# Response of Epoxy Adhesives when Stressed to Failure in Milliseconds

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## Synopsis

This investigation showed, as did an earlier investigation, that the adhesives tested exhibit greater resistance to rapidly applied stresses than they do to slower or gradually applied stresses. Also, the adhesives were shown to lose strength with test temperature whether tested rapidly or slowly. Within a region bounded approximately by a high-temperature second-order transition point (the ASTM heat distortion temperature) and a low-temperature second-order transition point, the test data fits an Arrhenius-type exponential equation, $S = Ae^{E/RT}$, where $S$ is the stress in the joint at failure and the other terms have their usual significance. Energies calculated from this expression are lower for dynamic (fast) than for static (slower) rates of testing. Further, it was shown that little change in bond strength occurs until time to failure is below 100 msec. Plots of stress versus $1/T$ for a series of test times show a decided discontinuity at $1/T = 0.0039$ or $-16°C$.

## Introduction

In an earlier investigation of the effects of rate of load application on adhesive bond strengths,[1,2] the adhesives tested exhibited greater resistance to rapidly applied or dynamic loads than they did to loads applied at quasi-static or slower rates. The differences observed between the dynamic and static strengths were shown to be dependent upon the formulation of the particular adhesive system. At low temperatures, where molecular motion is greatly reduced, the bond strengths obtained did not, as a rule, vary much with rate of load application. At higher temperatures, molecular motion is greatly increased and, unless some factor is present which will restrict molecular motion, the resistance to applied loads is more time-dependent. In effect, the adhesive-bonded joint exhibited properties which might have been attributed to the viscoelastic properties of the adhesive.

The initial study of rate effects on adhesive bond strengths led to the tentative conclusions cited above. Additional information was needed to further substantiate the conclusions drawn at the time and to extend the knowledge gained. This report reflects the subsequent work. The variations of adhesive bond strengths at rates, temperatures, and degrees of plasticization intermediate to some of those of formulations investigated in

TABLE I
Formulations

|                              | A    | B    | C    | D    | E    |
|------------------------------|------|------|------|------|------|
| Formulations, parts by weight |      |      |      |      |      |
| Epoxy resin                  | 100  | 90   | 80   | 70   | 60   |
| Flexibilizer                 | 0    | 10   | 20   | 30   | 40   |
| Curing agent                 | 20   | 19   | 18   | 17   | 16   |
| Flex, %                      | 0    | 8    | 17   | 26   | 34   |
| Cure conditions: 2 hr. at 80°C.; then 2 hr. at 150°C. |      |      |      |      |      |

the first report have been studied. In addition, a physical–chemical treatment of the data has been attempted.

## Discussion

In the previous investigation a number of curing systems were used. For this investigation, a commercial mixture of aromatic amines was used with a conventional bisphenol A epoxy resin and a reactive flexibilizer. Five variations in flexibilizer content were studied. The curing agent content was adjusted in each formulation to maintain stoichiometry. The formulations and cure conditions are given in Table I. The specimens used for all tests (Fig. 1) were a modification of those described in ASTM D2094-62T and D2095-62T. The modification was necessary to withstand the loads encountered at high rates.

Physical properties of polymeric materials may change markedly with small changes in temperature. At sufficiently low temperatures, a glassy state may be achieved; as the temperature is increased, there is
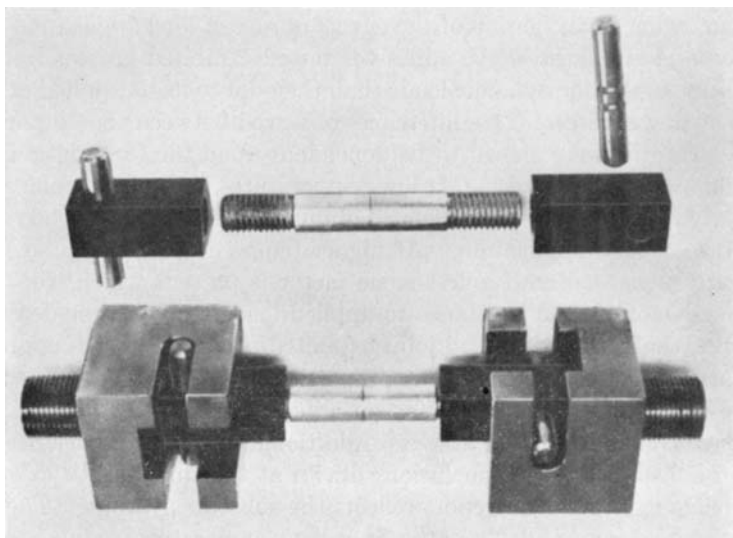


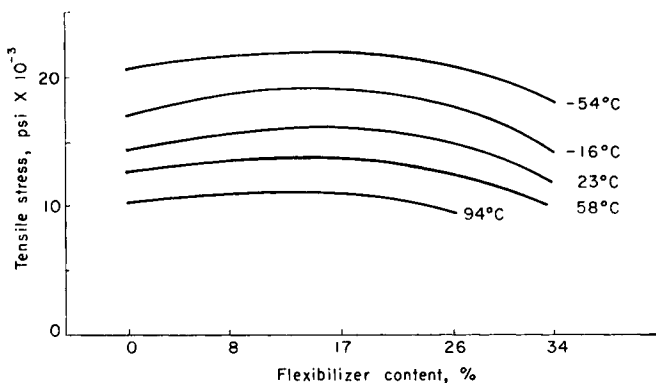Fig. 1. Adhesive-bonded test specimen with grips.

Fig. 2. Dynamic rupture stress vs. flexibilizer content.

a transition in properties from those of hard, brittle glassy materials to those of softer, more flexible materials. Such transitions are frequently referred to as either glass transitions, second-order transitions, or apparent second-order transition points, in contrast to the first-order transition point which is frequently associated with crystalline melting.

Plots of various properties of polymers such as specific volume against temperature may show abrupt changes at transition points. In fact, this technique is frequently used in locating second-order transition points. In the previous investigation, discontinuities in the data were observed at specific test temperatures; hence, for this investigation, definite temperature ranges were established. The upper limit was established as the heat distortion temperature (ASTM D648). The lower limits were found experimentally, as will be shown later, to be at some point between 23 and $-16°C$.

To evaluate more fully the effects of variations in rates of stressing upon the physical properties of adhesive bonds, it was felt that more information was required at flexibilizer contents, rates, and test temperatures intermediate to those described in the earlier report. To determine the effect of the flexibilizer content the tensile strength of the adhesive bonds, the data obtained at both dynamic and static rates of stressing, at the various temperatures, was plotted against the per cent flexibilizer (see Figs. 2 and 3).

Figure 2 shows the curves obtained under dynamic stress conditions. The curves show that the maximum tensile strengths were obtained when the adhesive system contained 11–16% flexibilizer. The curves also show that, at the lower temperatures, higher stress levels are obtained before failure.

The heat distortion temperatures of the two most highly flexibilized systems were determined to check the validity of using the data obtained for the five systems at the elevated test temperature. The heat distortion temperature (HDT) for the 34% flexibilized system was found to be 94–95°C. or just about at the upper test temperature. It was also noticed
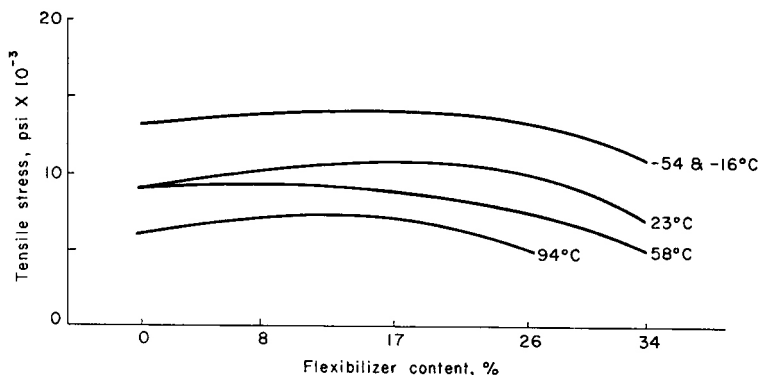
Fig. 3. Static rupture stress vs. flexibilizer content.

that the 34% flexibilized system appeared incompatible; the cured resin had an oily surface and was decidedly more translucent than similar compositions. Because this system was apparently over-flexibilized, it was dropped from this investigation. The HDT of the 26% flexibilized system was found to be 104–105°C. This was above the upper test temperature and therefore the system was considered acceptable for further studies. Inasmuch as the HDT of the 26% flexibilized system was above the upper test temperature, the HDT's for the other adhesive systems, all of lower plasticizer content, were not determined. The continuity of data observed later justified this action.

Figure 3 is a plot of the tensile stress versus flexibilizer content as obtained at static rates of stressing. The same general observation can be made as to the effects of the flexibilizer content upon the strength of the systems, i.e., the maximum tensile strengths were obtained when the adhesive system contained 11–16% flexibilizer. However, when the dynamic data was plotted (Fig. 2), the curves showed that the tensile strength continues to rise as the temperature is decreased. In the case of the static data (Fig. 3), it is noticed that at −54 and 16°C. the tensile strengths remained the same. This duplication of data at both test temperatures indicates that somewhere between 23 and −16°C. the adhesive experiences a transition. This transition may represent freezing-out of localized motion, thereby limiting the ability of the polymer to respond to the stress. Throughout the temperature ranges studied, higher strengths were obtained dynamically than statically, showing that the adhesives tested are rate sensitive, at least at the rates investigated thus far.

The results obtained when adhesive-bonded specimens were stressed to failure in milliseconds (i.e., at dynamic rates) are shown in Figure 4 as a series of curves obtained by plotting stress versus test temperature. As these curves indicate, the tensile strength at failure decreases as the test temperature increases. The points used to plot the 26% flexibilized curve were derived from the curves in Figure 2.

Figure 5 shows the curves obtained when the static stress data are plotted against the test temperatures. Again, the tensile strength at failure de-
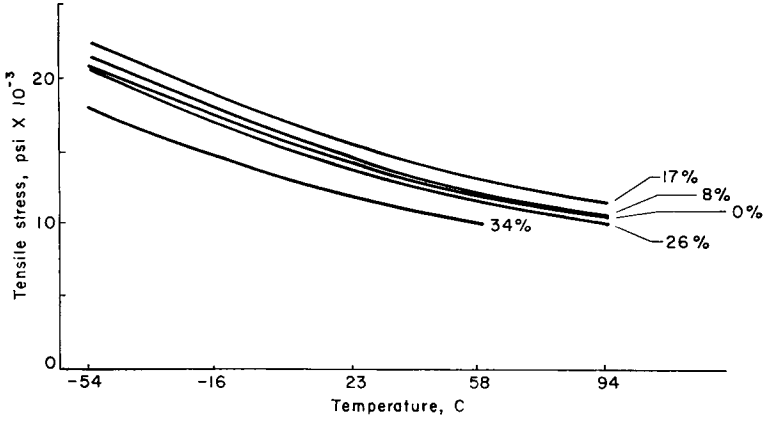
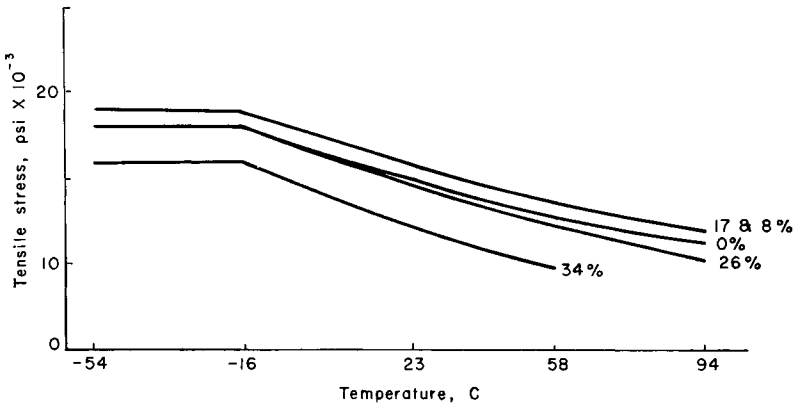Fig. 4. Dynamic rupture stress vs. test temperature.
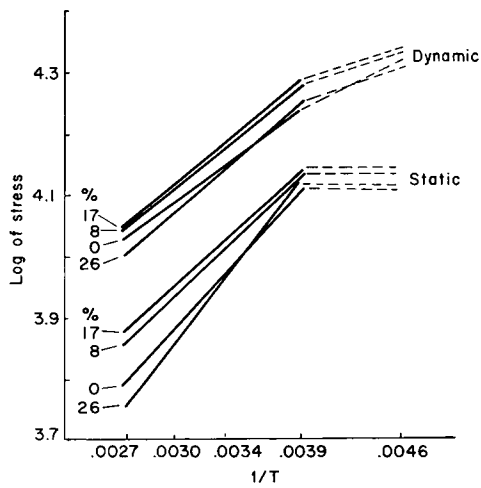


Fig. 5. Static rupture stress vs. test temperature.



Fig. 6. Plot of stress vs. $1/T$.

creased as the test temperature was increased, with the exception of the results obtained at $-16$ and $-54°C$. The stress at failure below this temperature remains constant as the temperature is decreased.

The general conclusions drawn from Figures 2 and 3 are reaffirmed by these curves. The range 11–16% flexibilizer content appears to be about optimum for this adhesive system. All of the adhesive systems will withstand higher stress levels at dynamic rates than at static rates.

Figure 6 shows the plots of the log of the tensile stress at failure versus $1/T$, where $T$ is the absolute temperature. The plots are linear between $1/T = 0.0027$ (94°C.) and $1/T = 0.0039$ ($-16°C.$). At $1/T = 0.0039$, the slope of the line changes, indicating a transition. By analogy with relationships of the Arrhenius type that have been found to apply to viscous flow,[3] e.g., $\eta = Ae^{E/RT}$, a relation of the form

$$\log S = \log A + E/2.303RT \tag{1}$$

was applied to the present work, where $S$ is the tensile stress at failure, $A$ is a constant and also the $y$ intercept, $R$ is the gas constant in calories per degree-mole and $E$ is the activation energy.

In applying eq. (1) to the data in this report, the $E$ value obtained is the apparent activation energy; the exact meaning of the value is not understood at this time.

As has been previously stated, the heat distortion temperature was selected as the upper limit of the tests for this investigation. As can be seen from Figure 6, the transition which takes place at the low temperature, where the slope of the line changes, is the other limit of the region in which the analogy to the exponential equation for viscous flow was applied. It is felt that below the low temperature second-order transition the adhesive is brittle and acts as a glassy solid. In the region above this transition and below the heat distortion temperature, the adhesive behaves as a viscoelastic material; above the heat distortion temperature, the adhesive behavior tends to be more like that of a viscous liquid.

It is in the region of viscoelastic behavior that the adhesive responds the most to variation in rates of stressing and is able to withstand higher stresses before failure. By determining the tensile strengths of an adhesive system at various temperatures, it is possible to calculate an overall energy, presumably related to bond rupture. It is also possible to calculate the tensile strength at a given temperature (apparently between the high temperature second-order transition and the low temperature second-order transition) by using the equation:

$$\log S = (E/2.303R) (1/T) + \log A \tag{2}$$

$E/2.303R$ is equal to the slope of the line from the log of stress versus $1/T$ curve. Therefore,

$$E = 2.303R \times \text{slope}$$

The overall energies calculated from the data in this investigation are shown in Figure 7 and in Table II.
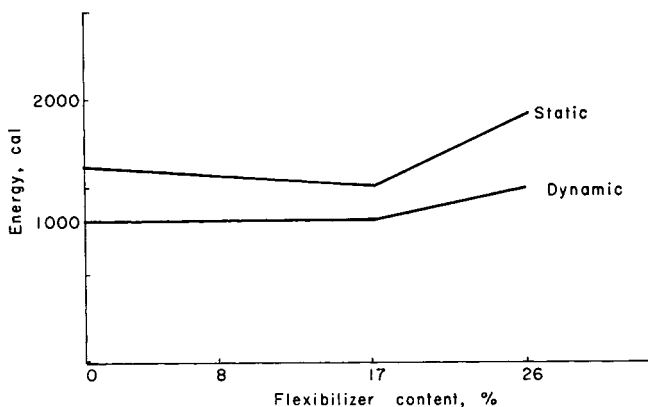
Fig. 7. Calculated energy.

From a comparison of the energies calculated from the data obtained at dynamic and static rates of stressing, it appears that more energy is required to rupture the bond during static stressing. This apparent increase in energy would be due to the energy absorbed by rearrangement and relaxation of the material under stress. The data obtained by static stressing generally has a wider spread between specimens than that obtained by dynamic testing. Therefore, the calculated slopes and energy values obtained from the static testing would be less accurate. It is considered possible that the negative slope in the first portion of the static energy curve is due to this inaccuracy and might be a straight line as in the case of the dynamic energy curve. As noted earlier in this report, between 11% and 16% flexibilizer appears to be optimum for strength properties, and here again an increase in energy is noticed, which might indicate that there is more movement within the polymer chain when the flexibilizer content is greater.

Figures 8 and 9 show the effect of changing the rate of stressing on the tensile strength of the adhesive at failure for two of the systems used in this investigation.

Figure 8 gives the curves obtained when the stress data at the various temperatures was plotted against time to failure for the unflexibilized epoxy adhesive.

Figure 9 represents the stress versus time to failure curves for the 17% flexibilized system. It can be observed from these curves that, as the rate

TABLE II
Calculated Energy Values for Dynamic and Static Results

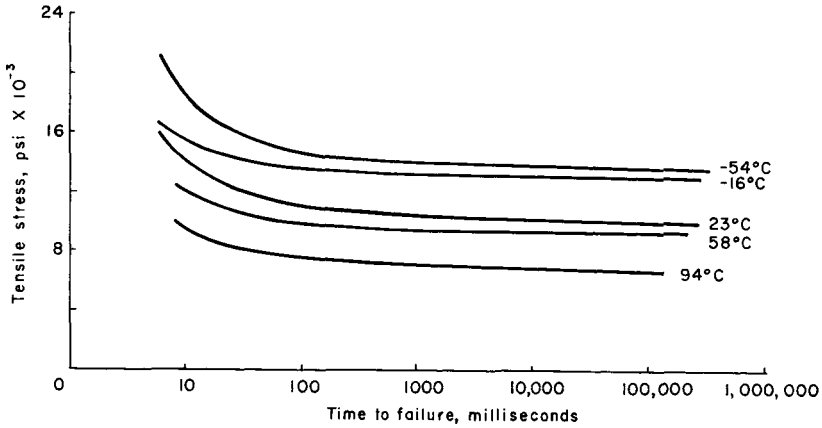|  | A | B | C | D |
| --- | --- | --- | --- | --- |
| Adhesive formulation |  |  |  |  |
| Percent flexibilizer | 0 | 8 | 17 | 36 |
| Dynamic energy, cal./mole | 810 | 820 | 805 | 980 |
| Static energy, cal./mole | 1130 | 1070 | 990 | 1400 |

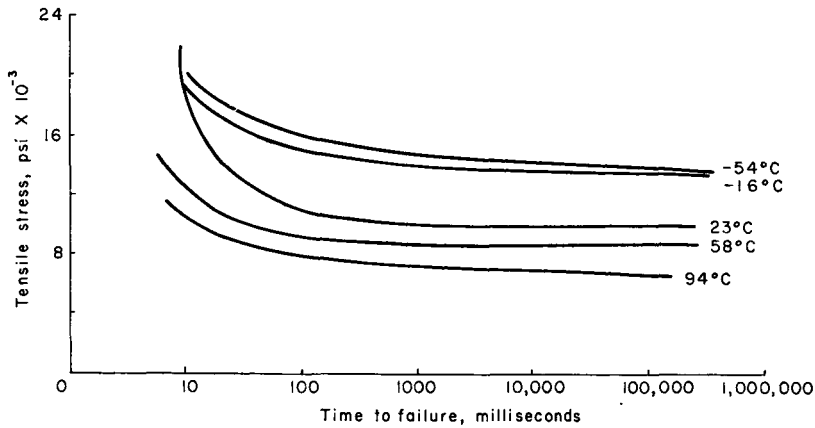Fig. 8. Plot of stress vs. time to failure for adhesive A.



Fig. 9. Plot of stress vs. time to failure for adhesive C.

of stressing is increased from the static to the dynamic, the effect of rate change does not become pronounced until the time to failure is below 100 msec. It appears that, if consideration is given to the relationship of the change in stress to the change in time to failure, eq. (3) would apply:

$$dS/dt = kt \tag{3}$$

or

$$S = (kt^2/2) + C \tag{4}$$

If this is true, a plot of stress versus the square of the time to failure would result in a straght line. Figure 10 shows a plot of $S$ versus $t^2$ for the results of tests of the 17% flexibilized adhesive at room temperature. The plot shows that for the region from about 50 msec. to failure on to about 250,000 msec., the curve is essentially a straight line. This indicates that the
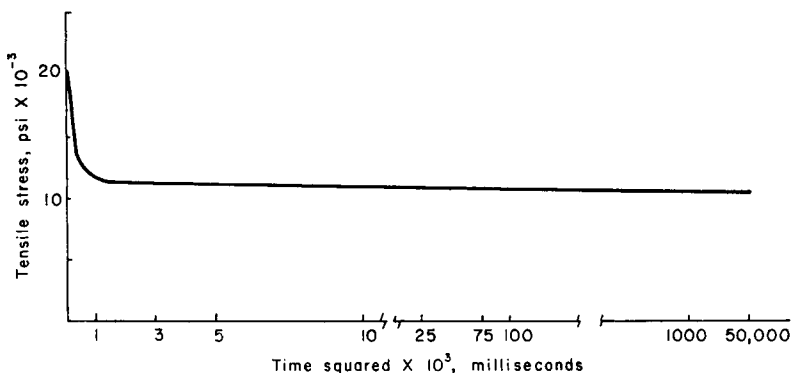
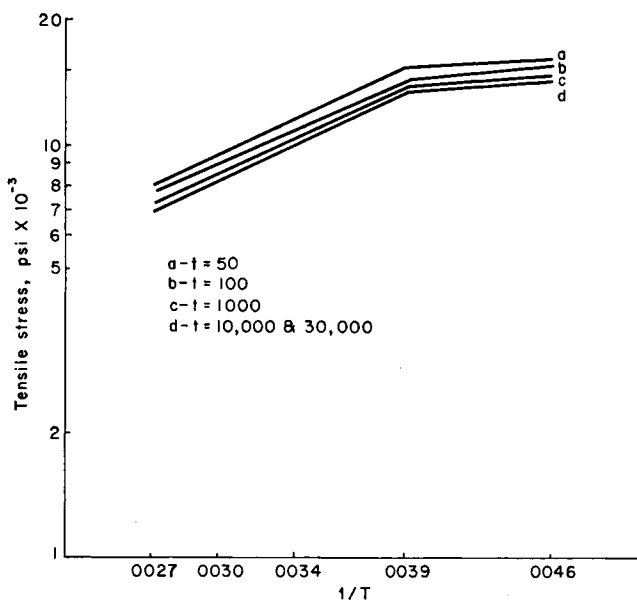Fig. 10. Plot of stress vs. $t^2$ for adhesive C at 23°C.



Fig. 11. Plot of log stress vs. $1/T$ for adhesive C.

strengths of the adhesives are not generally affected by time until the rate of stress becomes so fast that rearrangement of the polymer cannot take place.

Figure 11 shows a series of plots of the log of $S$ versus $1/T$ data which were derived from Figure 8 at various times to failure, i.e., $t = 50$, $100$, $1000$, $10,000$, and $30,000$ msec. The curves show the same trend at the various rates. However, calculation of energy values appears to be best accomplished from data obtained at dynamic rates of stressing since there seem to be fewer sources of error in the test procedures and the resulting data at these high rates.

## Experimental Procedure

The 1020 steel rods were submerged in a solution of 1 part by weight (pbw) sodium dichromate, 10 pbw concentrated sulfuric acid, and 30 pbw distilled water for approximately 5 min. at room temperature. The rods were then washed with paper wipers (Kimwipes) under running water to remove the black scale formed during the treatment. After washing, the rods were rinsed first in distilled water and immediately afterward in acetone. They were then wiped dry and heated at 175°C. for $1/2$ hr. After the rods were cooled to 23°C., the adhesive was applied with a wooden applicator and the specimens assembled in the bonding jig. The adhesive formulations and curing cycles are shown in Table I.

Test temperatures were −54, −16, 23, 58, and 94°C. The rate of load application in the static tests was 2400 psi/min. to failure; in dynamic testing the rate was in milliseconds to failure. Intermediate tests were run at various rates from 6 to $3 \times 10^5$ msec. to failure.

## References

1. Wegman, R. F., and W. C. Tanner, paper presented at the Fourth Pacific Area National Meeting, ASTM, Los Angeles, California, October 1–5, 1962.

2. Tanner, W. C., and R. F. Wegman, Picatinny Technical Report 3054, March 1963.

3. Billmeyer, F. W., Jr., *Textbook, of Polymer Chemistry*, Interscience, New York, 1957.

## Résumé

Cette recherche montre, ainsi que l'on montré des études antérieures, que les adhésifs essayés manifestent une plus grande résistance à des tensions appliquées rapidement que celles dues à des tensions plus lentes ou appliquées graduellement. Les adhésifs perdent aussi leurs forces avec la température d'essai qu'ils soient essayés rapidement ou lentement. Au dedans d'une région limitée approximativement par le point de transition de second ordre à haute température (la température de distorsion à la chaleur ASTM) et une température basse correspondant au point de transition de second ordre, les données des essais s'accordent avec une équation exponentielle du type Arrhénius égale à $S = Ae^{E/RT}$, où $S$ est la tension au sein du joint à la cassure et les autres termes ont leur signification habituelle. L'énergie calculée au départ de cette expression est plus faible pour des vitesses d'essai dynamiques (rapides) que pour des essais statiques (plus lents). En outre, on montre qu'il y a peu de changement dans la force de liaison tant que le temps de cassure reste inférieur à 100 sec. Les diagrammes de la tension en fonction de $1/T$ pour une série de temps d'essais indiquent une discontinuité à $1/T = 0.0039$ c.à.d. −16°C.

## Zusammenfassung

Die vorliegende Untersuchung zeigt ebenso wie eine frühere, dass die untersuchten Klebestoffe gegen rasch einwirkende Spannung eine grössere Festigkeit zeigen als gegen langsamer oder stufenweise einwirkende Spannung. Weiters verloren die Klebestoffe sowohl bei rascher als auch bei langsamer Testung mit steigender Testtemperatur an Festigkeit. In einem etwa durch einen Hochtemperaturmwandlungspunkt zweiter Ordnung (die ASTM-Hitzebeständigkeitstemperatur) und einen Tieftemperaturumwandlungspunkt zweiter Ordnung begrenzten Bereich entsprechen die Testdaten einer

Arrheniusgleichung $S = Ae^{E/RT}$, wo $S$ die Bruchspannung in der Verbindung ist und die übrigen Terme ihre übliche Bedeutung besitzen. Aus diesem Ausdruck berechnete Energien sind für dynamische (schnelle) Testgeschwindigkeiten niedriger als für statsiche (langsamer). Weiters wurde gezeigt, dass bei Bruchdauern oberhalb 100 msec nur eine geringe Änderung der Bindungsfestigekeit auftritt. Bei der Auftragung der Spannung gegen $1/T$ für eine Reihe von Testzeiten ergab sich eine entschiedene Diskontinuität bei $1/T = 0,0039$ oder bei $-16\,°C$.