JOURNAL OF APPLIED POLYMER SCIENCE VOL. 7, PP. 1325–1339 (1963)

Failure Criteria for Some Polyurethane Propellants

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INTRODUCTION

The objective of this paper is to describe the experimental and theoretical studies carried on at Aerojet-General Corporation to establish failure criteria applicable to simple case-bonded hollow cylindrical grain and evaluate these criteria by cycling such cylinders to failure. The concept of failure necessarily includes a study of the behavior of those members of a population most likely to fail. The usual measurement of properties and correlation of data centers around consideration of mean behavior, estimates of variability being made to assess the measurement quality. Stress and strain calculations also focus on the use of mean values of the parameters and comparison with the mean of observed deflections. Failure, however, is concerned with the likelihood of occurrence of a particular stress or strain at the point where the material properties are least adequate. The formation of yield bands in propellants gives particular point to this problem. The data suggest that as the strains increase, yield bands occur and change the distribution of strains to produce regions in which failure will occur before further strain is produced in the unyielded regions. Thus, the usual elastic stress calculations and techniques, such as photoelasticity, do not directly lead to predictions of failure.

This paper will cover (*1*) the results of studies on the batch-to-batch variability of breaking strain of uniaxial tensile test over a range of temperatures, (*2*) the correlation of breaking strain of uniaxial tensile test with rate and temperature, and (*3*) the correlation of uniaxial tensile elongation to break with failure by grain cracking as a result of the thermal cycling of a case-bonded hollow cylinder of propellant.

BATCH VARIABILITY OF FAILURE BEHAVIOR

The large variability associated with propellant properties suggests that certain batches, and certain portions of these batches, will be more susceptible to failure than others. A related hypothesis is immediately suggested for experimental testing: the failure behavior under different types of stress-strain environments are related such that those batches with the highest incidence of failure in one environment will have the highest incidence in another. It is clear that we lack the knowledge at this time to define failure mechanisms in detail for different batches or

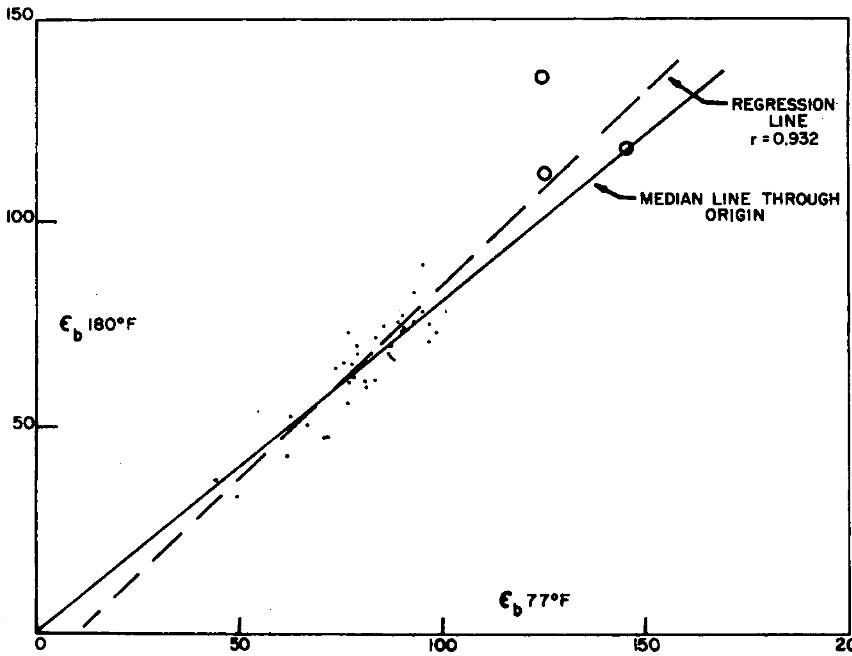

Fig. 1. Correlation of failure strain at 180°F. with that at 77°F. for same batch; (O) rejected for poor cure.

even different compositions. A possible procedure is to compare property measurements with small-scale motors, and validate the results as full-scale motor data become available. It is evident that during the validation process the small-scale motor data and the property data would become increasingly firm as a basis for acceptance criteria.

The production of polyurethane propellant for several programs at the Sacramento Solid Rocket Plant of the Aerojet-General Corporation offers the possibility of taking data on different batches of propellant and determining the correlation between failure values of different mechanical property tests. Instron data at one strain rate are taken from −75 to 180°F. in these several programs. A study has been completed of data taken on one carton from each of forty batches of a polyurethane propellant.

Figures 1–4 show correlation graphs of the elongation at failure at 77°F. versus the failure value at the other test temperatures for each of the cartons studied. The data were also analyzed numerically to give the correlation coefficient shown on each figure. Except for −75°F., the data gave high correlations and, in particular, the three cartons giving highest elongations and the two giving lowest elongations (except as shown in Figure 4 for −75°F.) were the same in all cases. This indicates that a test at any one of the test temperatures would have screened out the same extreme cartons of the population as it would have at any other test temperature, except −75°F. The −75°F. data are in question at this time because of a

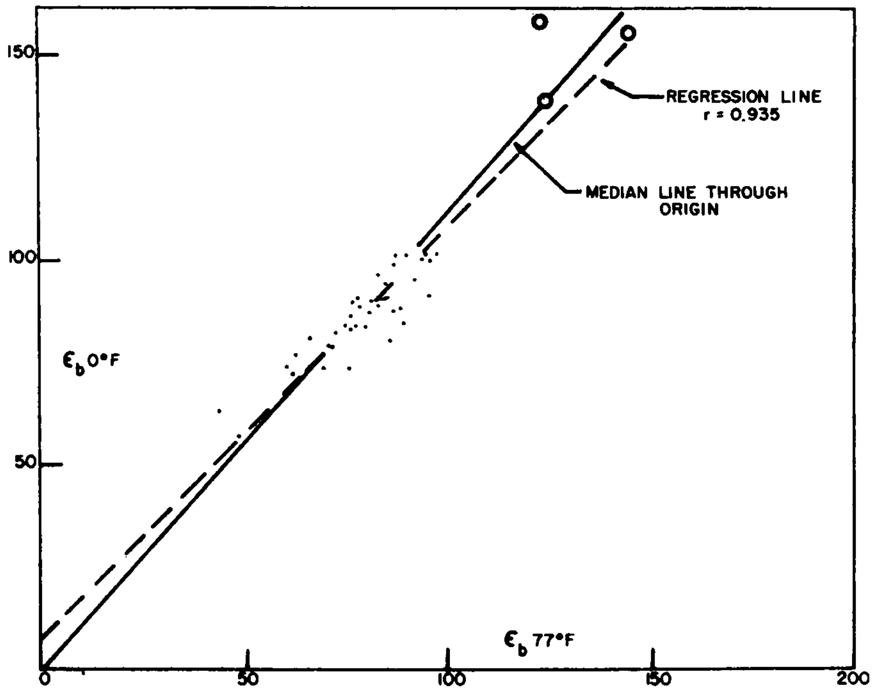

Fig. 2. Correlation of failure strain at 0°F. with that at 77°F. for same batch; (O) rejected for poor cure.

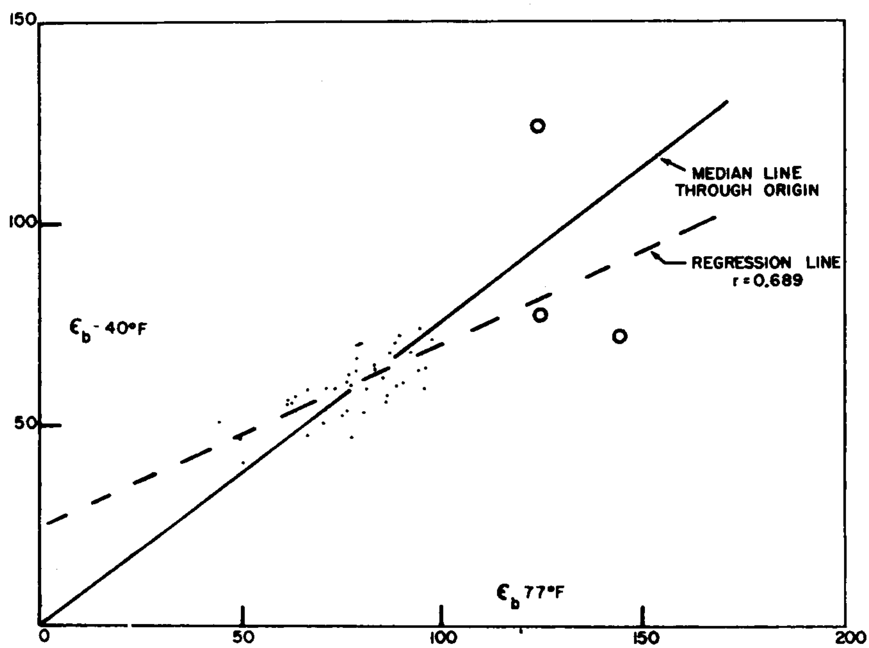

Fig. 3. Correlation of failure strain at −40°F. with that at 77°F. for same batch; (O) rejected for poor cure.

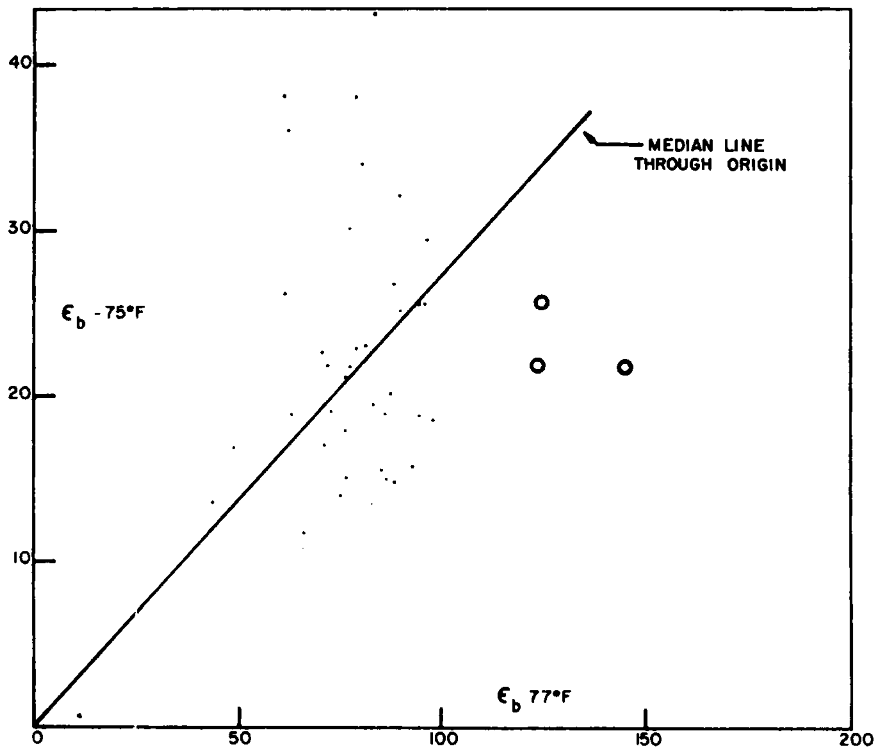

Fig. 4. Correlation of failure strain at −75°F. with that at 77°F. for same batch; (O) rejected for poor cure.

particularly strong effect of pretest humidity exposure on −75°F. test results; these tests were run on specimens experiencing a fairly wide range of humidity prior to being placed in −75°F. conditioning for test.

The variability of this propellant was also statistically analyzed in more detail for three cartons of each of three widely different batches. It was found that the variability tended to decrease between batches and increase within cartons as the test temperature decreased. When the three batches were considered together, coefficients of variation between batches ranged from 51% at 180°F. down to 26% at −75°F., contrasting with the between-replicate variation which increased from 7 to 15% over the same temperature range. Table I contains the mean values for the three-batch three-carton three-replicate analysis, and the variability analysis data are given in Table II.

An additional analysis of two of the batches, 18-M-1 and 21-M-1, was made. In this case, test data from two additional cartons from each of these batches were available. The means of these two batches were more nearly alike at the middle temperatures and tended to diverge at the extremes, which would have minimized variability at the middle temperatures. The between-replicate values, however, followed patterns identical

TABLE I
Mean Values of Breaking Strain for Three Batches of a Polyurethane Propellant
(Each value represents the average of 9 samples)

Temp., °F.	1 Batch 15-M-2	2 Batch 18-M-1	3 Batch 21-M-1
180	19.9	98.0	73.0
77	28.1	93.6	93.3
0	35.7	113.3	104.0
−40	33.1	69.8	61.7
−75	18.2	26.6	23.3

TABLE II
Coefficients of Variation for Three Batches, Three Cartons, Three Replicates of a Polyurethane Propellant

Temp., °F.	Between batches, %	Between replicates, %
180	51.0	7.1
77	46.0	9.8
0	50.0	8.8
−40	35.0	9.8
−75	26.3	14.9

TABLE III
Coefficients of Variation for Two Batches, 18-M-1 and 21-M-1, Five Cartons, Three Replicates of a Polyurethane Propellant

Temp., °F.	Between batches, %	Between replicates, %
180	22.0	4.3
77	8.9	7.1
0	—	12.0
−40	7.2	10.0
−75	21.0	14.0

with those from the initial analysis of all three batches. Table III contains the results of the variance analysis in terms of coefficients of variation. All of the coefficients of variation listed had a significance level of 0.95 or greater.

CORRELATION OF FAILURE BEHAVIOR

WLF Rate Shift Factor Correlation

The correlation of mechanical property behavior at different rates and temperatures has been performed on many polymers by following the shift factor technique (WLF) of Williams et al.[1] Correlation of failure behavior for a rubber was shown by Smith and Stedry.[2] Correlation of failure in the highly filled polyurethane systems has not been reported in the literature. From consideration of available test data on propellants, it appeared

TABLE IV
Uniaxial Tensile Failure Strains for a Polyurethane Propellant

Temp., °F.	Strain at failure, %, for strain rate (min.$^{-1}$)						
	0.074	0.74	7.4	100	500	1000	2000
180	46.4	52.4	65.0	81.8	92.5	92.2	90.1
140	50.8	56.9	66.5	85.4	88.6	100	92.7
110	55.8	67.8	71.4	84.9	88.6	91.4	107
80	66.4	66.1	81.4	92.2	95.3	98.8	99.9
40	71.1	76.4	79.6	98.1	91.8	90.0	88.1
0	70.6	84.2	79.2	76.0	65.8	62.5	68.1
−40	58.3	56.4	47.6	65.8	44.4	26.2	22.8
−60	50.2	53.0	48.4	—	23.9	15.5	14.8
−75	35.1	27.0	17.0	9.4	8.9	5.2	3.5

that the maximum elongations at failure at any rate for different temperatures were not the same, this maximum decreasing as the temperature decreased. A test of the correlation is difficult, since for only a few temperatures and rates generally studied do the elongations go through a maximum, so only a portion of any set of data can provide data applicable directly to the question. Uniaxial tensile failure data for one batch of this propellant were available at temperatures from −75 to 180°F. and strain rates from 0.074 to 1000 min.$^{-1}$. The values are given in Table IV, each value being an average of five specimens. The analysis of the data

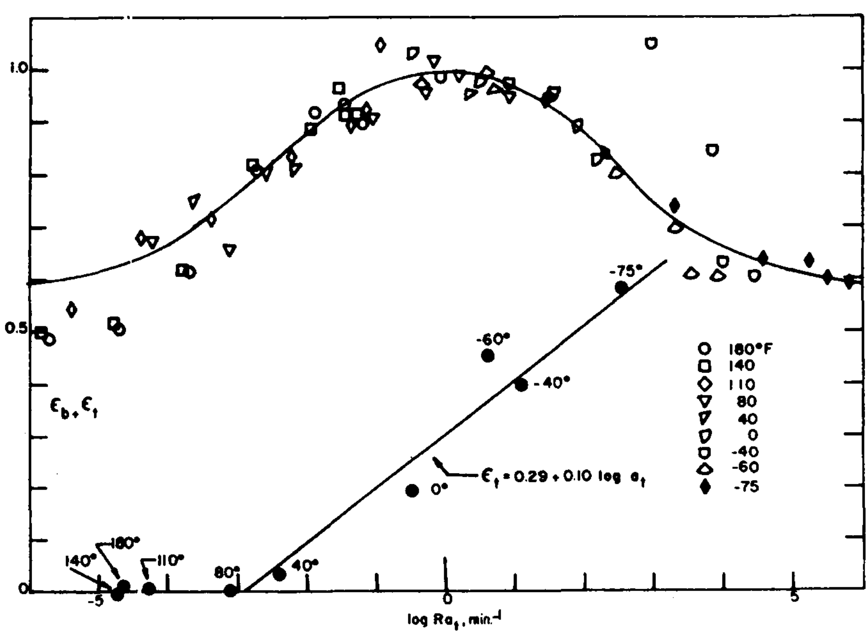

Fig. 5. Failure strain of a polyurethane propellant with reduced rate obtained with vertical shift factor.

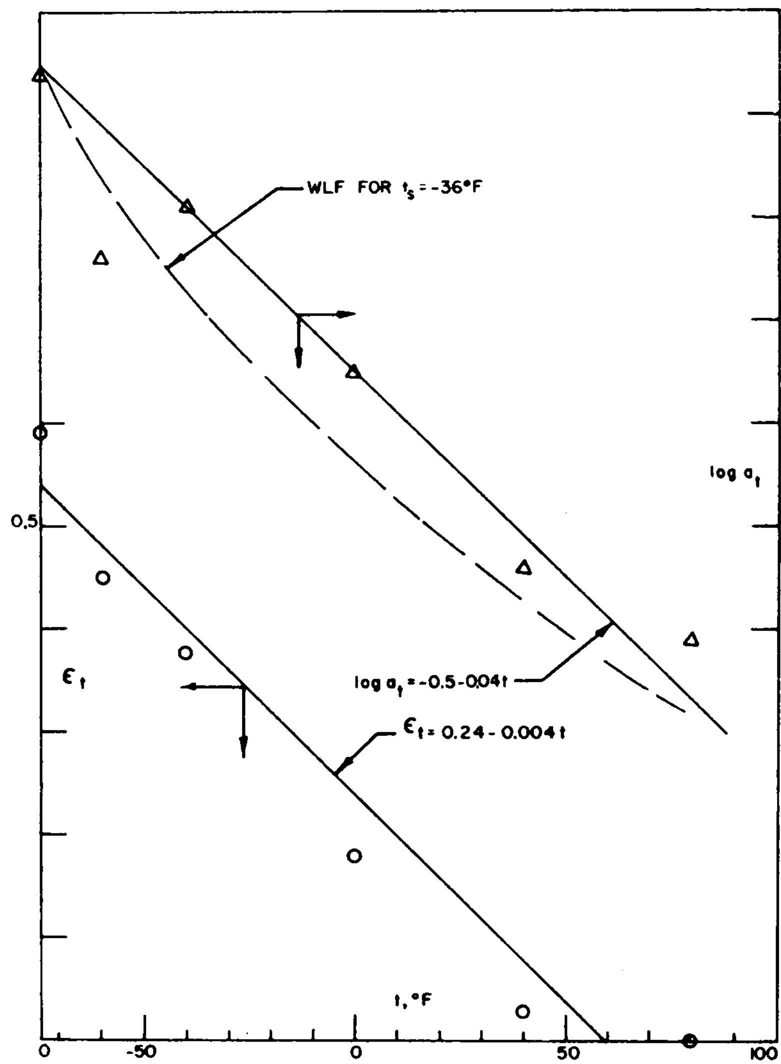

Fig. 6. Relationships of shift factor and temperature.

was performed graphically in the WLF technique by shifting the points, plotted as ϵ_b versus log R for each temperature, horizontally and also vertically as required, to produce a continuous curve of ϵ_b versus log Ra_T. Analysis started with the 180°F. data and proceeded systematically down to −75°F. The vertical shift, not required for elastomers without filler, was done without regard to fitting a particular pattern, and the results are shown in Figure 5 where the experimental locations of the point $\epsilon_b = 0$, $R = 1$ min.$^{-1}$, are shown. The final reduced scale, log Ra_T, was selected for a shift factor based on the WLF equation, as discussed below. The vertical shift required, as described by the term ϵ_T, was apparently zero for

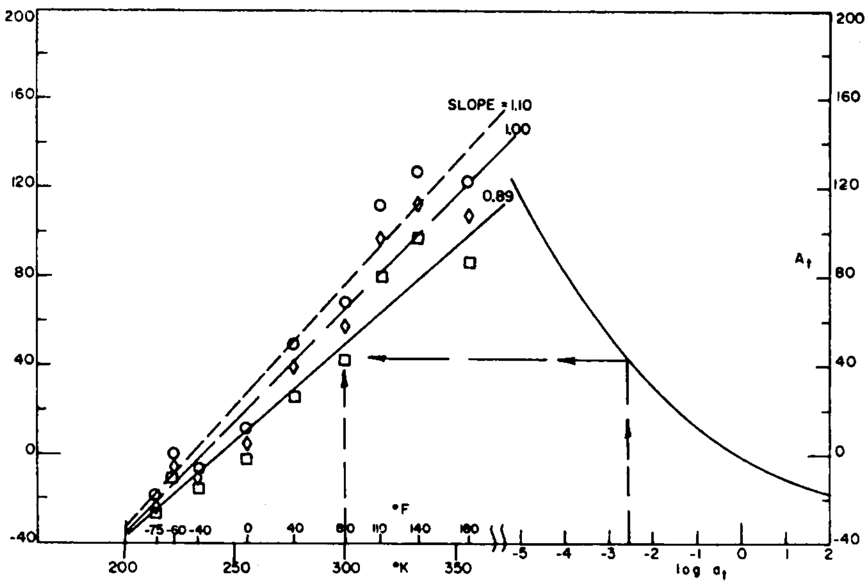

Fig. 7. Determination of reference temperature T_s by using shift values and linearized shift function.

temperatures of 80°F. and above, but increased as the temperature approached −75°F. The equation shown in Figure 5 describing the line drawn for ϵ_T is

$$\epsilon_T = 0.29 + 0.10 \log a_T \quad (1)$$

The same points used to define the line given by eq. (1) are shown in a different way in Figure 6, e.g., the vertical shift ϵ_T versus temperature, and the corresponding value of the shift factor, log a_T, versus temperature. The equations are:

$$\epsilon_T = 0.24 - 0.004t \quad (2)$$

and

$$\log a_T = -0.5 - 0.04t \quad (3)$$

The line positions were selected to make the constants of eqs. (1), (2), and (3) consistent among themselves; e.g., any two of the equations will define the third.

Considering now the usual WLF shift factor, the WLF equation can be rearranged to give

$$T = T_s - 101.6/[1 + 8.86/\log a_T] = T_s - A_T \quad (4)$$

In this form, it can be seen that a graph of T versus A_T will be a straight line of unit slope. Such a graph is Figure 7, log a_T versus A_T being shown at the right for convenience. With the data of Figure 5, before T_s was selected and the data were normalized, an arbitrary shift was made by assuming a value of log a_T at -75°F. and thus determining the relative value of log a_T for all the other reference data points on Figure 5. When these are plotted on Figure 7, the data gave a line of slope 0.89, and T_s = 243°K. Selection of a second estimate of log a_T at -75°F. gave a second line of slope 1.10 and T_s = 230°K. Interpolation, which was found to be nonlinear, finally gave data which produced a line of slope 1.00 and T_s = 235°K. (t_s = -36°F.).

If a WLF shift factor relation holds in this case for the low-temperature data, then the straight-line relation of eq. (3) would not be expected to apply. Comparison of the straight line with the WLF curve for t_s = -36°F. from Figure 7 is shown in Figure 6.

Temperature Shift Correlation

The scatter of the shift data for this propellant system led to an examination of the data when plotted versus temperature at each rate. It was discovered that the data could be superimposed to give a lower variability when an arbitrary origin was shifted both horizontally and vertically, as shown in Figure 8. Not only do the data show good agreement with two straight-line segments, but the shift points of the origin—selected at 0°F. and zero strain—are remarkably consistent and show none of the scatter characteristic of the rate shift data of Figure 5. When plotted as log R

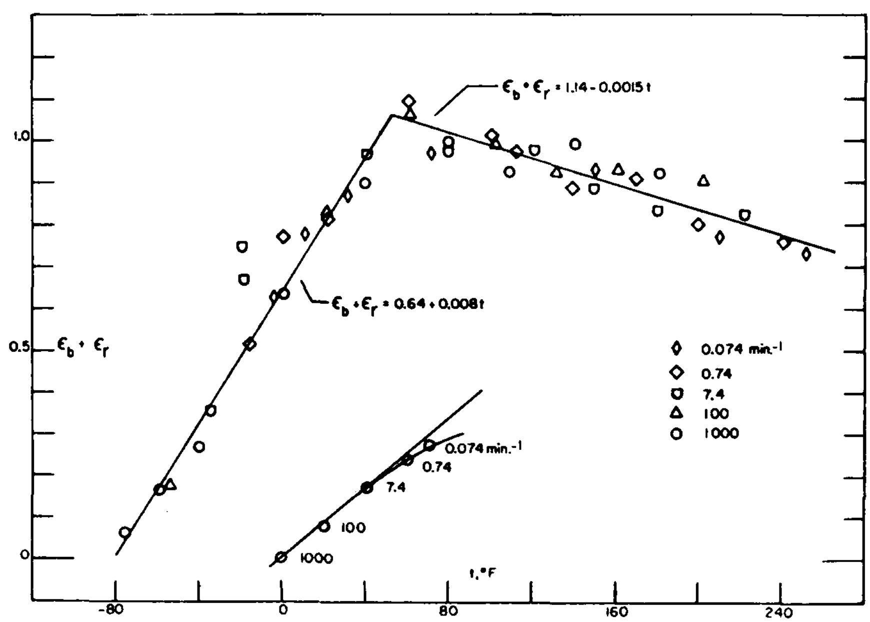

Fig. 8. Failure strain of a polyurethane propellant with temperature, rate shift factor used.

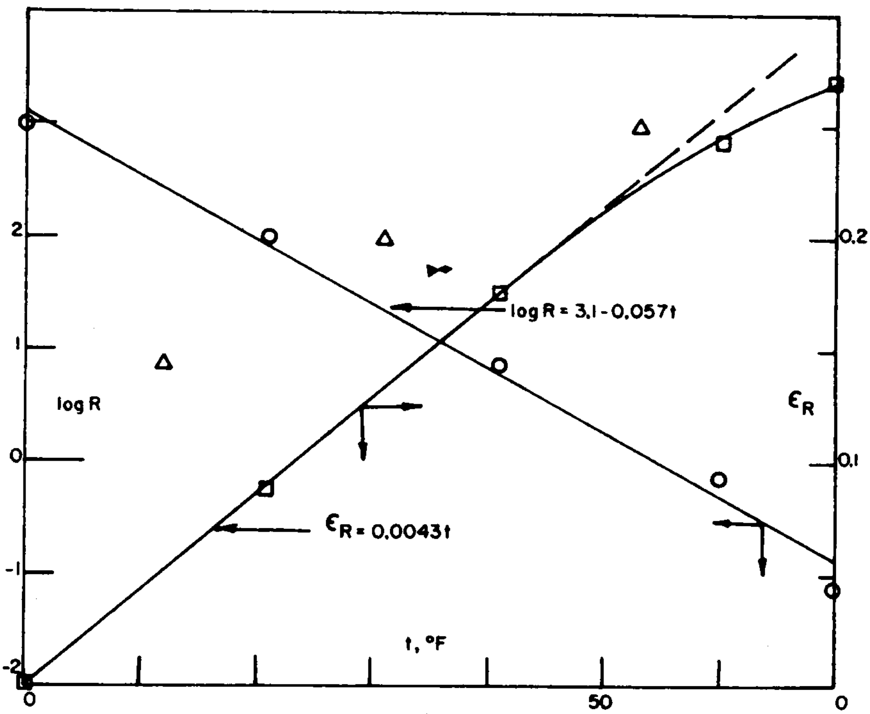

Fig. 9. Relation of log rate and rate shift factor ϵ_r to temperature.

versus the temperature shift required, Figure 9, a good straight line is obtained having the equation:

$$\log R = 3.1 - 0.057t \qquad (5)$$

Plotting the ϵ_R value at each point against the temperature does not, however, give a straight line but rather a curve, suggesting that ϵ_R does not increase above some limiting value even for very low rates of testing. This possibility may be evaluated by tests on the Very Low Rate Tester, but is already suggested by the values obtained in constant-strain failure testing, equivalent to extremely low rates of loading.

The two straight line segments of Figure 8 give

$$\epsilon_b + \epsilon_R = 0.64 + 0.008t \qquad t < 50°\text{F. at } 1000 \text{ min.}^{-1} \qquad (6)$$

$$= 1.14 - 0.0015t \qquad t > 50°\text{F. at } 1000 \text{ min.}^{-1} \qquad (7)$$

It is of interest to note that the maximum occurs near 0°F. for $R = 0.74$ min.$^{-1}$, a general characteristic of many polyurethane propellant systems.

A useful relation is obtained by taking the approximation relation from Figure 9,

$$\epsilon_R = 0.0043t \qquad (8)$$

and substituting for t from eq. (5), giving:

$$\epsilon_R = 0.23 - 0.075 \log R \tag{9}$$

Substituting for ϵ_R from eq. (9) in eqs. (6) and (7), we have:

$$\epsilon_b = 0.41 + 0.008t + 0.075 \log R \tag{10}$$

for temperatures below that giving the maximum ϵ_b, and

$$\epsilon_b = 0.91 - 0.0015t + 0.075 \log R \tag{11}$$

for temperatures above. This maximum shifts with temperature, occurring at 53°F. for 1000 (min.$^{-1}$), 31°F. for 100, 12°F. for 7.4, −7°F. for 0.74, and −18°F. for 0.074.

The excellent correlation obtained by the temperature shift method will be tested on other systems. It would be expected that a difference would be observed in the basic constants of the relations, analogous to the rate shift produced by variations in the glass temperature for the WLF type of correlation.

CORRELATION OF FAILURE DATA WITH MOTOR FAILURES

Small motors with cast-in-case cylindrical grains have been used for studies of strain produced in motors, and some of these motors have experienced failures. It appeared possible to test a failure hypothesis by study of these failures. A survey was made of forty-one of these small case-bonded motors containing three different polyurethane propellants that had been thermally cycled to −75°F.; b/a ratios from 4 to 12.5 were tested. Of these forty-one motors, fifteen failed by longitudinal cracking of the

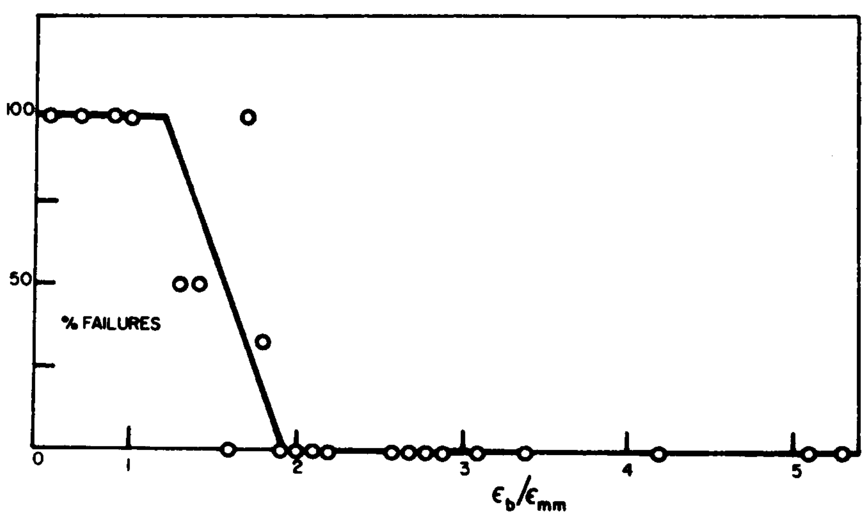

Fig. 10. Relation of failure strain in tensile specimens to cracking of subscale tubular case-bonded grains at −75°F.

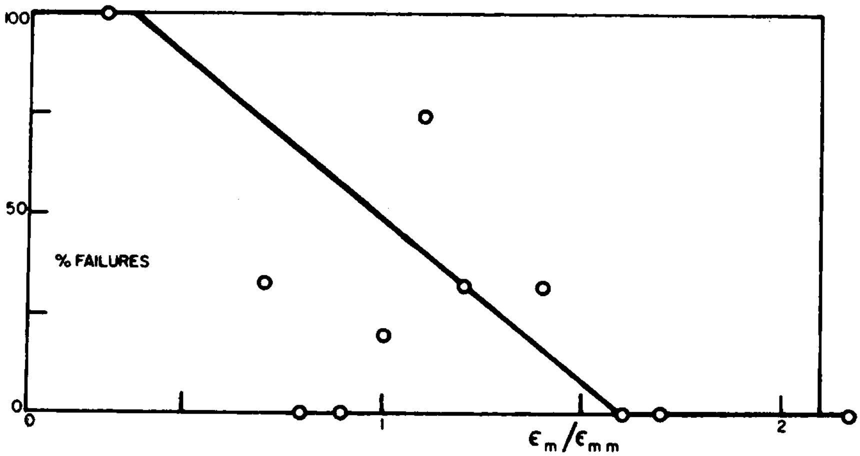

Fig. 11. Relation of strain at maximum stress in tensile specimens to cracking of subscale tubular case-bonded grains at −75°F.

propellant grain. The strain in the motor was compared at −75°F. with the standard Instron data in the hope of establishing a correlation between the propellant failure strain under the condition, as seen in the motor, and the failure strain, as encountered in uniaxial tensile tests.

The propellant property used was the lowest tensile strain at break reported from the two or three tensile tests taken at −75°F. Since some of the motors had been stored for various lengths of time at 0°F. before cycling to −75°F., an estimated correction for embrittlement was added to the strain at break as measured on unembrittled propellant. The strain at break corrected for embrittlement was divided by the measured strain in the motor on its first cycle to −75°F., to give a ratio called ϵ_b/ϵ_{mm}. The ratio of ϵ_b/ϵ_{mm} is shown plotted against the per cent of motors cracking at that ratio in Figure 10. When the ratio ϵ_b/ϵ_{mm} was 1 or less, all of the motors failed; when the ratio was 2 or more, none of the motors failed. The region between 1 and 2 is the expected area of doubt caused by the wide distribution of propellant properties.

The embrittlement corrected value of strain at nominal maximum stresses was also divided by the measured strain of the motor on the first cycle to −75°F. and plotted against the per cent of motors failed, Figure 11. From a comparison of Figures 10 and 11, the strain at break appears to be a much more discriminating value to use for predicting failure due to thermal cycling.

The correlation shown in Figure 10 by means of the relation ϵ_b/ϵ_{mm} emphasizes the importance of adequate data on ϵ_b within and between batches, and the probable importance of measuring ϵ_b under environmental conditions closely approaching those in the motor. The success of the correlation with uniaxial data suggests that a concentration on uniaxial failure behavior is warranted for correlation with failure data on small charges having unrestrained ends. The data on yield bands also suggest that study of the number of yield bands produced in tubular grains is pertinent in this type of correlation, as is a general study of the production of yield bands at various temperatures or, more specifically, the formation of such bands in tensile specimens due to simultaneously straining and changing temperature.

GRAPHICAL REPRESENTATION OF FAILURE BEHAVIOR

The distribution of failure elongations at the various measurement temperatures can be combined with the expected strain in the motor, as shown in Figure 12, to give a graphical representation of the expected failure behavior. This figure is drawn with the lower 3σ limit of individual failure values to describe the failure value expected in the poorest batch used in the

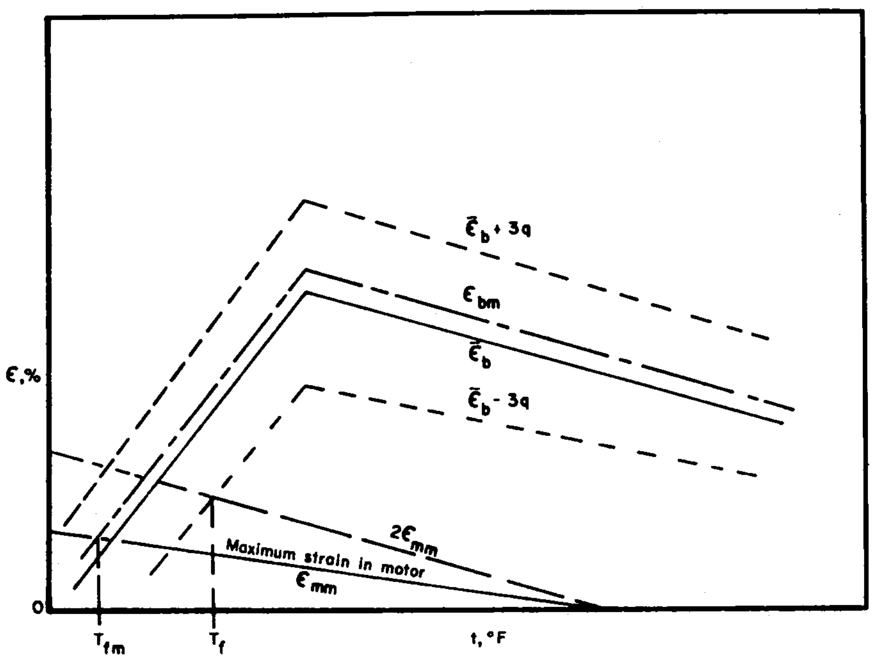

Fig. 12. Hypothetical propellant properties related to motor strain.

motors. From the correlation of Figure 10, the intersection of the lower 3σ curve with the line corresponding to twice the maximum expected motor strain should be the highest temperature, T_f, at which failure could be expected. Similarly, the intersection with the calculated strain in the motor of the lowest failure elongation expected from the best batch of propellant, ϵ_{bm}, would give the lowest temperature, T_{uf}, to which any of the motors could be expected to cycle before failure.

The work described here was accomplished under contract with the Air Material Command, USAF, and the permission of the USAF to publish this material is gratefully acknowledged.

The assistance of K. W. Bills, Jr. in supplying high-rate tensile data and of H. P. Briar in statistical analysis is gratefully acknowledged. The analytical studies reported here were supported under Air Force Contract AF 33(600)–40314 S.A. No. 1.

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Synopsis

Experimental and theoretical studies were made on failure criteria applicable to simple case-bonded hollow cylindrical grains. The minimum strain at break at −75°F. for uniaxial tensile test was found to be at least twice the hoop strain at −75°F. of a thermally cycled, case-bonded hollow cylinder of propellant when no failures were observed, whereas, when the minimum strain at break was equal to or less than the hoop strain of the cycled cylinder, the grain always cracked. For uniaxial tension, where the rate of elongation and temperature are controlled variables, the failure elongation varies from specimen to specimen and from batch to batch. A study of batch variability of the uniaxial test showed that a test at any test temperature from −40 to 180°F. could be used to characterize batch quality. The correlation of breaking strain at different rates and temperatures with the use of the WLF technique on one batch was found to be improved if an additional vertical shift factor was added to account for the lowering of the maximum failure elongation for temperatures below 0°F. However, by using a diagonal shift with rate, a graph of failure elongation versus temperature shows lower variability than does the WLF analysis.

Résumé

Des études expérimentales et théoriques ont été faites pour établir des critères de rupture applicables à des grains cylindriques creux pressés entre eux. La tension minimum à la cassure à −75°F pour un test de tension uniaxiale était égale au moins au double de la tension circulaire à −75°F pour un cylindre creux de propellant, lorsqu'aucune félure n'était observée; lorsque la tension minimum à la rupture était égale ou plus petite que la tension circulaire du cylindre, les grains cassent toujours. Pour une tension uniaxiale, lorsque la vitesse d'elongation et la température sont des variables contrôlées, l'élongation à la rupture varie d'un échantillon à l'autre et d'une préparation à l'autre. Une étude de variabilité des préparations par test uniaxial a montré que le test effectué à une température de −40 à 180°F peut être utilisé pour caractériser la qualité de la préparation. La corrélation entre la tension de rupture à différentes vitesses et températures, en se basant sur la technique WLF sur une préparation, peut être améliorée si on ajoute un facteur supplémentaire de glissement vertical afin de rendre compte de l'abaissement de l'élongation maximum à la rupture pour des températures inférieures à 0°F. Toutefois, en utilisant un glissement diagonal pour la vitesse, on obtient un graphique de l'élongation à la rupture en fonction de la température qui présente une variabilité plus petite que pour l'analyse WLF.

Zusammenfassung

Experimentelle und theoretische Untersuchungen der für einfache, einsatz-gebundene, hohlzylindrische Fasern anwendbaren Bruchkriterien wurden ausgeführt. Die Mindestbruchverformung bei −75°F betrug beim uniaxialen Zugtest wenigstens das doppelte der "Hoop"-verformung eines wärmebehandelten, einsatz-gebundenen Propellant-

Hohlzylinders ohne Auftreten von Fehlstellen; sobald die Mindestbruchverformung gleich oder geringer als die "Hoop"-verformung des behandelten Zylinders war, trat immer eine Rissbildung ein. Bei uniaxialer Spannungsbeanspruchung mit kontrollierter Dehnungsgeschwindigkeit und Temperatur variiert die Bruchdehnung von Probe zu Probe und von Ansatz zu Ansatz. Eine Untersuchung der Abhängigkeit des uniaxialen Tests vom Ansatz zeigte, dass ein Test bei beliebiger Temperatur zwischen −40° und 180°F zur Charakterisierung der Qualität eines Ansatzes brauchbar war. Die Korrelation der Bruchverformung bei verschiedener Geschwindigkeit und Temperatur mit dem WLF-Verfahren wurde durch Anwendung eines zusätzlichen vertikalen Verschiebungsfaktors zur Berücksichtigung der Erniedrigung der maximalen Bruchelongation bei Temperaturen unterhalb 0°F verbessert. Ein Diagramm Bruchdehnung gegen Temperatur zeigt jedoch bei diagonaler Verschiebung mit der Geschwindigkeit eine geringere Variabilität als nach der WLF-Analyse.

Received April 10, 1962