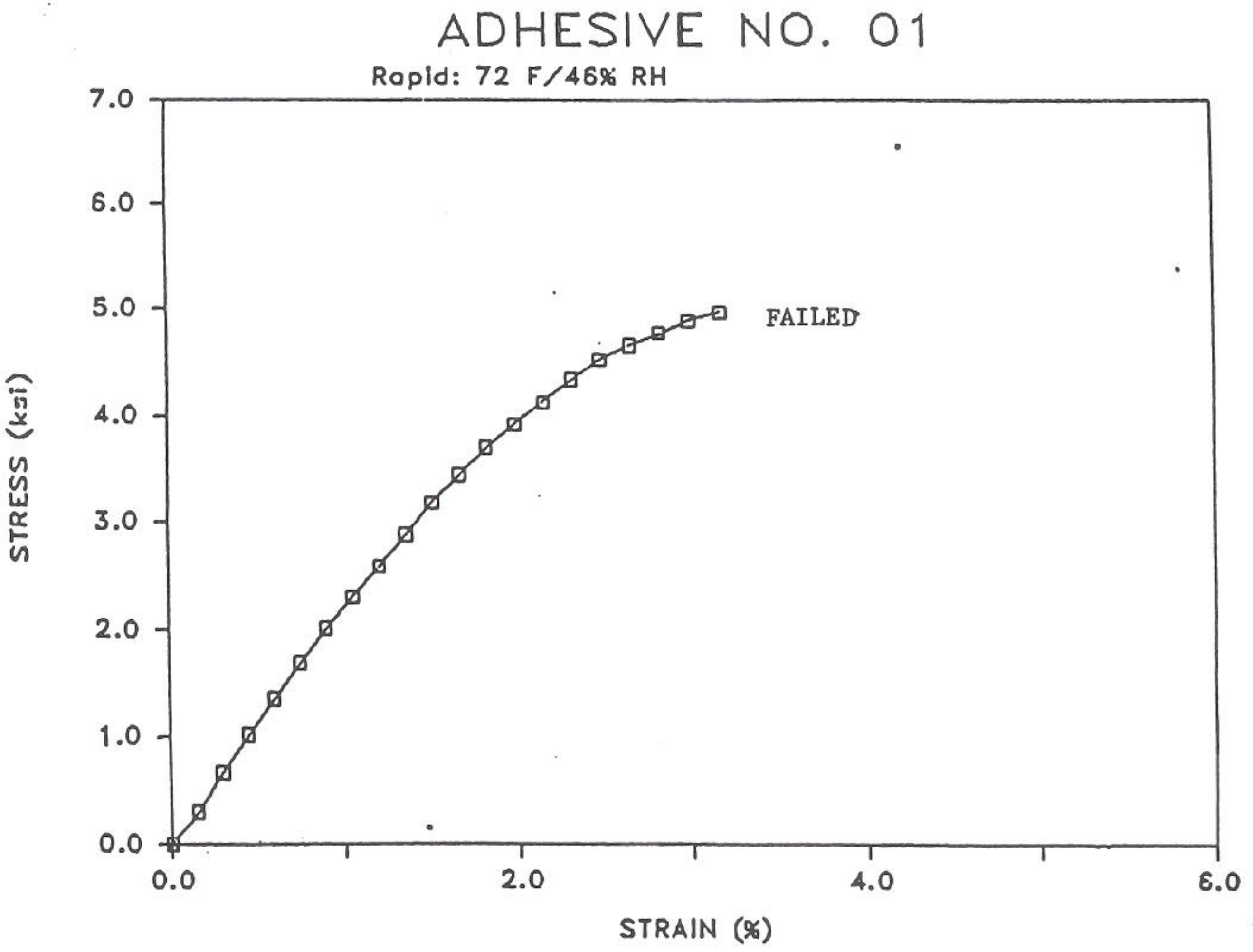

Fig. 9 Rapid test of two-part epoxy adhesive

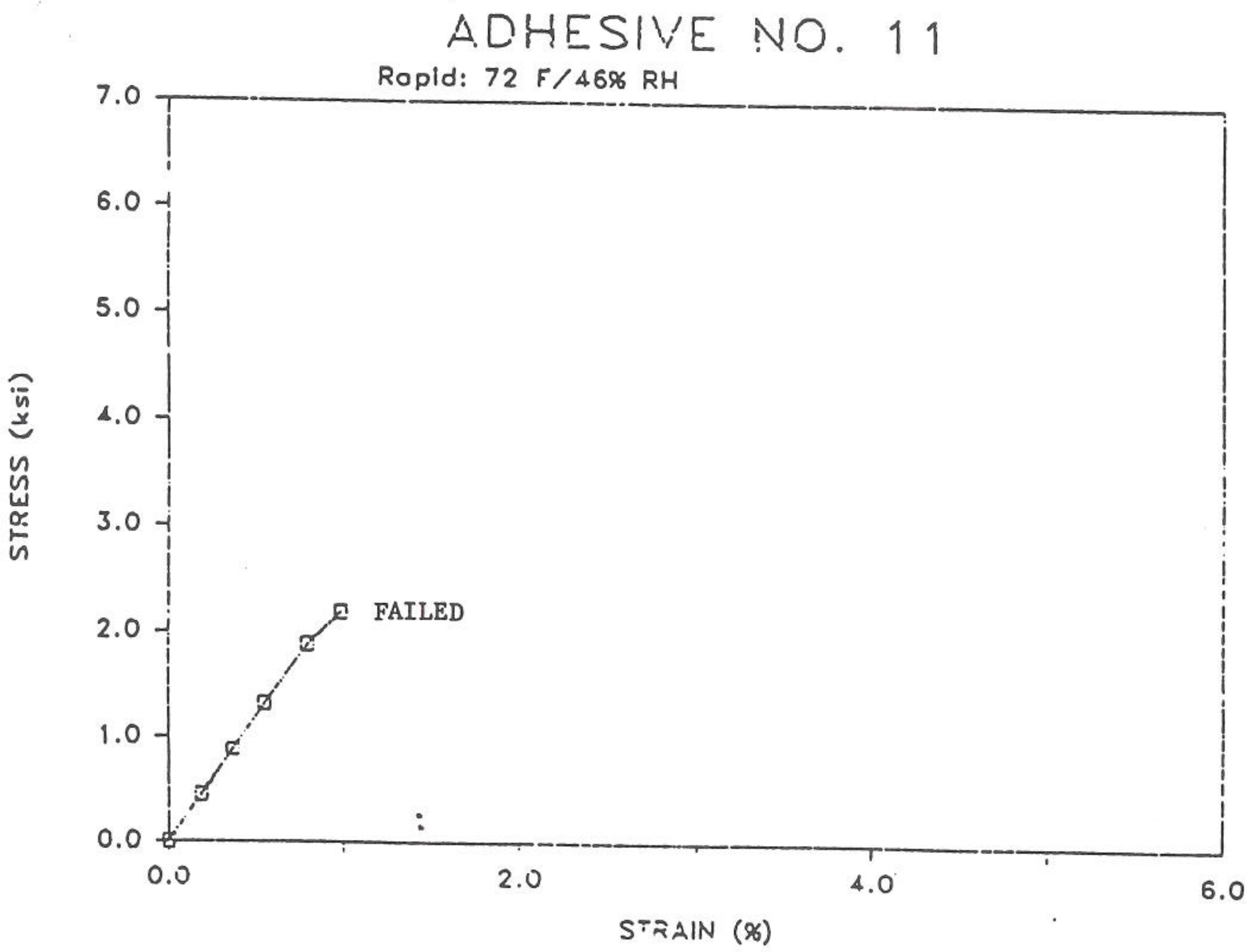

Fig. 10 Rapid test of one-part film epoxy adhesive

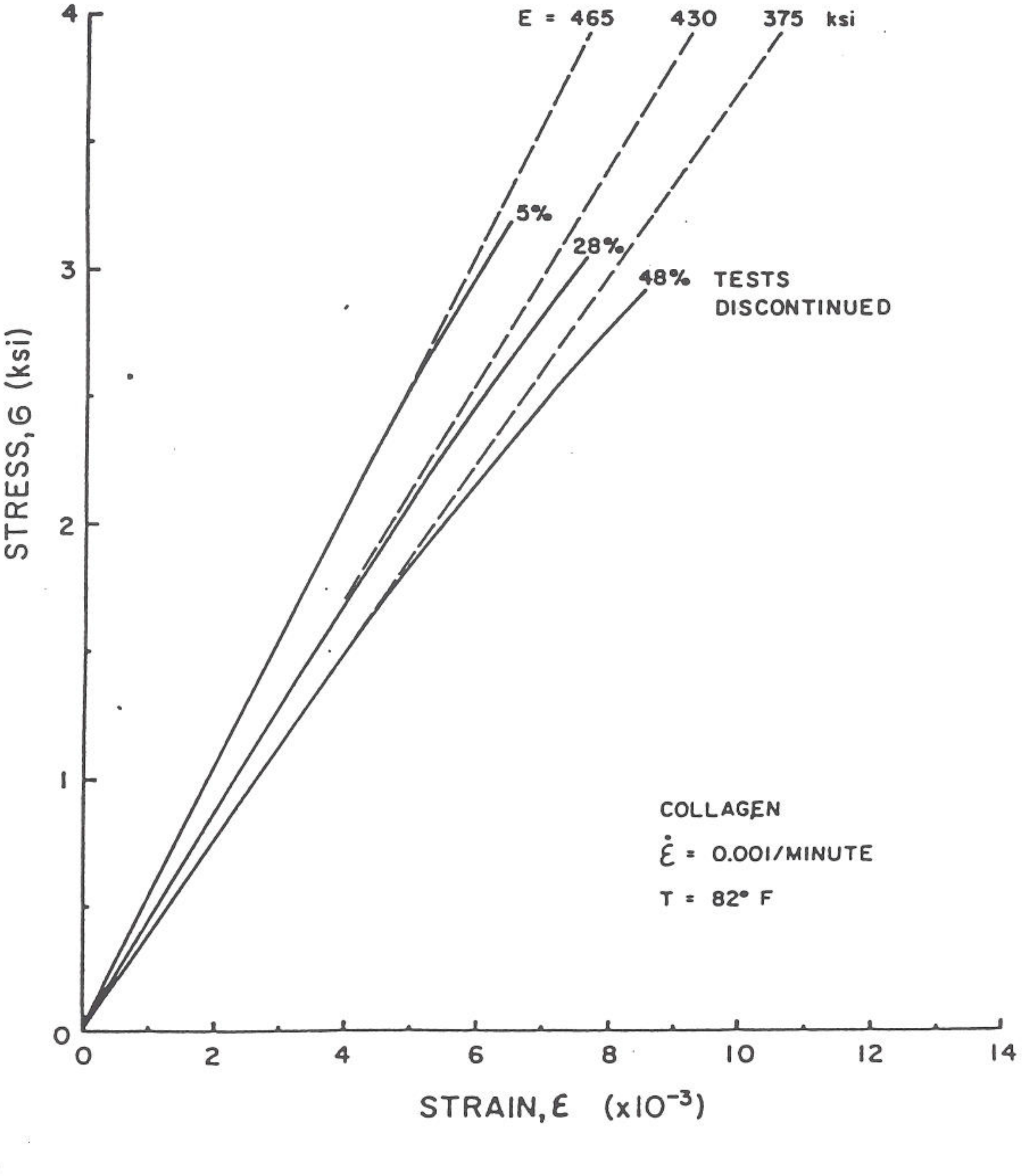

Fig. 11 Rapid loading stress-strain curves for collagen

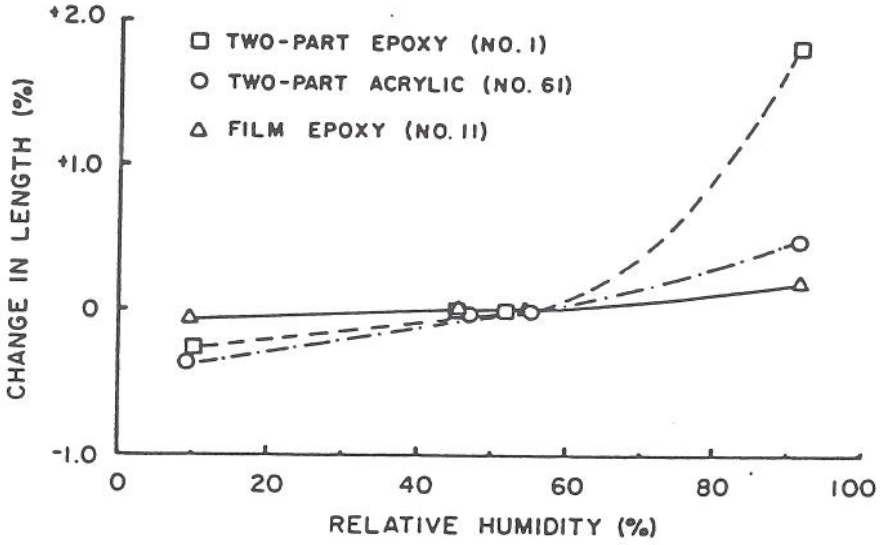

Fig. 14 Equilibrium swelling isotherm for three adhesives

NYLON

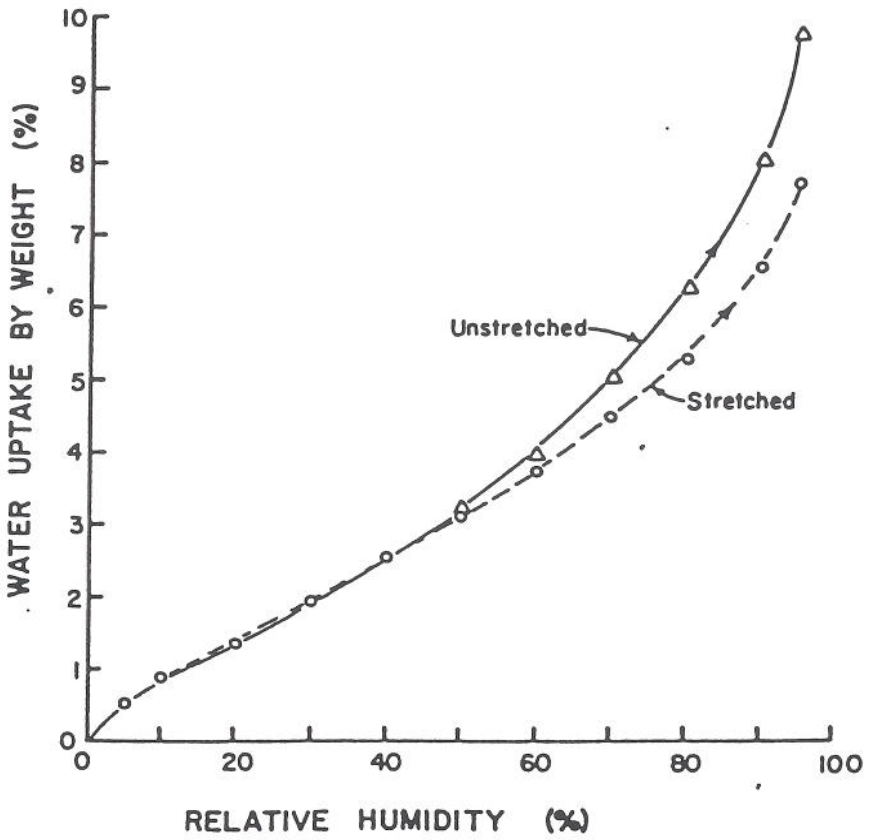

Fig. 15 Equilibrium moisture isotherm for nylon adapted from Bull (13)

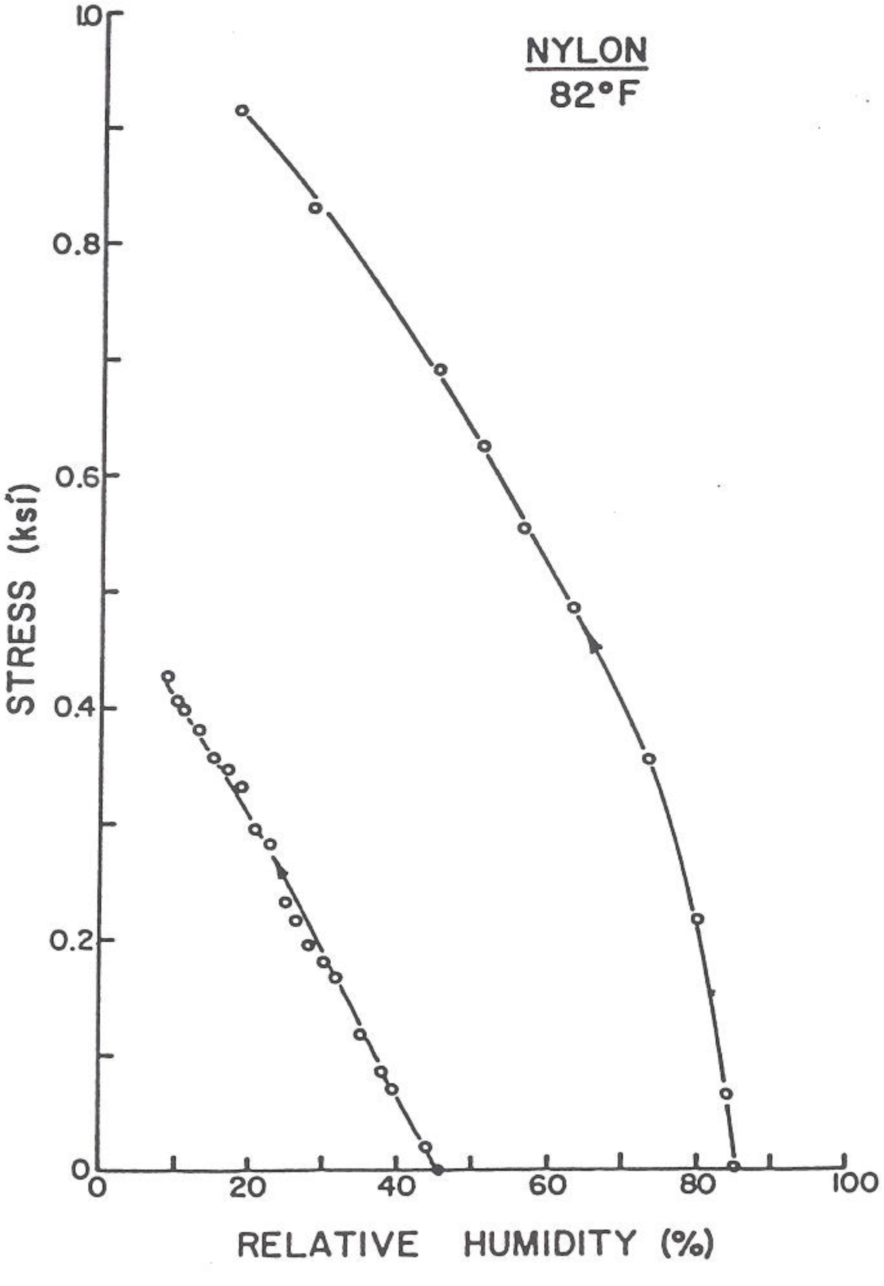

Fig. 17 Effect of changes in RH on stress of restrained nylon specimens

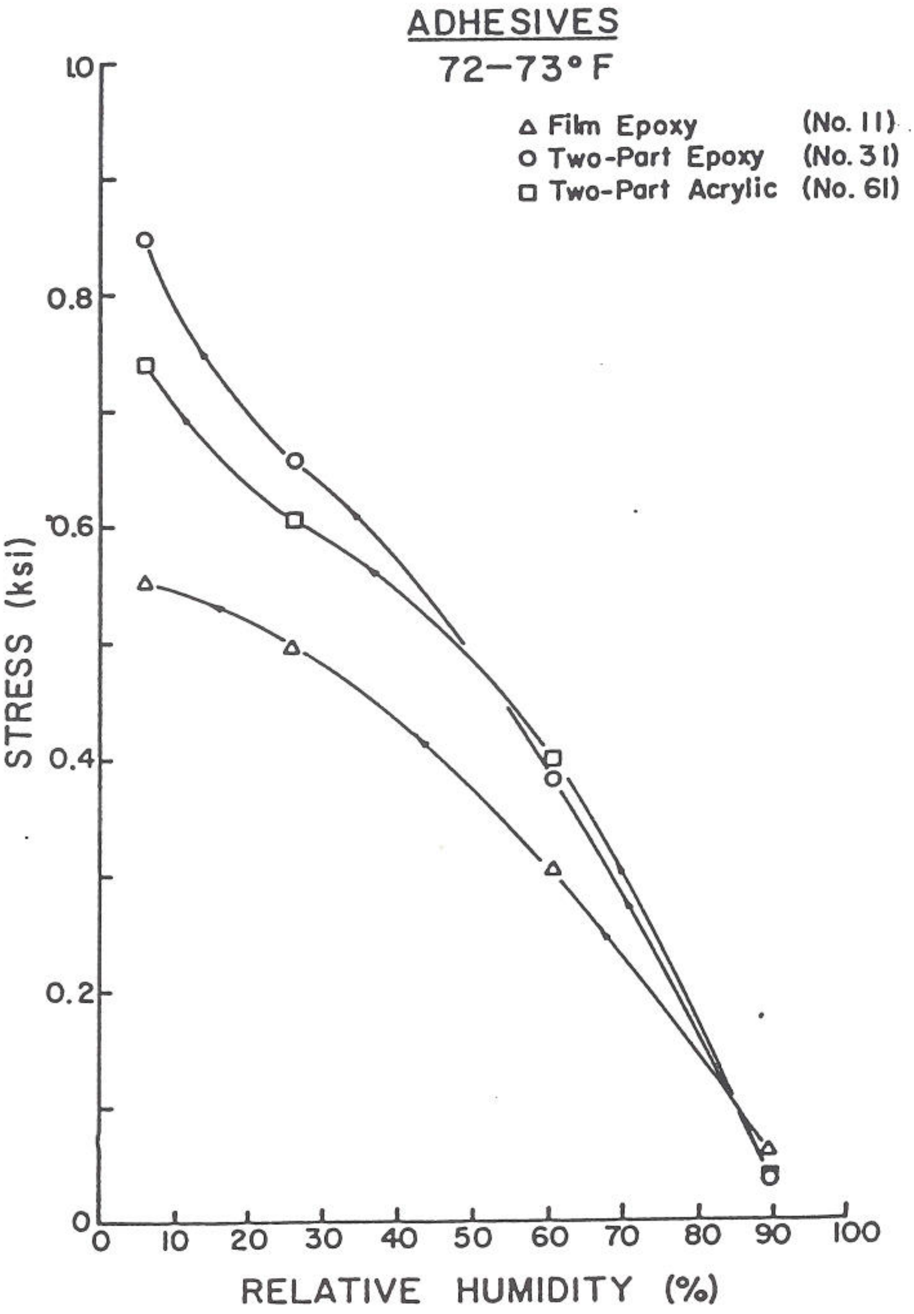

Fig. 18 Effect of changes in RH on stress of restrained adhesive specimens

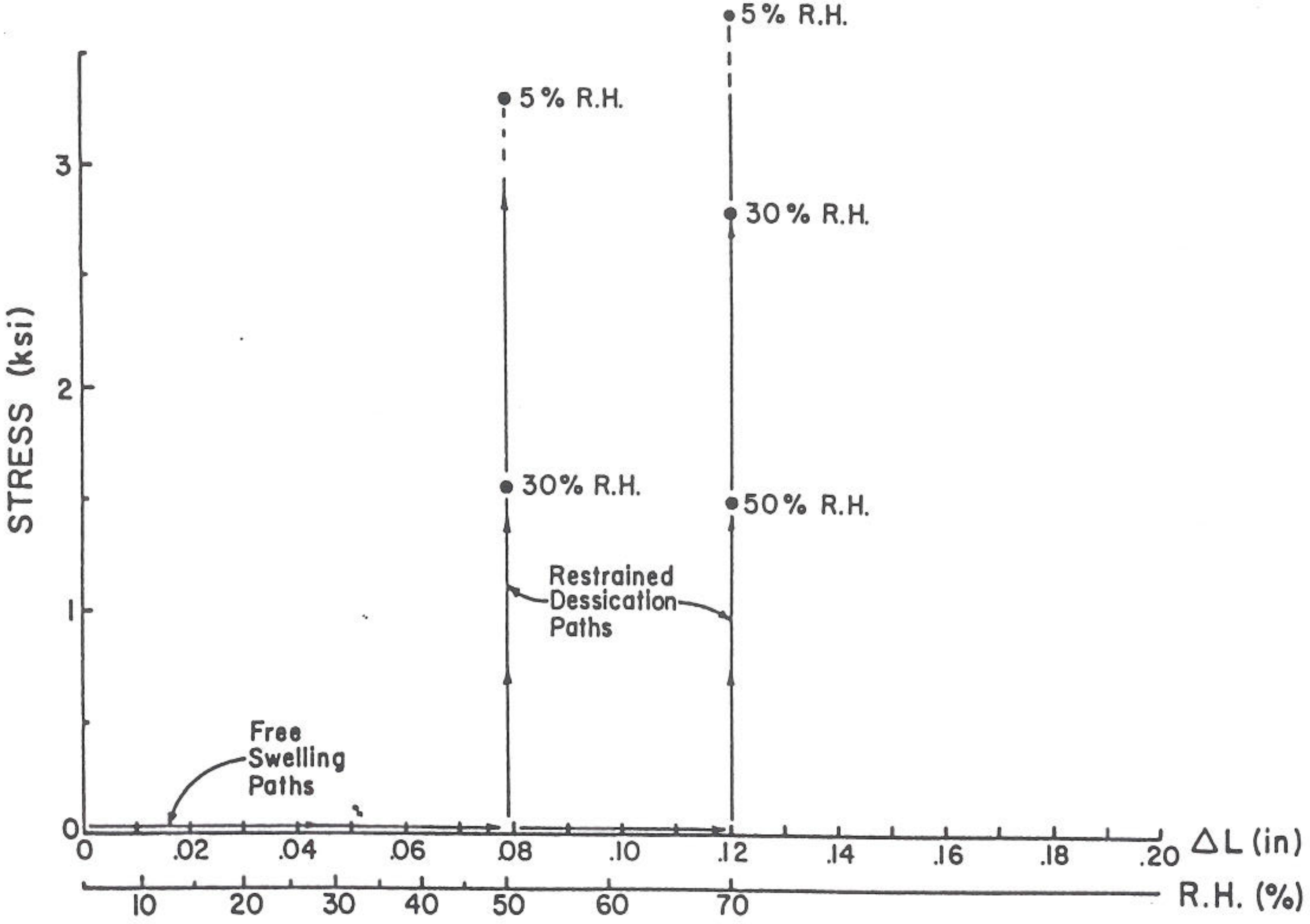

Fig. 20 Equilibrium stress-elongation curves for collagen subjected to environmental loading at 82°F

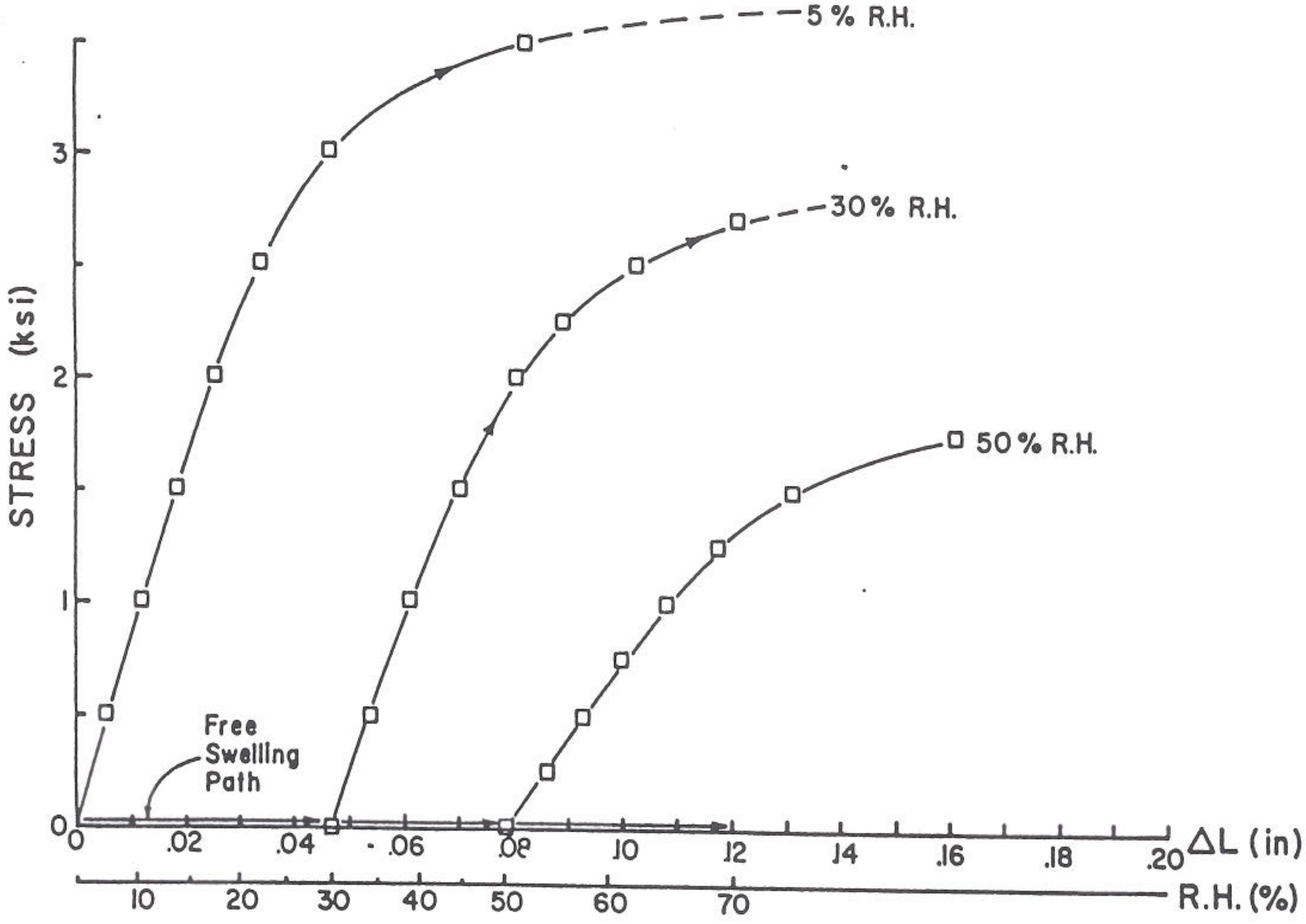

Fig. 19 Equilibrium stress-elongation curves for collagen subjected to tensile loading at 82°F

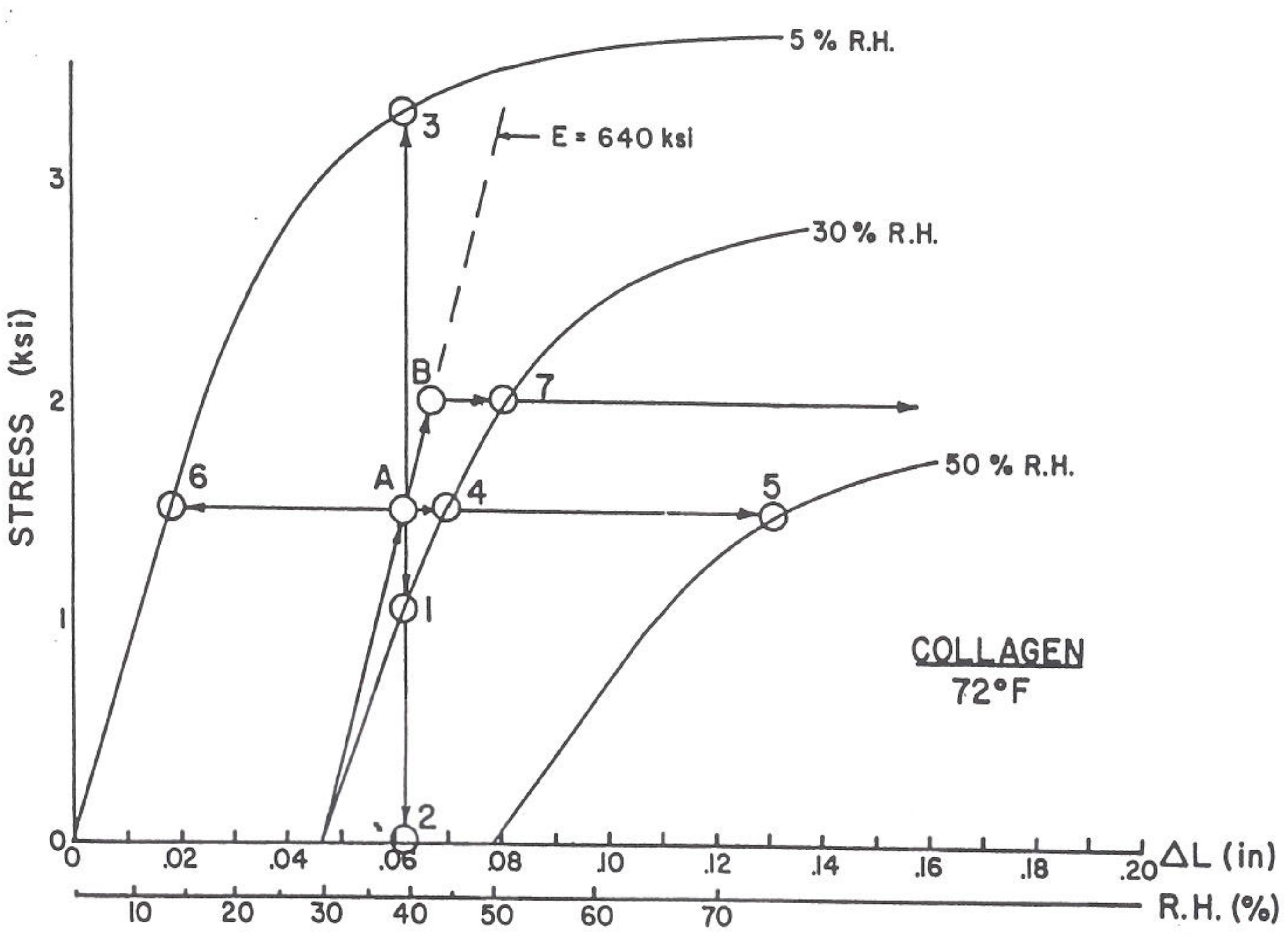

Fig. 22 Illustration of performance under constant stress and fixed length loading

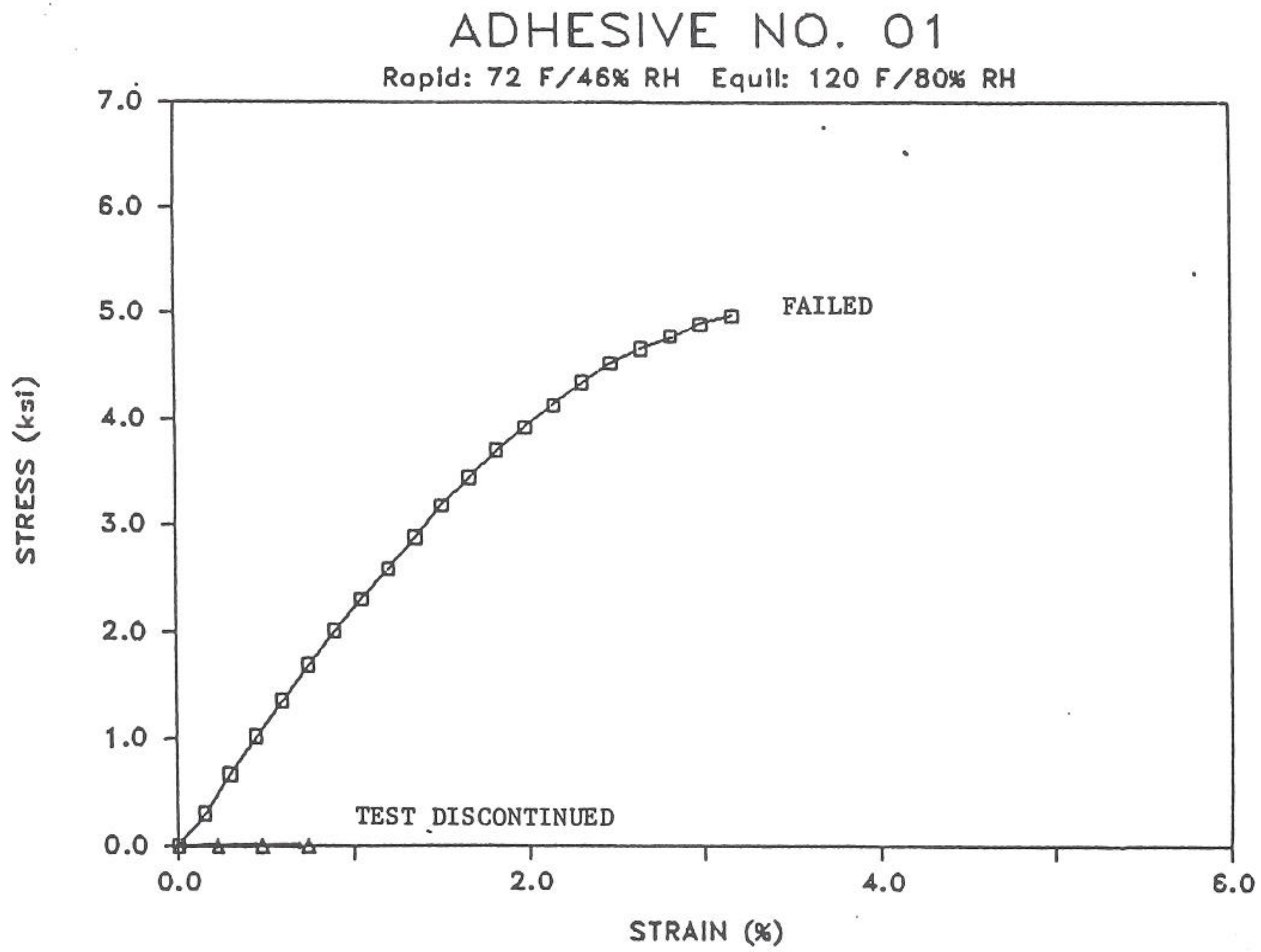

Fig. 23 Screening test for tw0-part epoxy adhesive cured 2 hours at 160°F

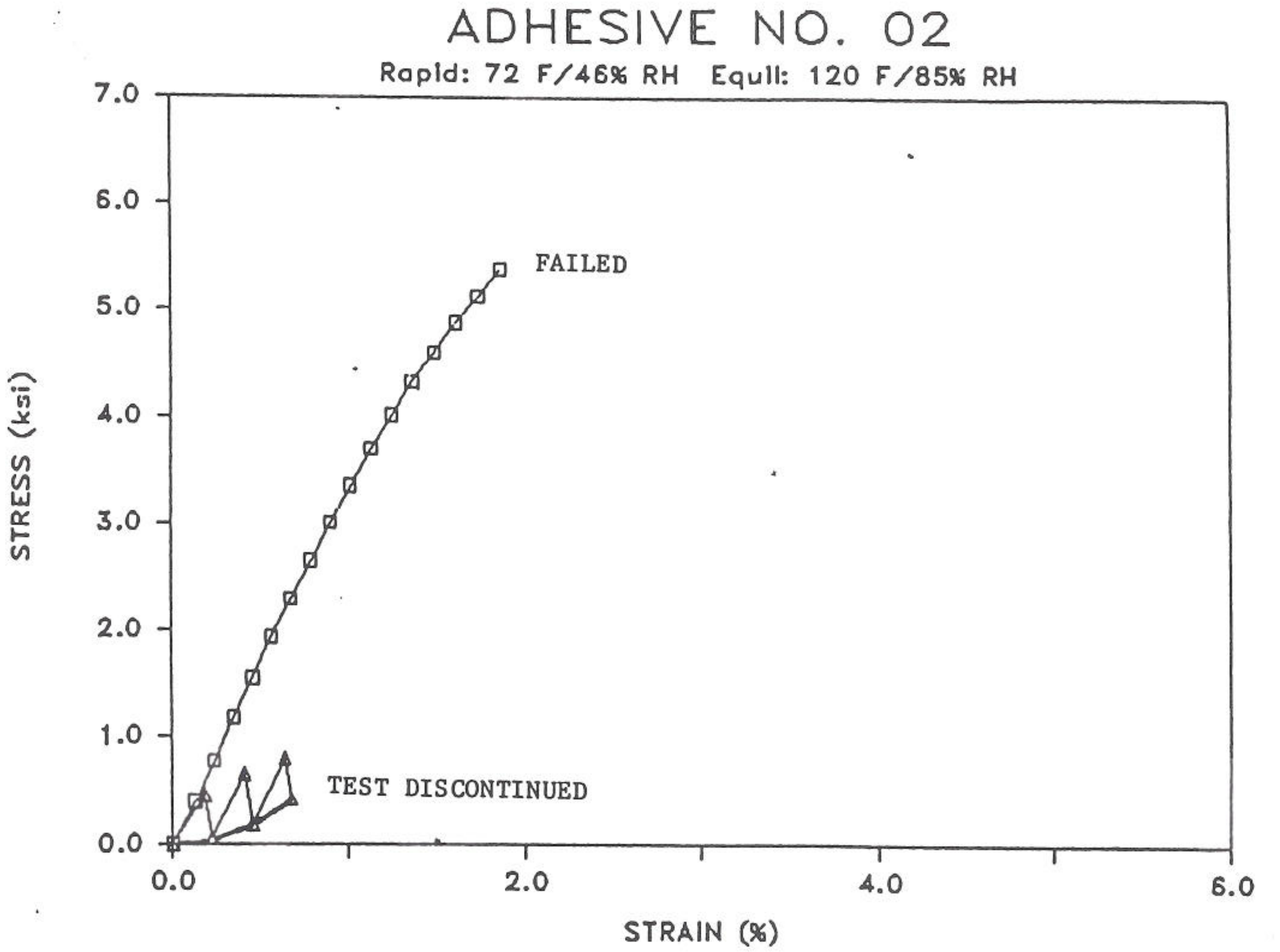

Fig. 24 Screening test for film epoxy adhesive cured 80 minutes at 250°F

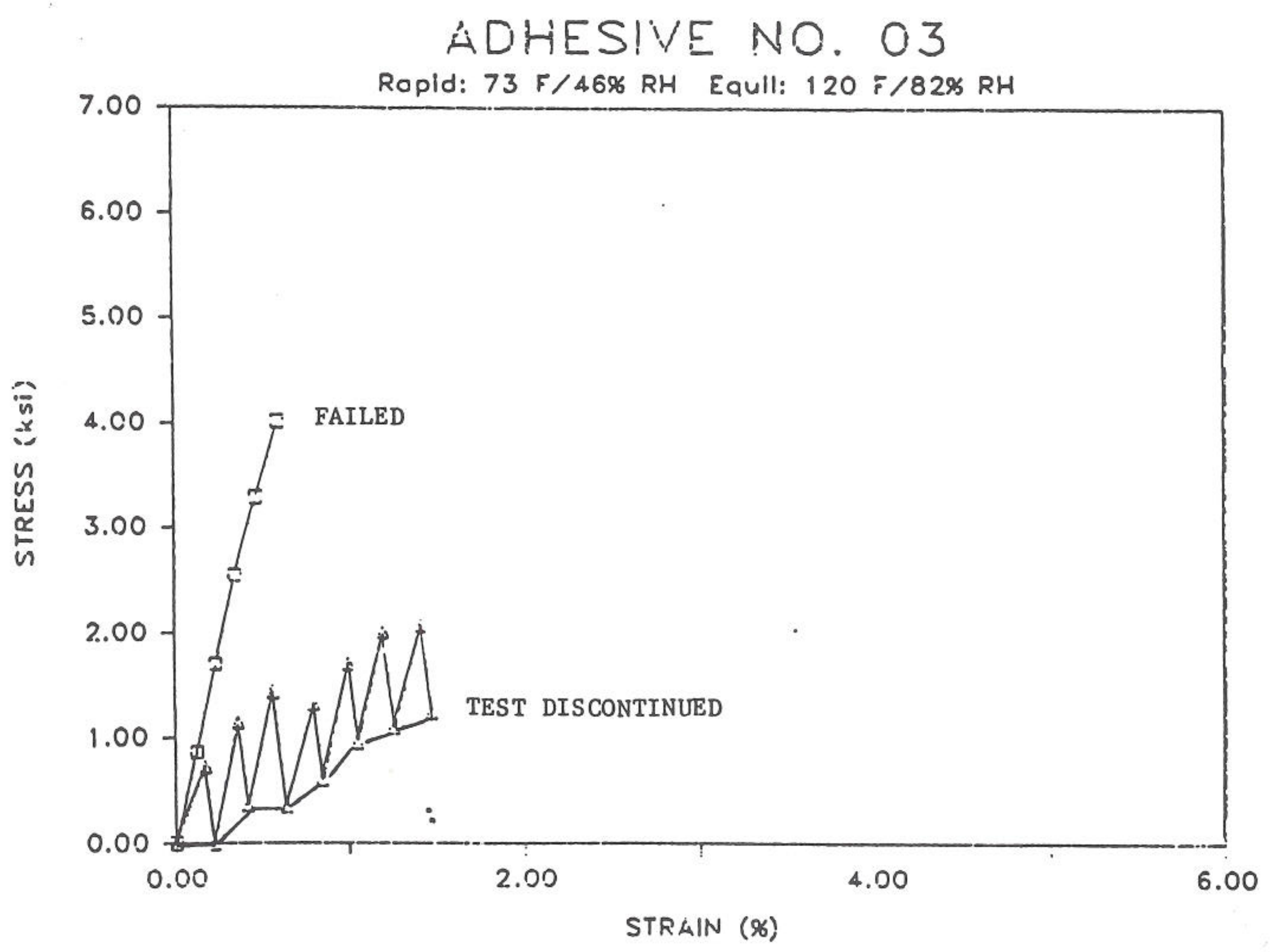

Fig. 25 Screening test for film epoxy adhesive cured 75 minutes at 350°F

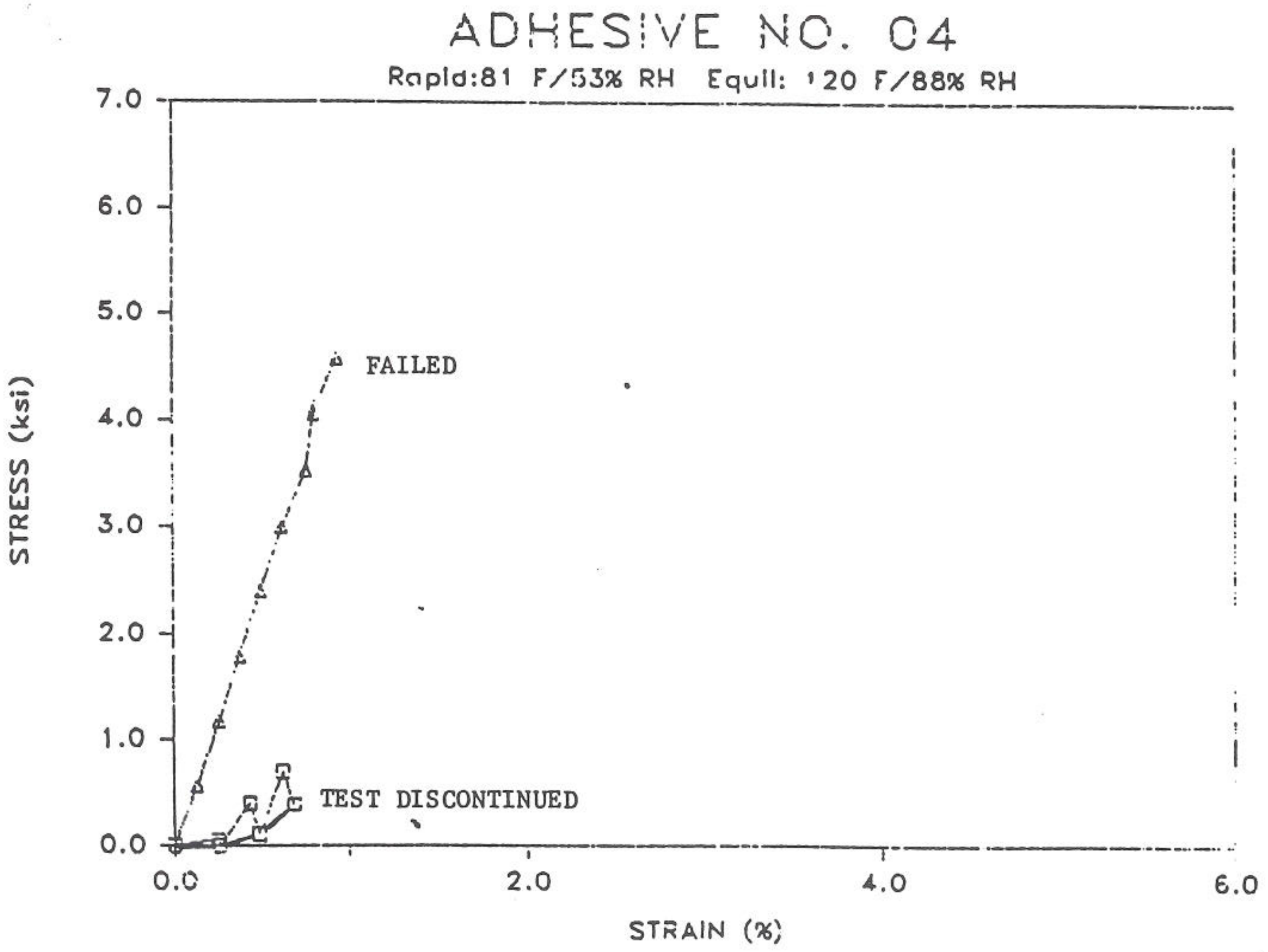

Fig. 26 Screening test for two-part epoxy adhesive cured 1 hour at 200°F

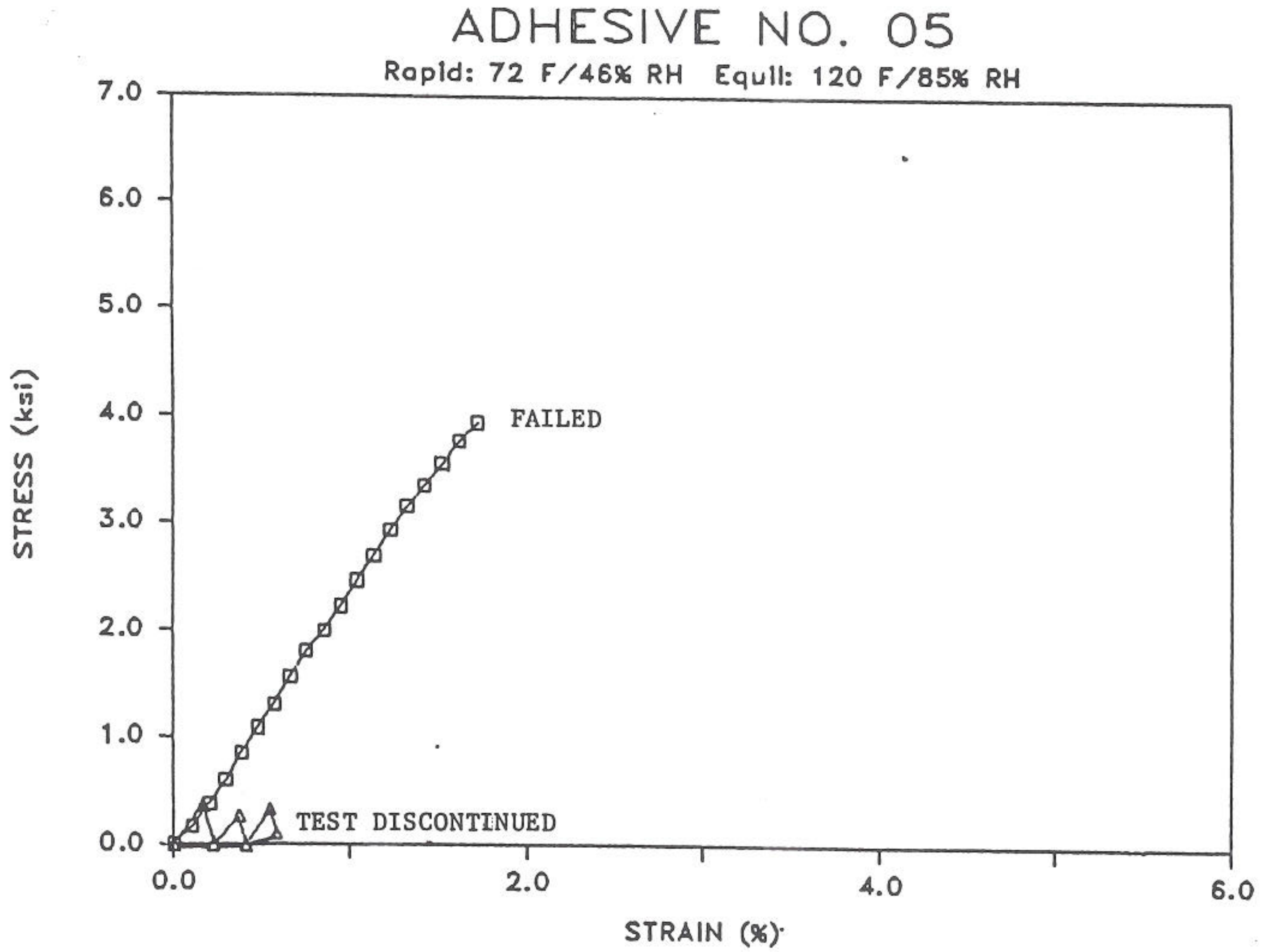

Fig. 27 Screening test for film epoxy adhesive without scrim cured 80 minutes at 250°F

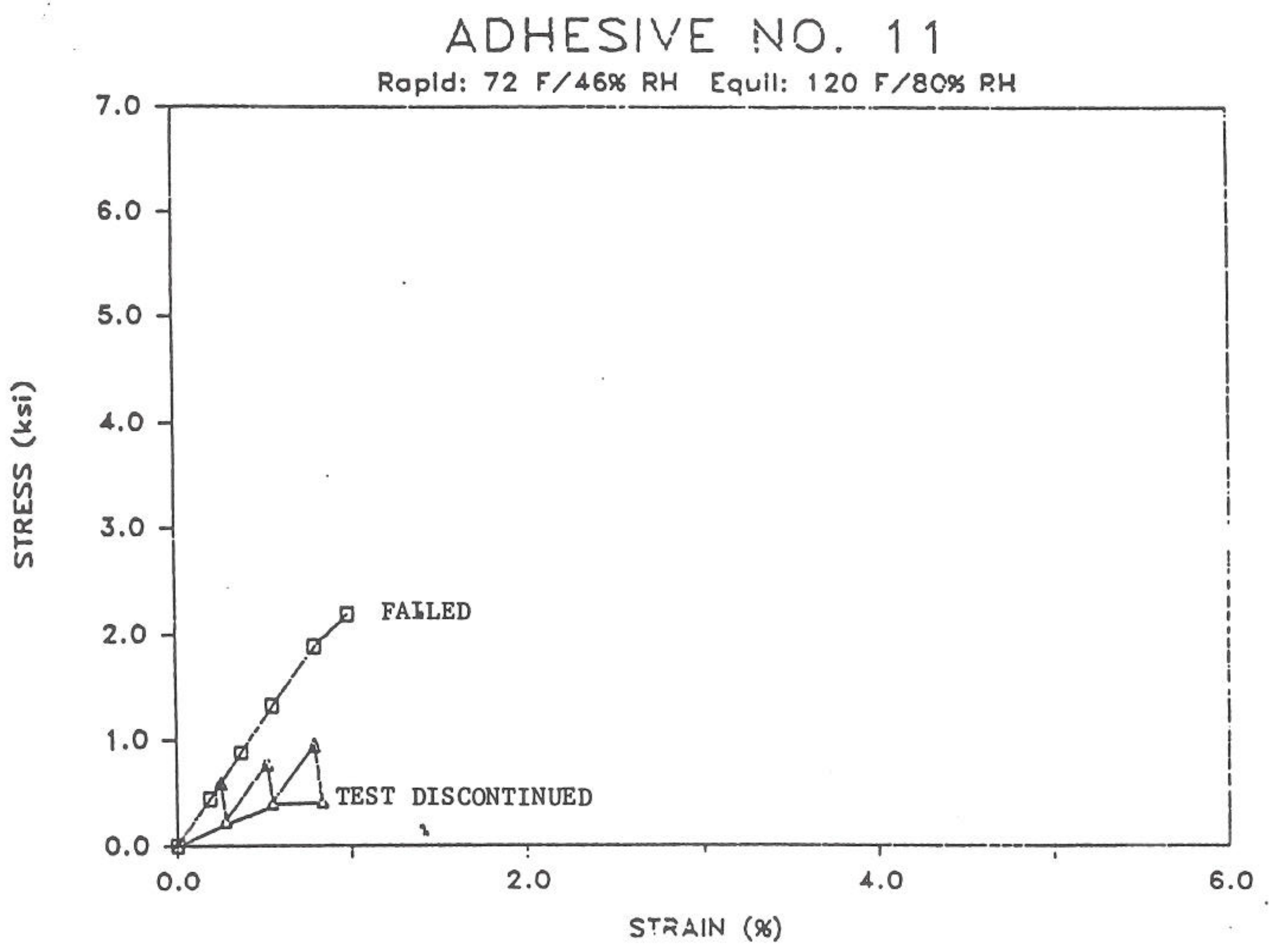

Fig. 28 Screening test for film epoxy adhesive cured 65 minutes at 250°F

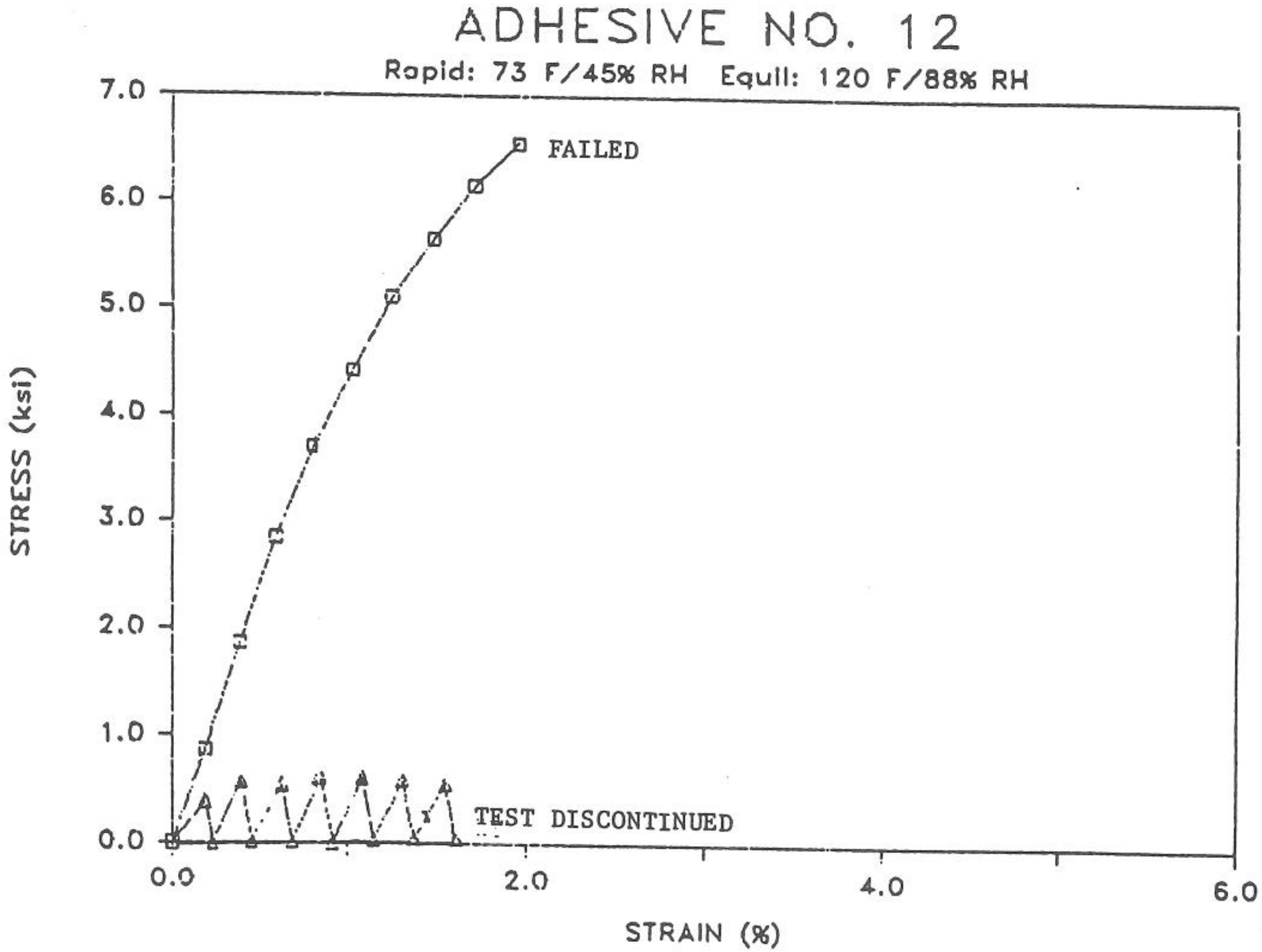

Fig. 29 Screening test for one-part epoxy adhesive cured 60 minutes at 300°F

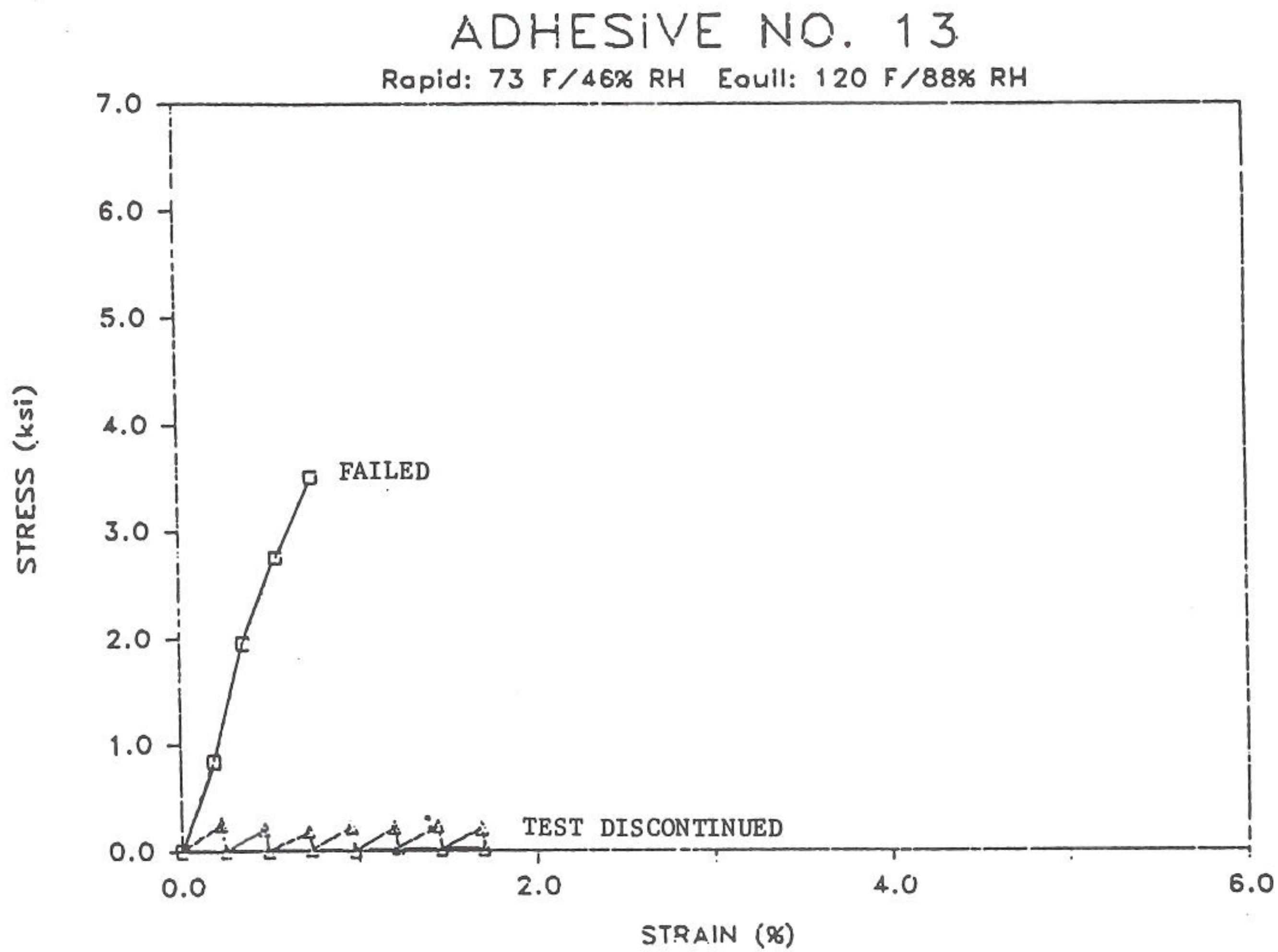

Fig. 30 Screening test for one-part epoxy adhesive cured 40 minutes at 250°F

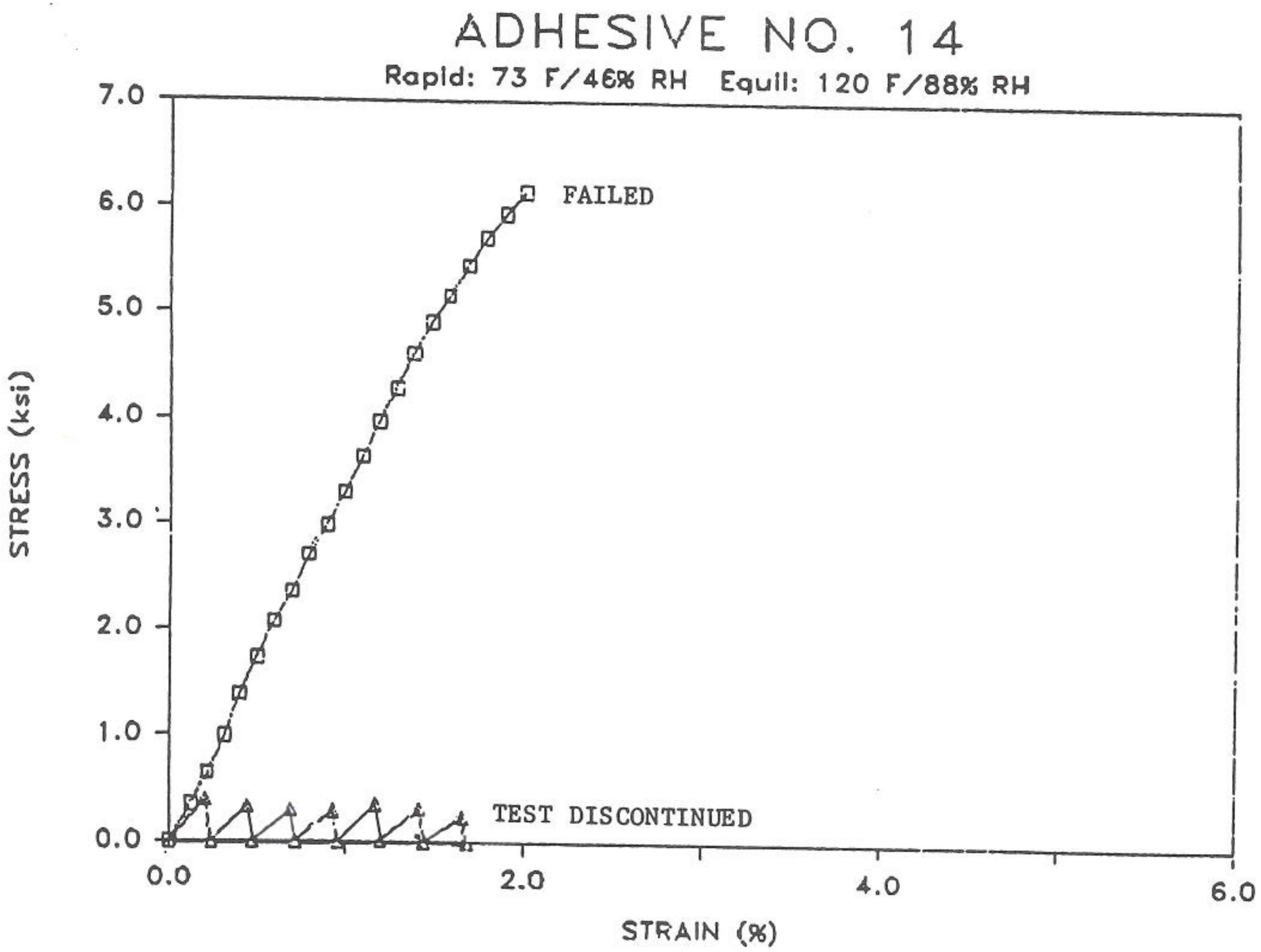

Fig. 31 Screening test for one-part epoxy adhesive cured 80 minutes at 250^oF

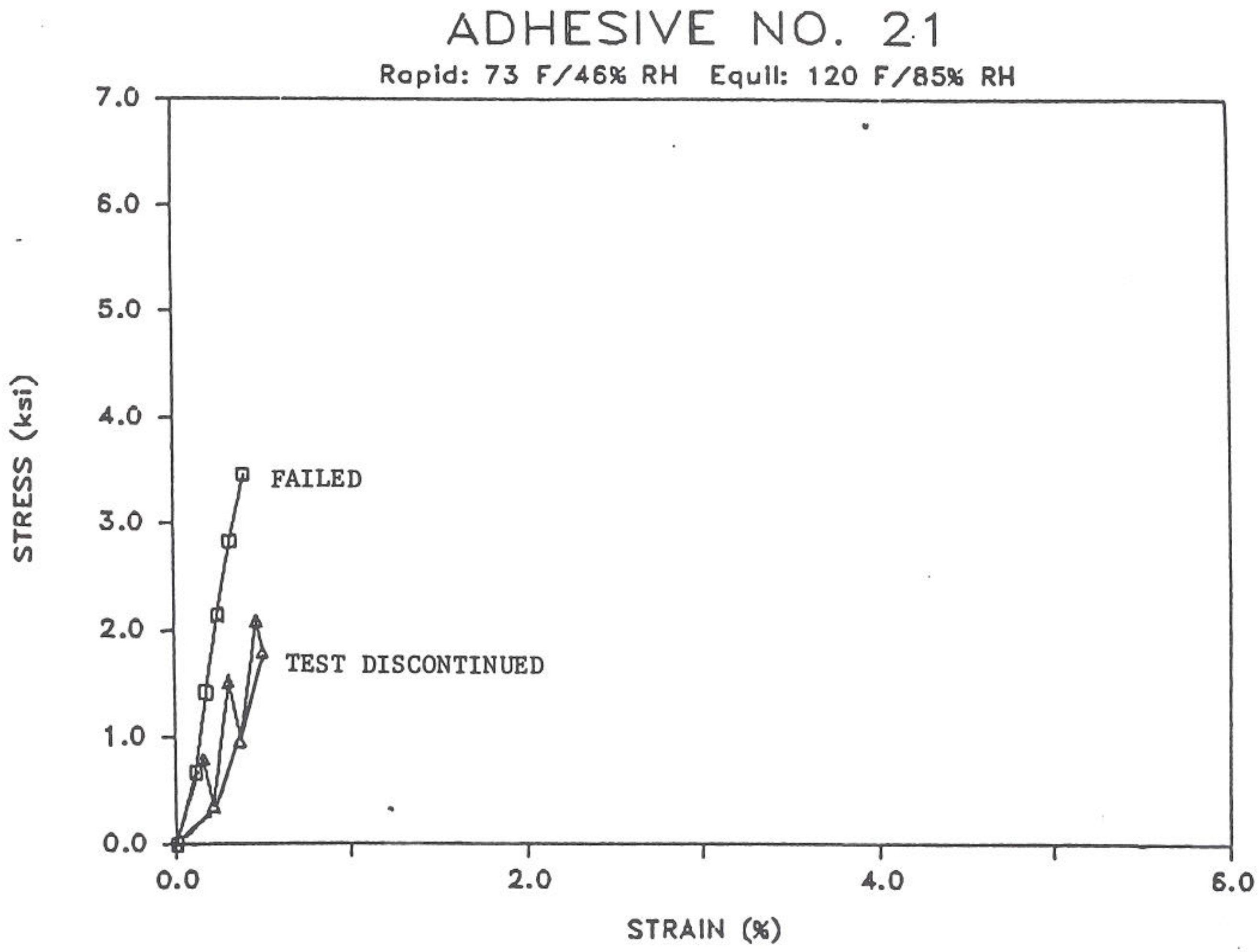

Fig. 32 Screening test for two-part epoxy adhesive cured 4 days at 80°F

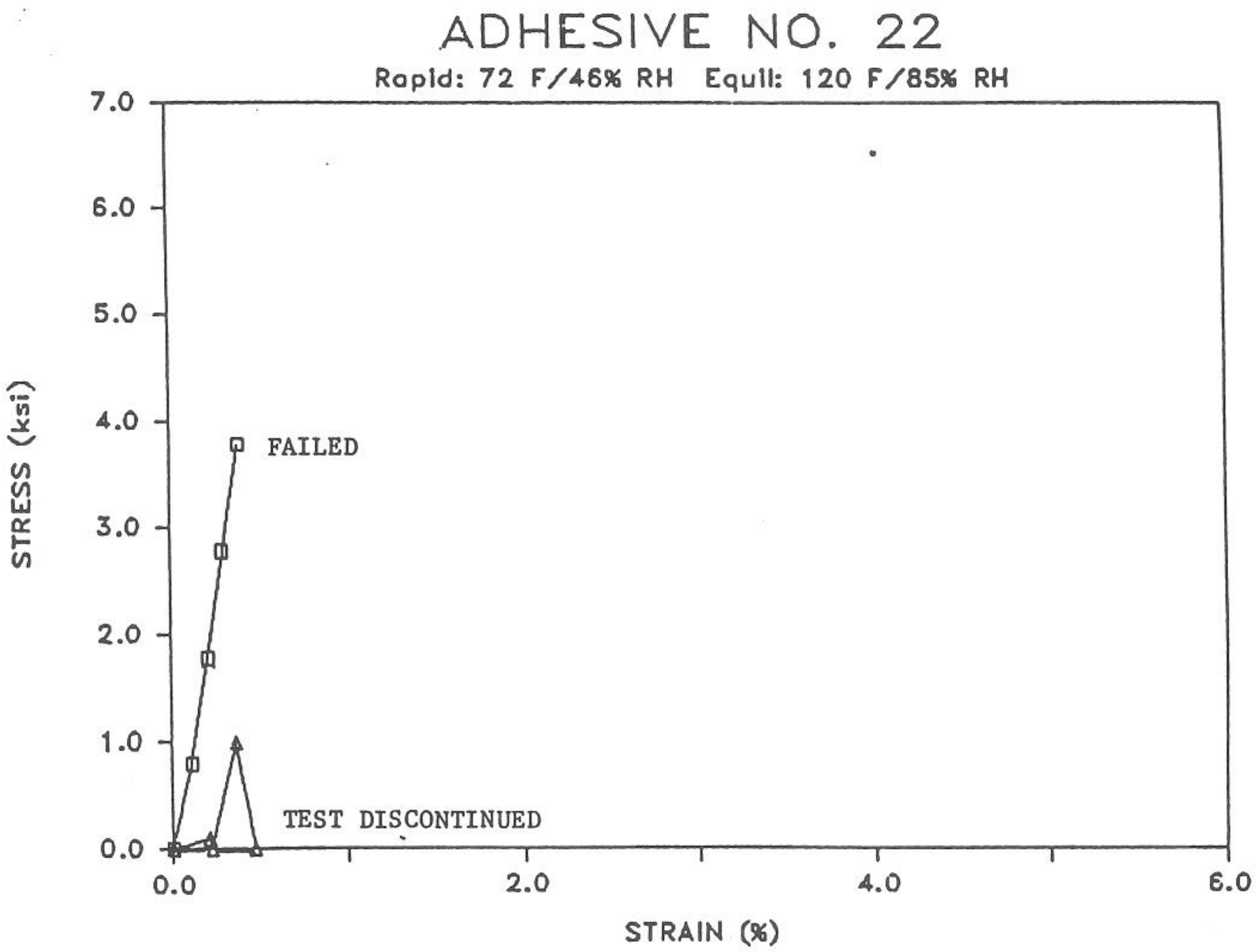

Fig. 33 Screening test for two-part epoxy adhesive cured 2 hours at 260°F

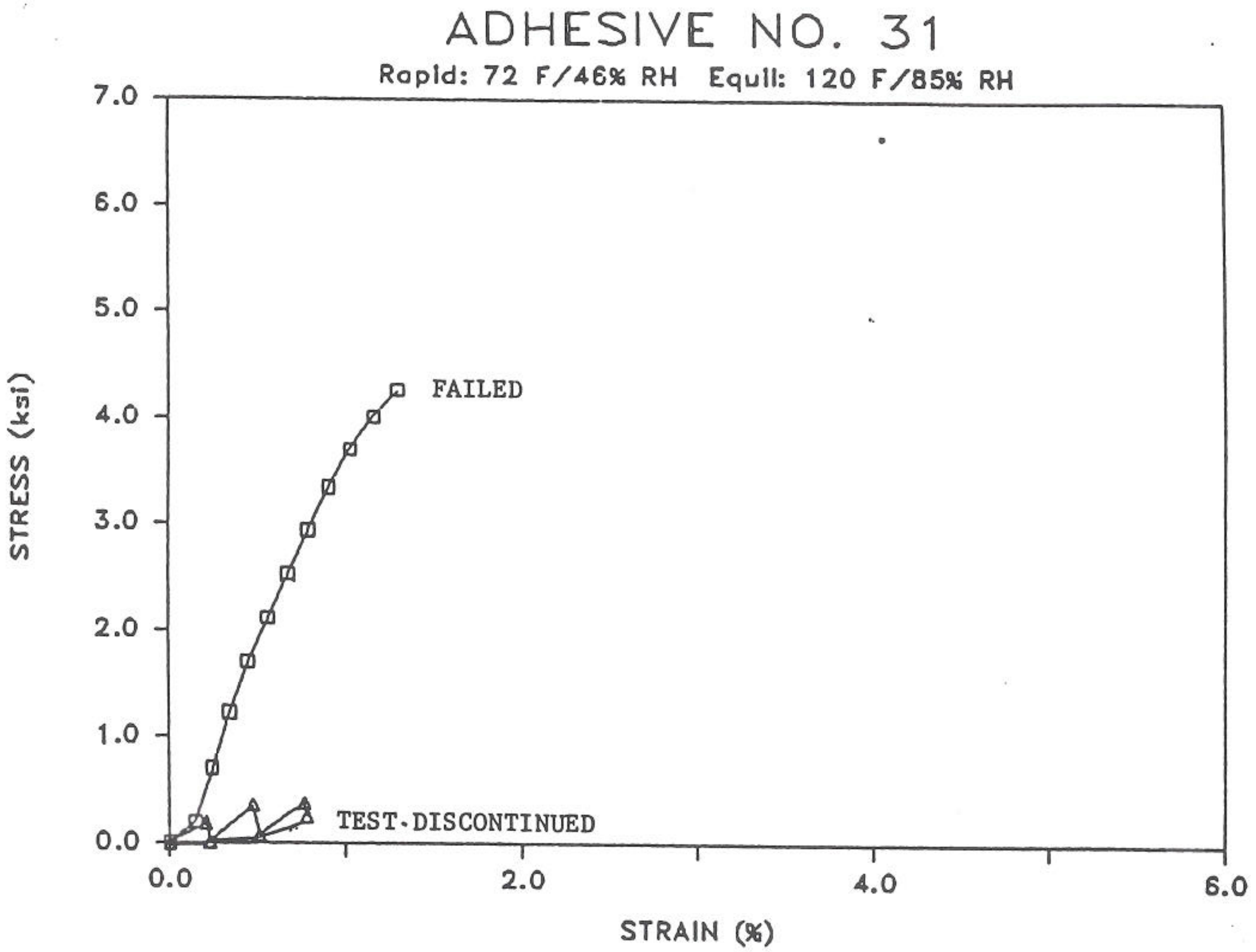

Fig. 34 Screening test for two-part epoxy adhesive cured 4 days at 80^oF

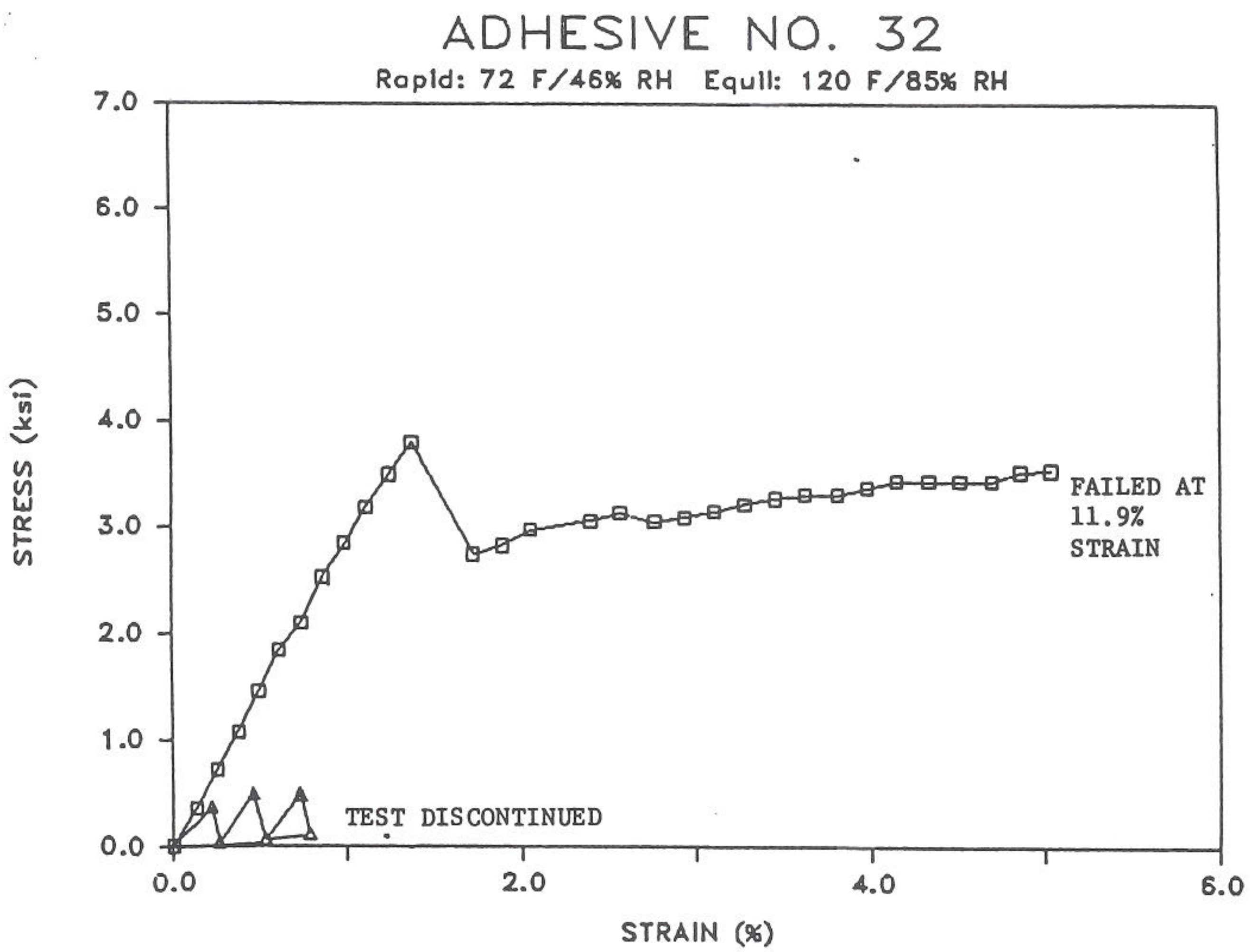

Fig. 35 Screening test for two-part epoxy adhesive cured 4 days at 80°F

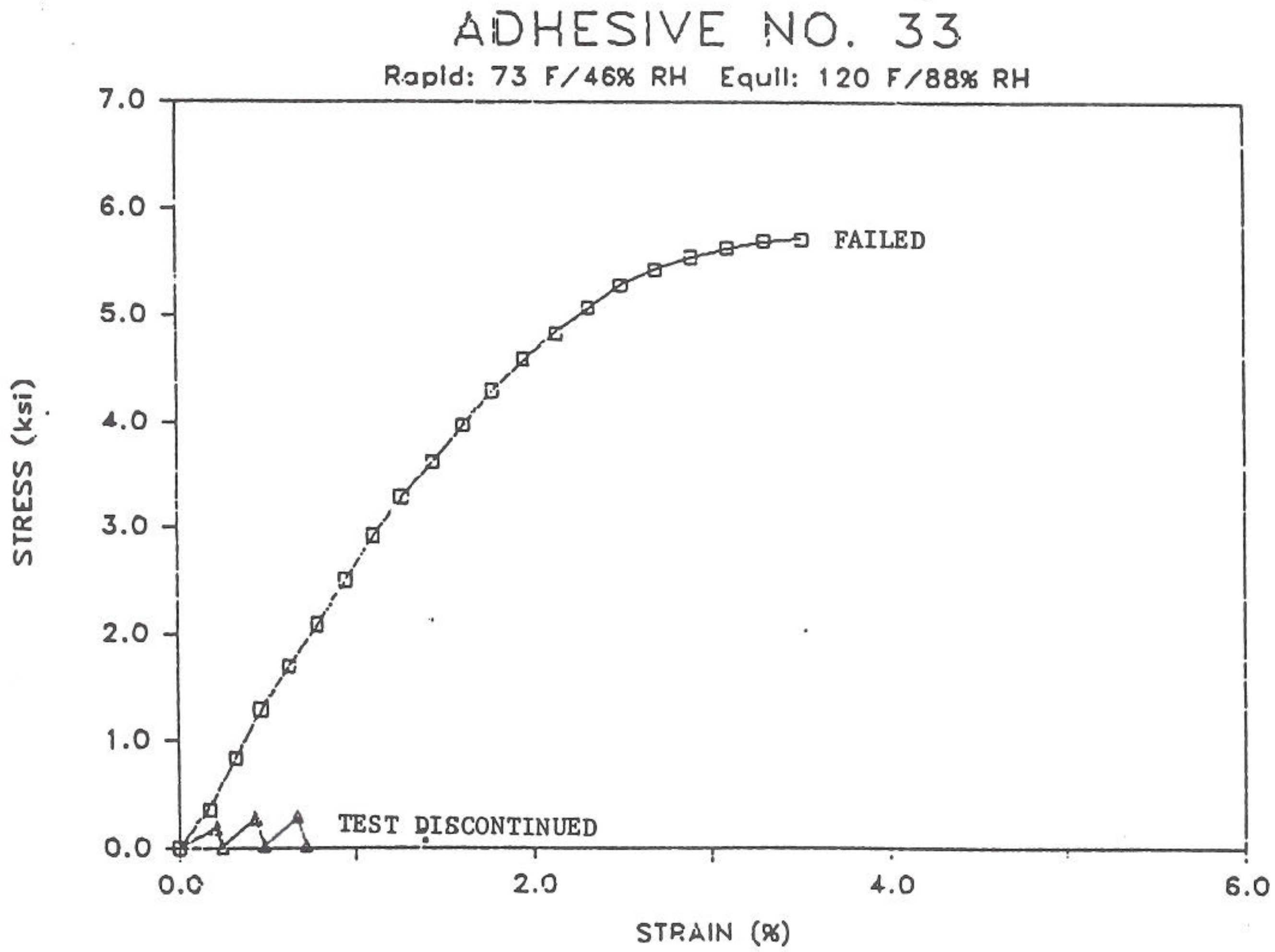

Fig. 36 Screening test for two-part epoxy adhesive cured 38 minutes at 259°F

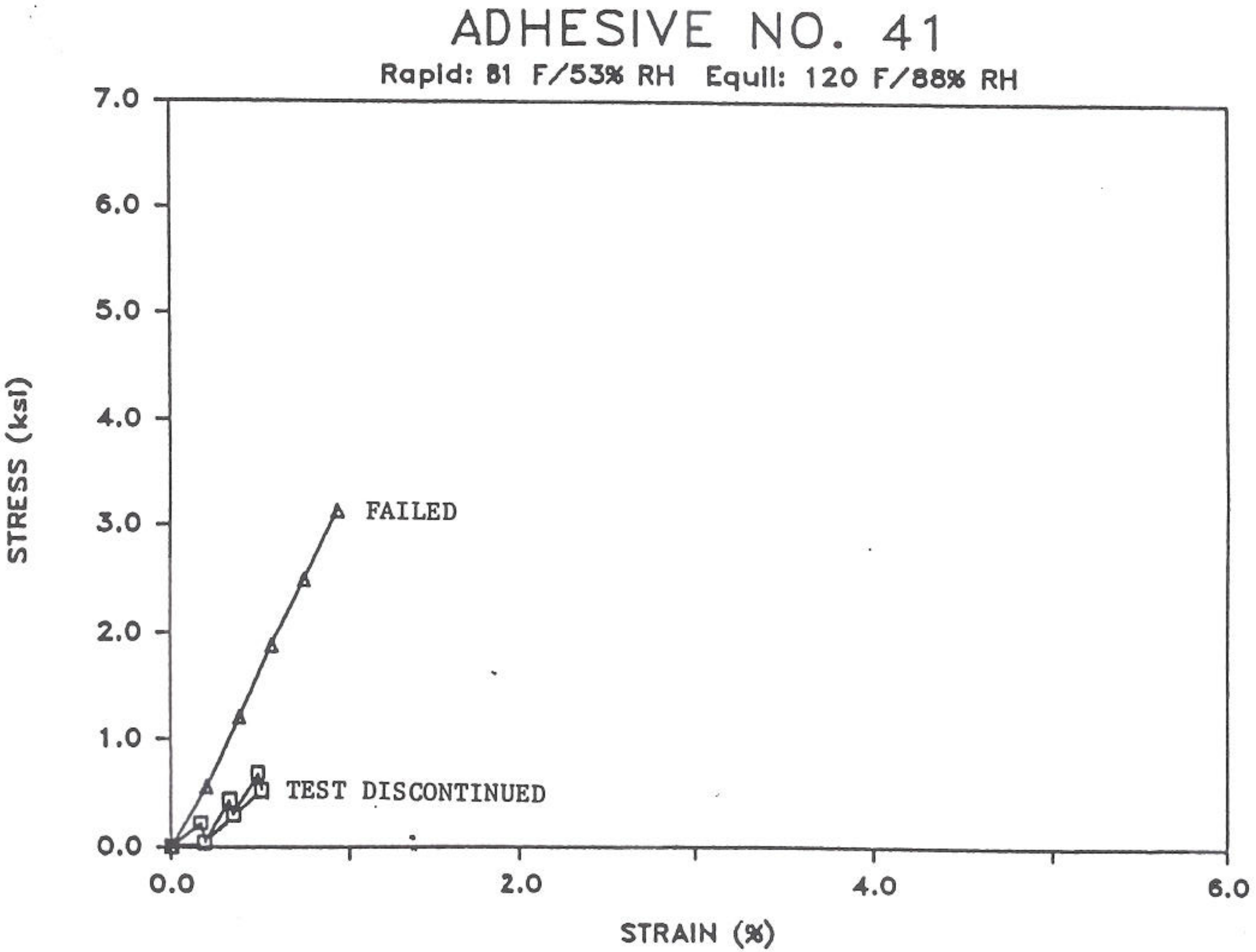

Fig. 37 Screening test for film epoxy adhesive cured 1 hour at 350°F

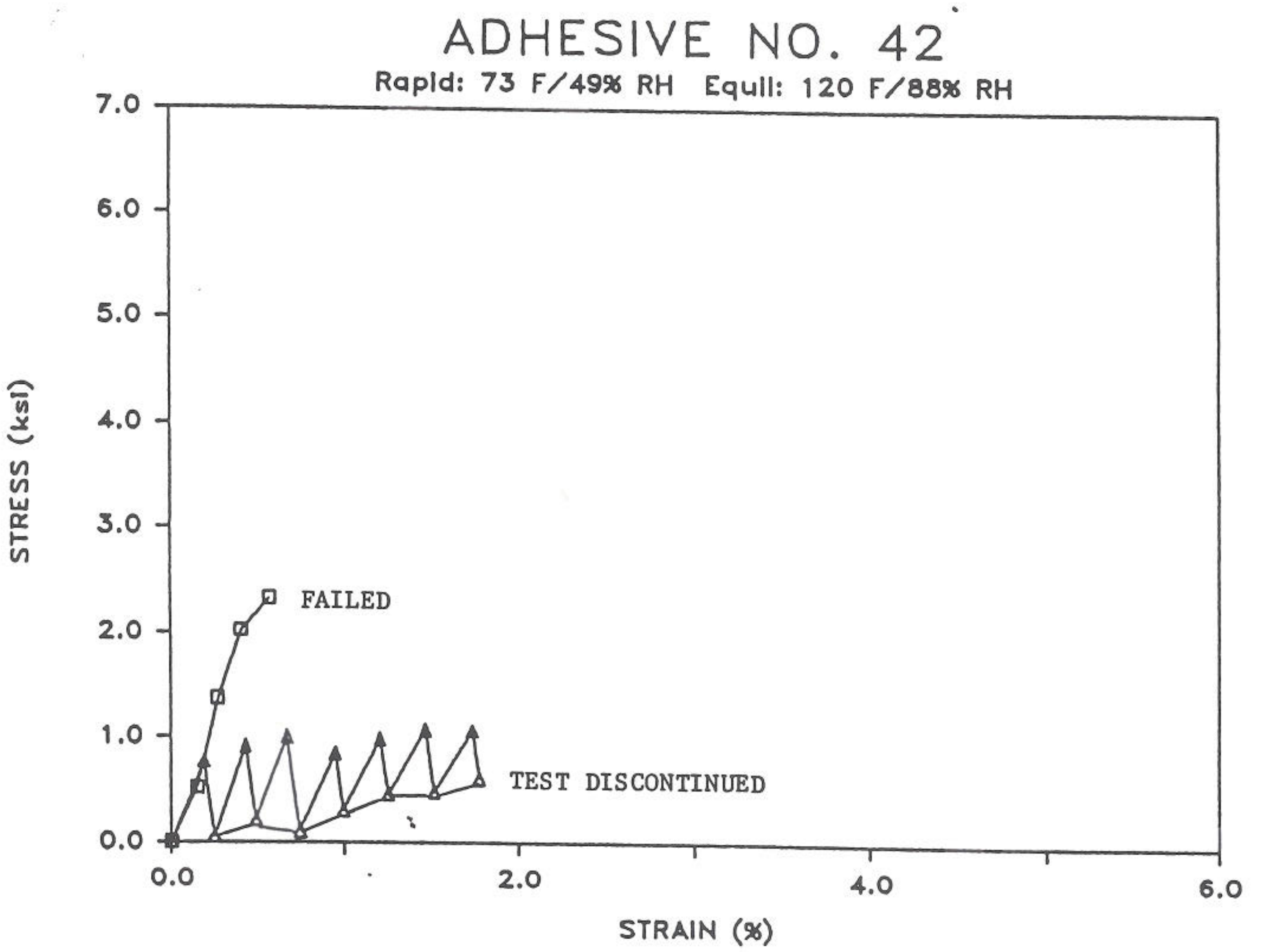

Fig. 38 Screening test for film epoxy adhesive cured 75 minutes at 350°F

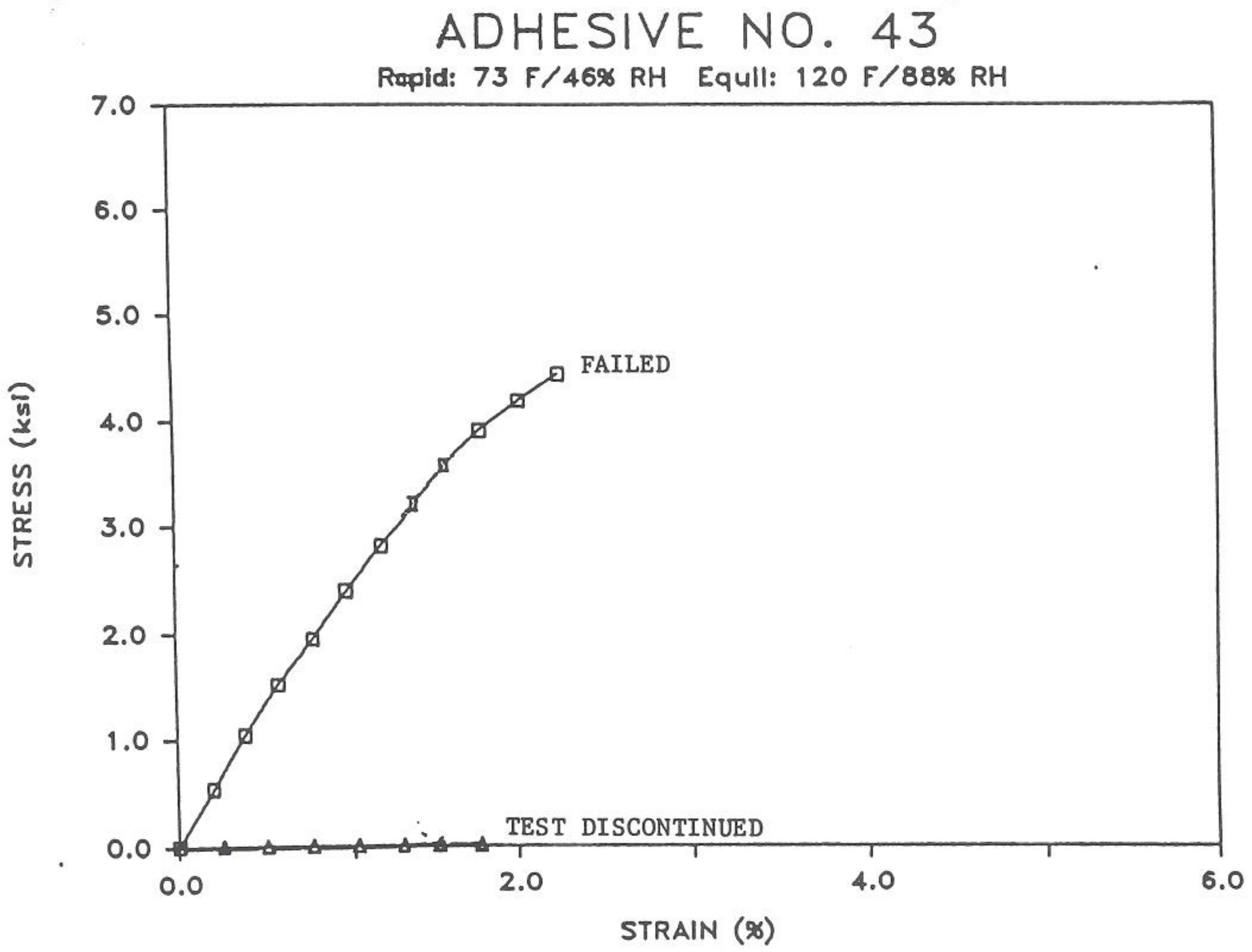

Fig. 39 Screening test for two-part epoxy adhesive cured 60 minutes at 200^oF

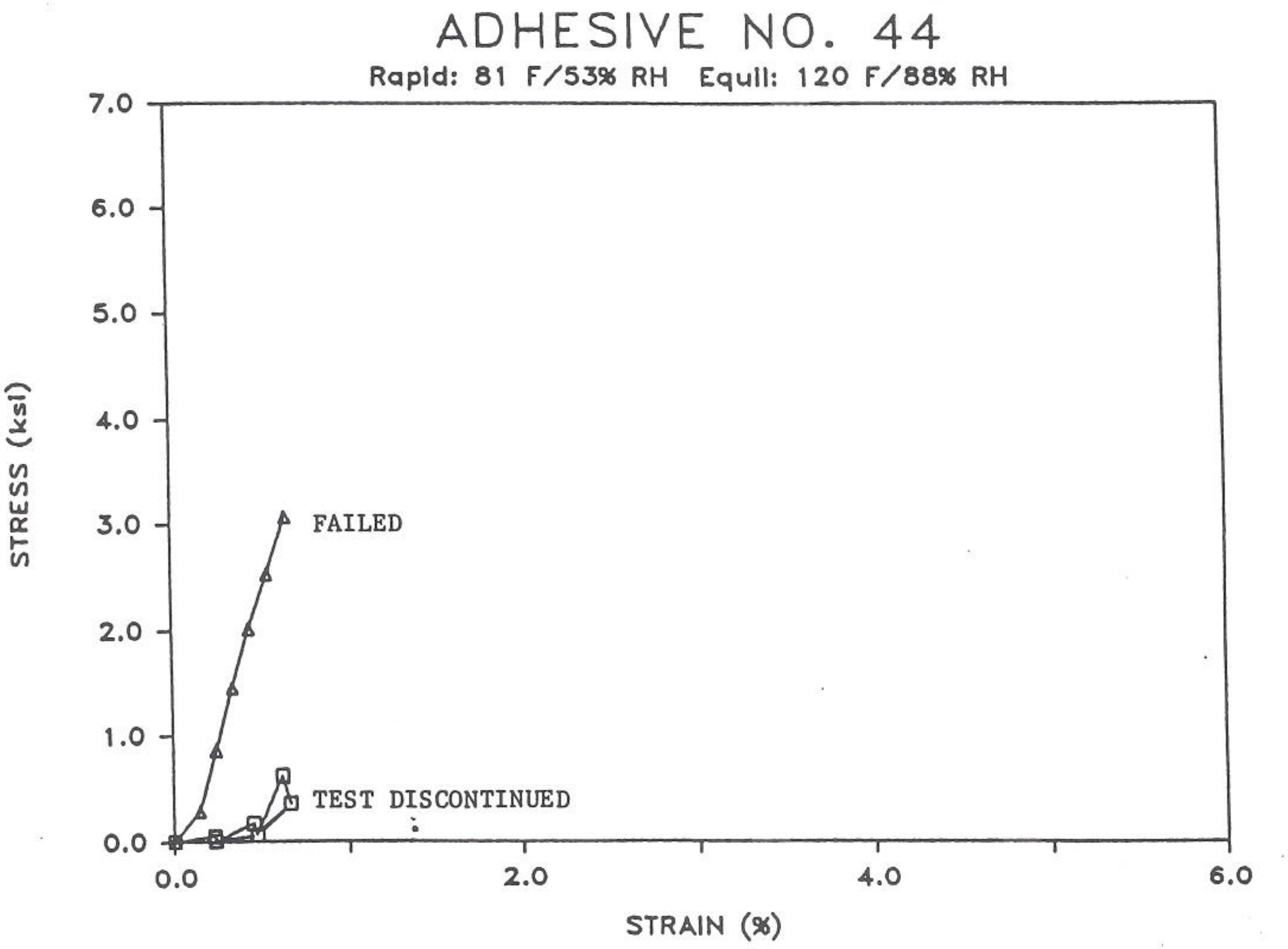

Fig. 40 Screening test for two-part epoxy adhesive cured 1 hour at 200°F

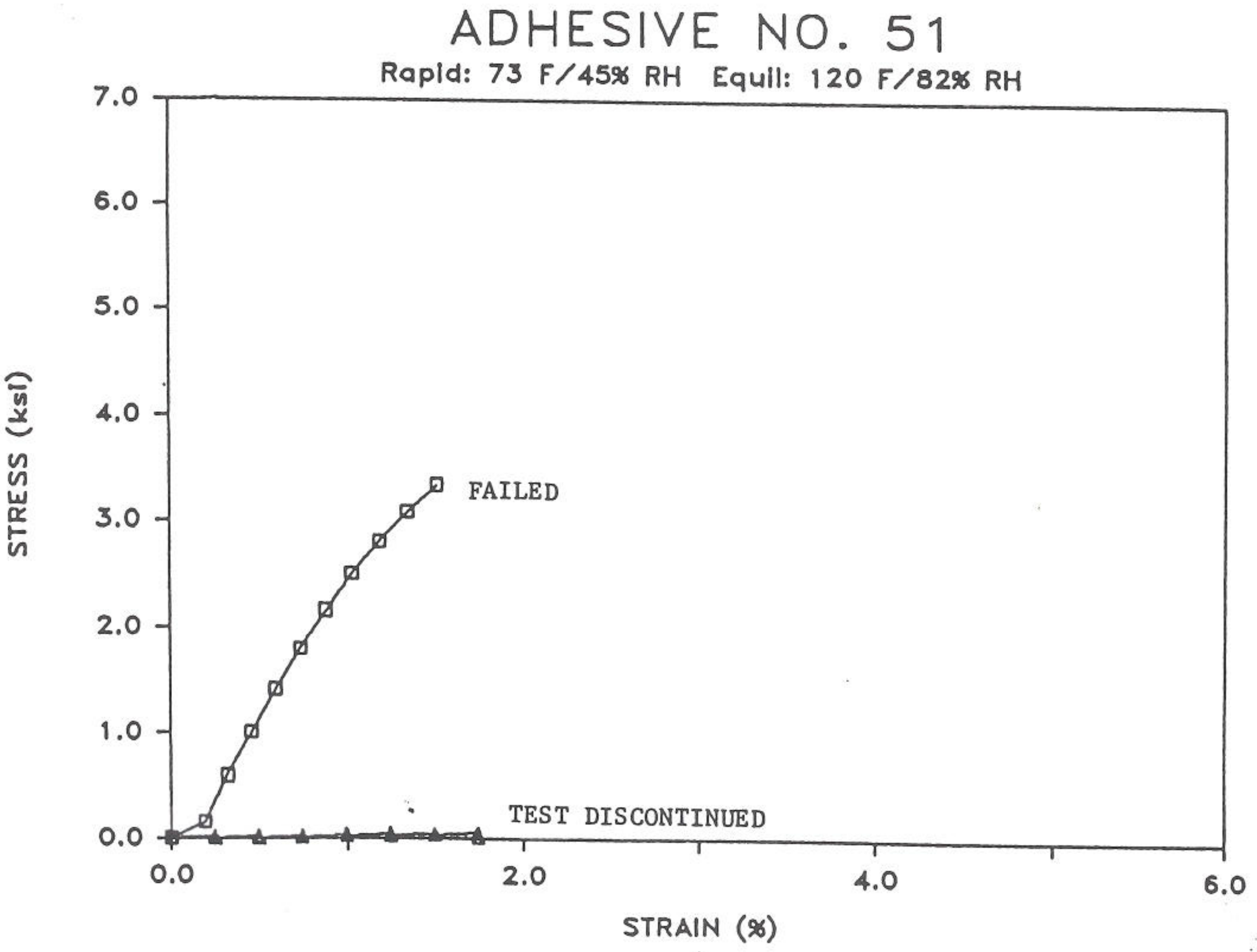

Fig. 41 Screening test for two-part epoxy adhesive cured 48 hours at 78°F

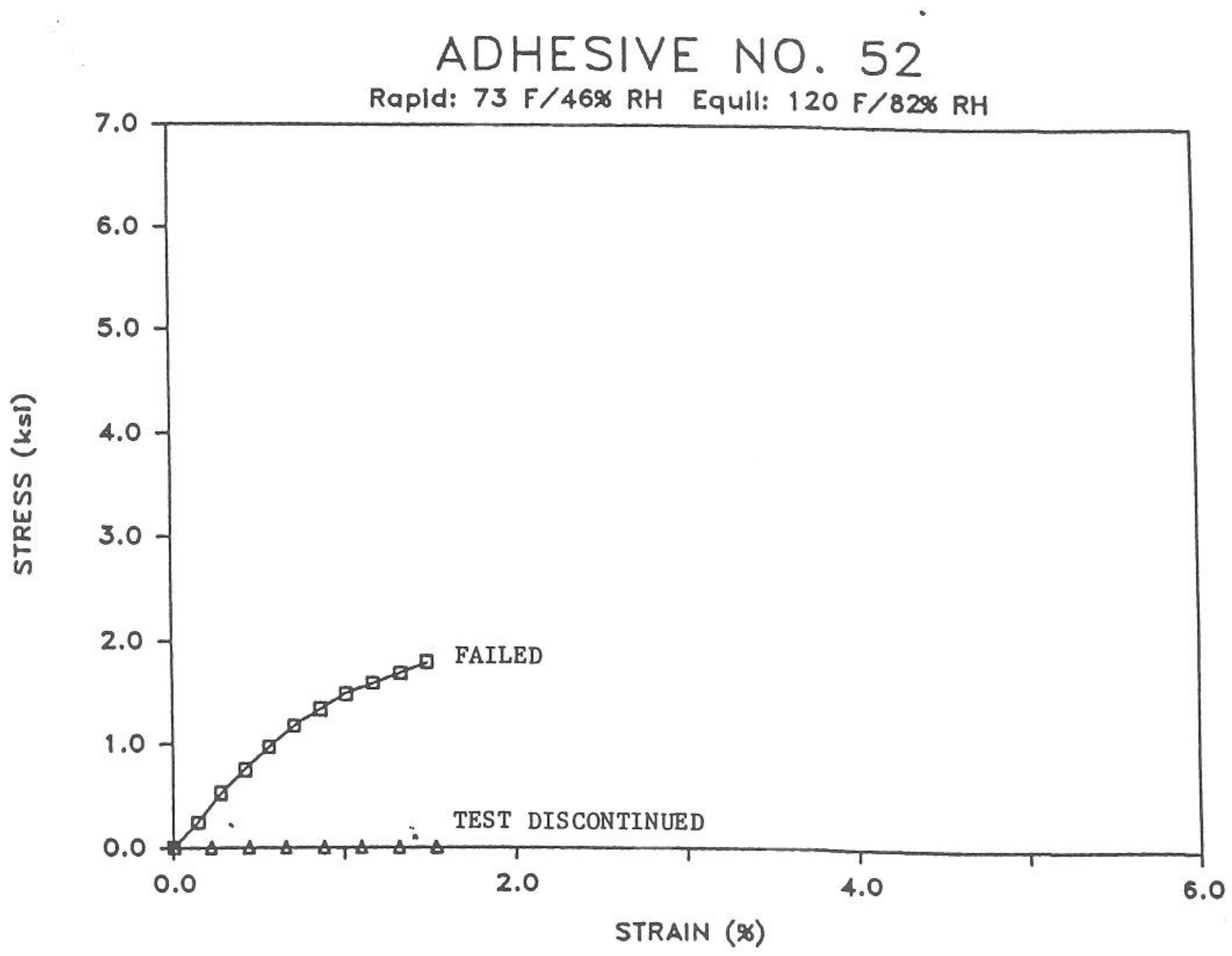

Fig. 42 Screening test for two-part epoxy adhesive cured 48 hours at 78°F

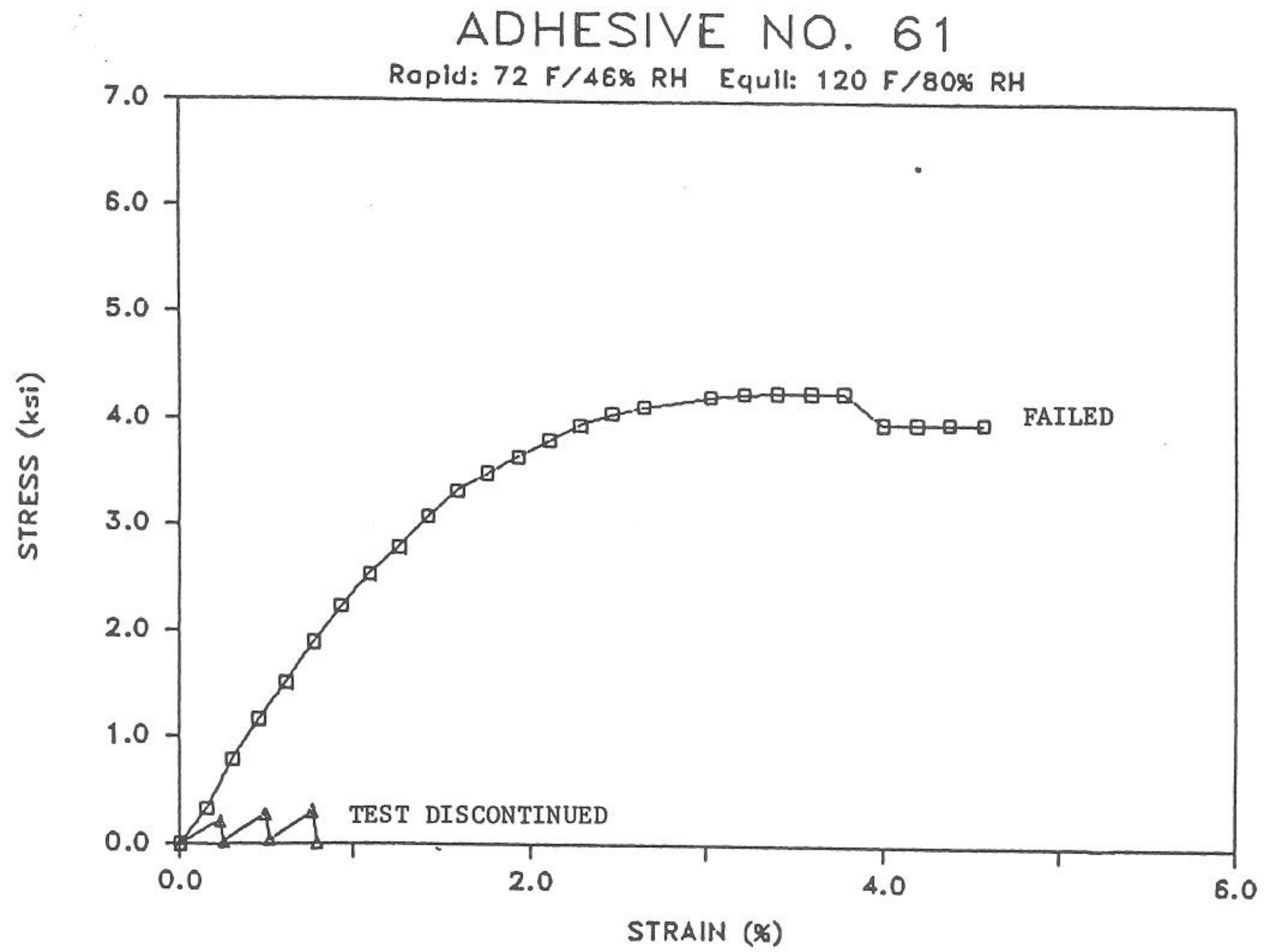

Fig. 43 Screening test for two-part acrylic adhesive cured 24 hours at 78°F

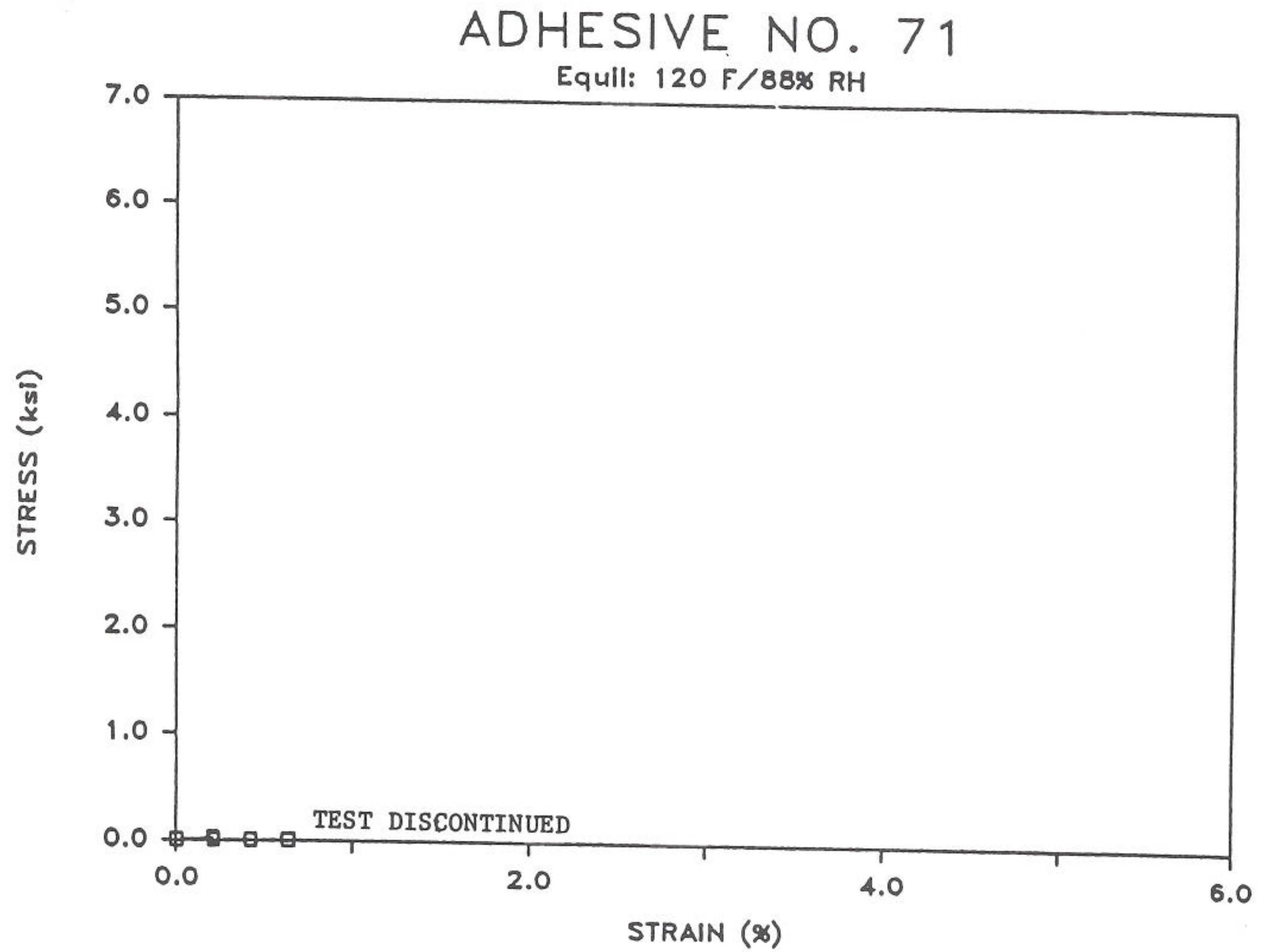

Fig. 44 Screening test for two-part epoxy adhesive cured 4 days at room temperature

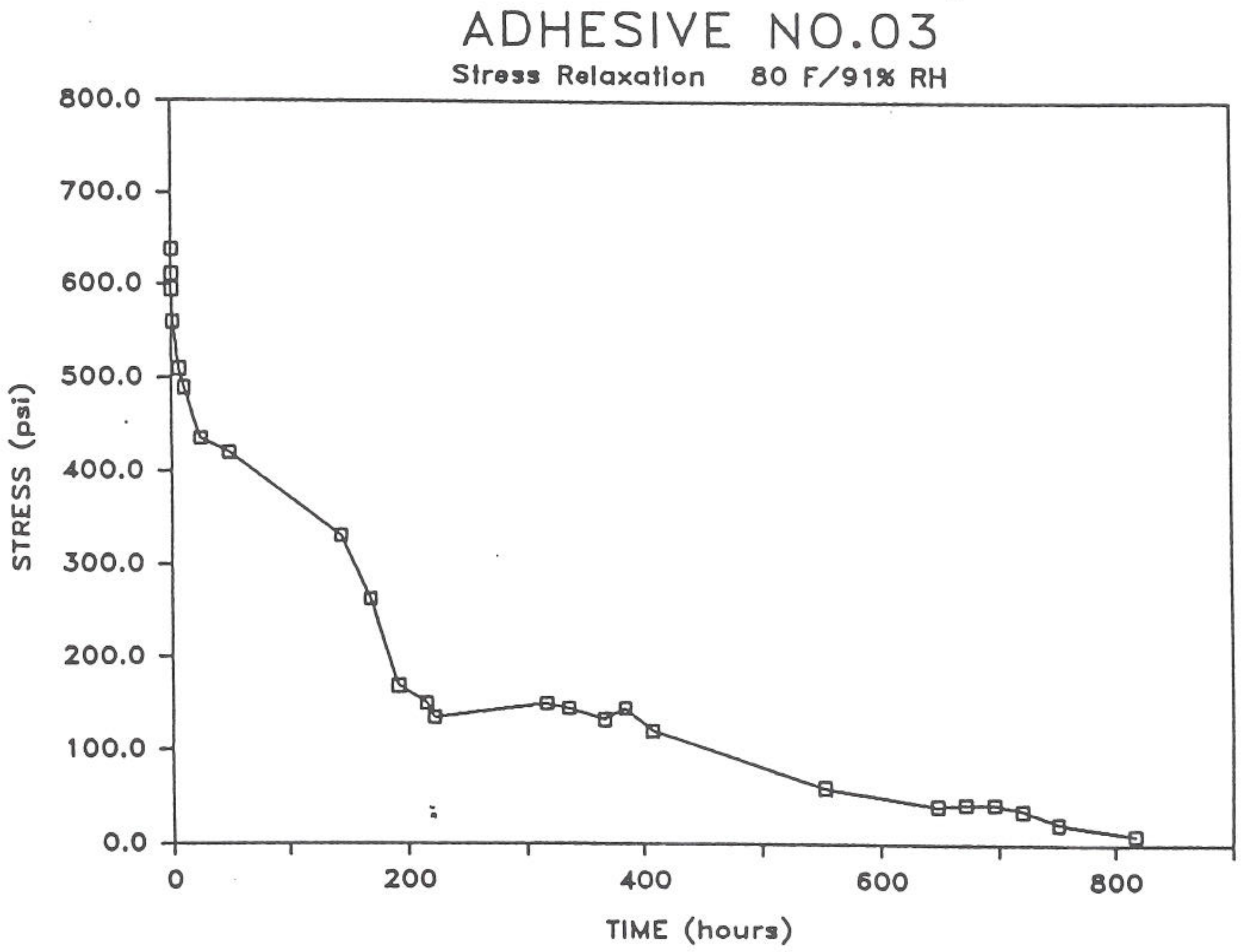

Fig. 45 Extended stress relaxation plot, epoxy adhesive

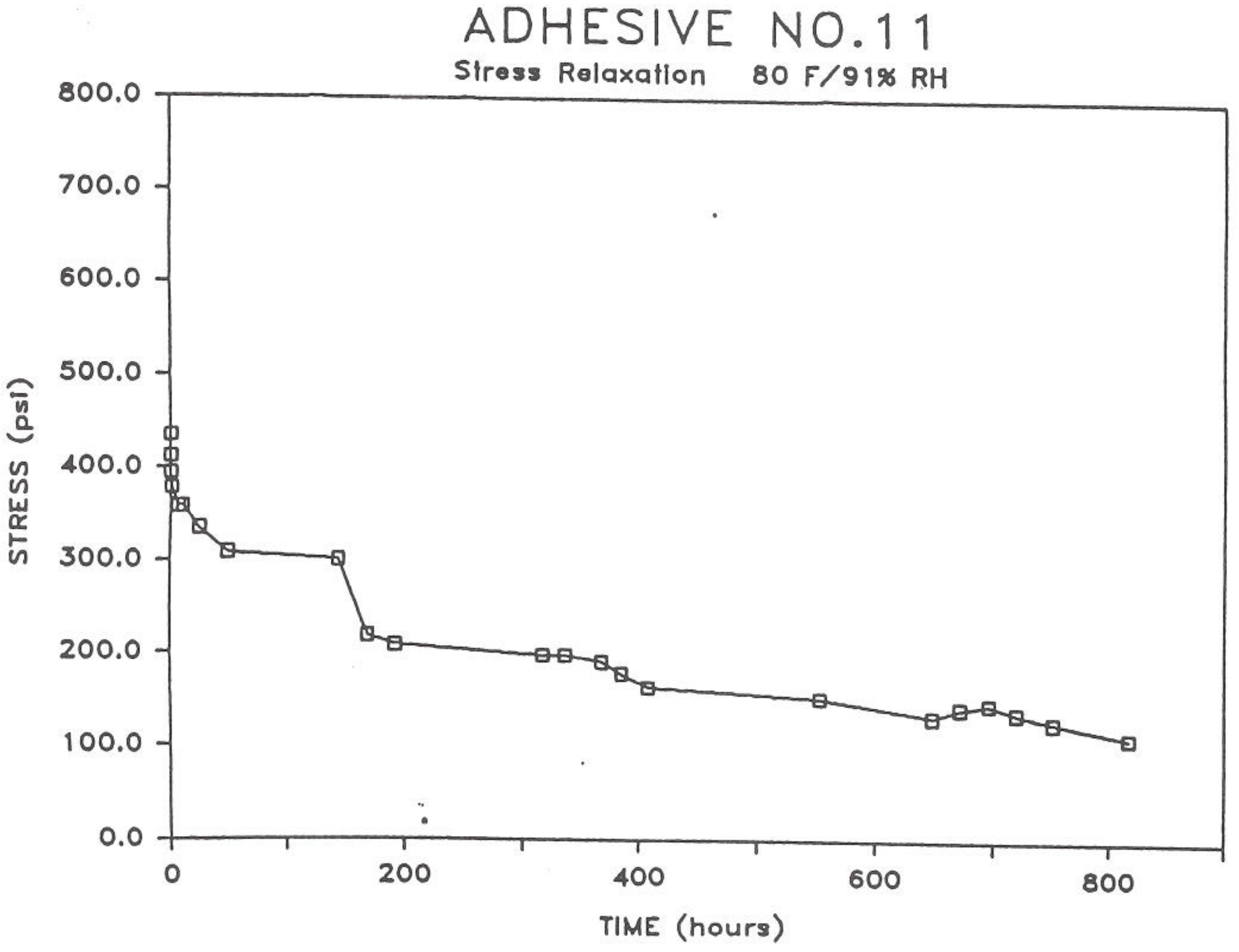

Fig. 46 Extended stress relaxation plot, epoxy adhesive

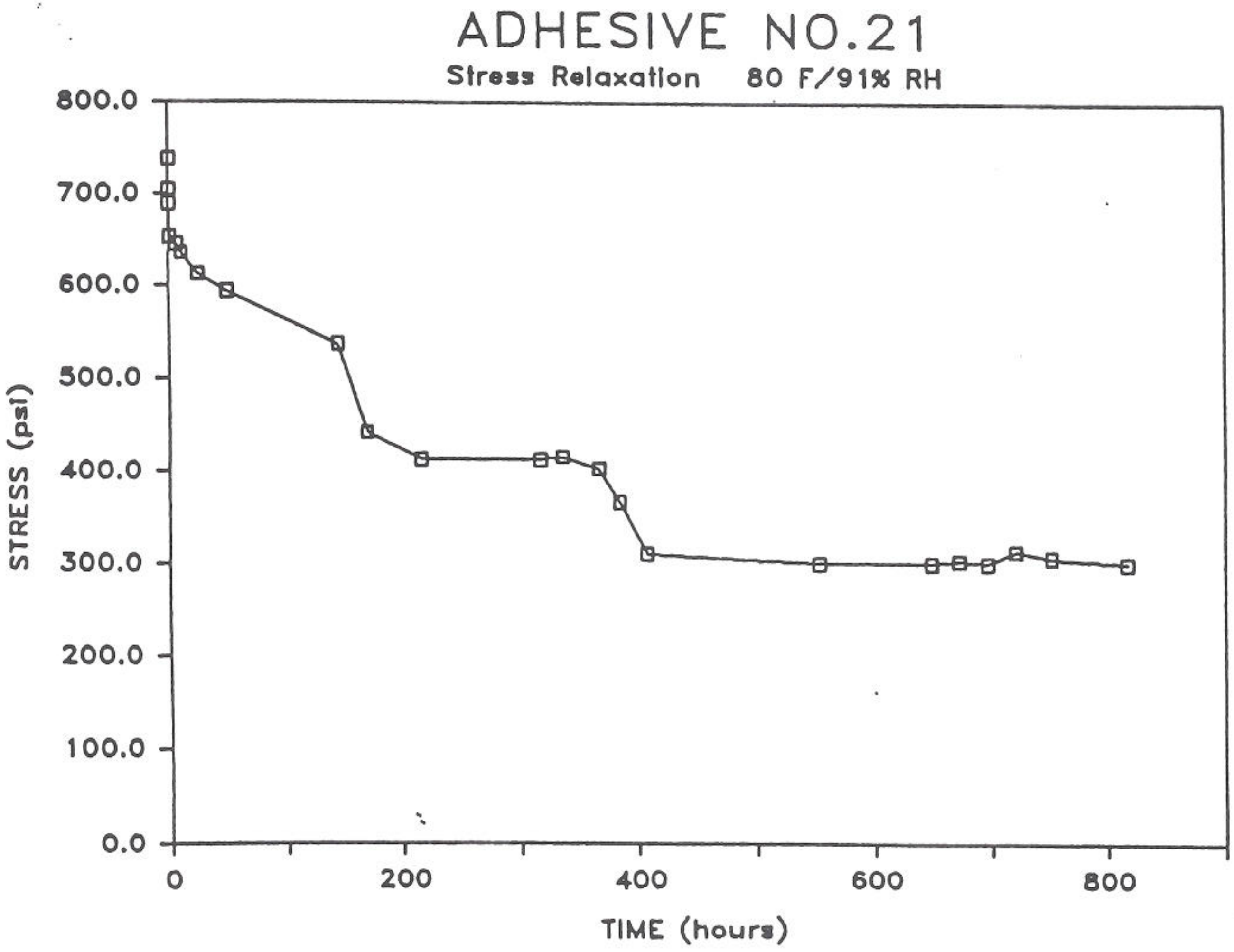

Fig. 47 Extended stress relaxation plot, epoxy adhesive

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