

Energy Balances and Uniaxial Damage of Highly Filled Elastomers

ALBERT H. LEPIE and ARNOLD ADICOFF, *Naval Weapons Center, China Lake, California 93555*

Synopsis

A propellant sample undergoes internal damage while it is tested at finite deformation. The damage consists of broken molecular chains and void spaces which form around the filler particles and contribute to failure of the propellant. Attempts were made to determine the amount of this damage from the viewpoint of energy dissipations. Mechanical energy losses, called damage energy, were computed from energy changes during tension cycling experiments carried out at different temperatures and straining rates. Shift procedures were applied to the experimental results, and a double-reduced master curve for damage energies was obtained by using time-temperature and strain shift factors. The reduced master curve can be used to predict the extent of damage accumulated in a propellant sample during tensile tests at different straining rates and temperatures.

INTRODUCTION

It has been postulated that the interaction between the binder and the oxidizer is responsible for the mechanical behavior of propellants.¹ In general, it is difficult to differentiate between the various microstructural phenomena that lead to ultimate failure of a propellant. The extremely high surface-to-volume ratio of about 3000 of an average 85% solids propellant leads one to suspect the role of the surface in failure.

Most workers in the field relate the high local binder stress fields in a finitely deformed propellant to the microstructural damage effect, called dewetting. In a strict sense, the dewetting refers to a debonding between the solid substrate and the binder.^{2,3} In actual fact, one should include chemical bond scission at a point distant from the interface. Finite deformation then results in formation of voids near the vicinity of the particles.

The purpose of this paper is to present the damage effects in a somewhat different perspective. Therefore, in this paper we examine a term which we call damage energy and determine the dependence of this energy on temperature, straining rate, and extent of strain.

THEORETICAL CONSIDERATIONS

A uniaxial tensile test on an end-bonded specimen from 0% strain to failure results in a single stress-strain curve which is characteristic for the material.

The area under the curve represents the total mechanical energy input (E_t) required to break the sample:

$$E_t = \int_{\epsilon_0}^{\epsilon_1} \sigma(\epsilon) d\epsilon. \quad (1)$$

A part of this energy is elastic and recoverable and causes contraction of the end pieces of the elongated sample after breaking. Another part of the energy is not recoverable and is consumed by an irreversible damage process during the straining experiment. Thus, the total input energy can be divided into two parts:

$$E_t = E_e + E_l \quad (2)$$

E_e is the elastic part and E_l is the lost part of the energy.

If a tensile experiment is interrupted at finite strain and the same sample is strained again, a different stress-strain curve is obtained, indicating a lower stress at the same value of strain.^{4,5} The difference between the virgin and second stress-strain curves is assumed to be caused by molecular chain scissions and dewetting which took place during the first stretch. The amount of dissipated energy during repeated straining is called damage energy (ΔE_D) in this paper:

$$\Delta E_D = E_n - E_{n+1}. \quad (3)$$

The total damage energy, $\Sigma \Delta E_D$, which is absorbed by a propellant sample from 0% to 40% strain has been determined from tension cycling experiments in which the percent of strain is increased in steps. The total damage energy is defined as the sum of the fractional damage energies obtained from the increasing strain cycling tests under isothermal conditions:

$$E_D = \Sigma \Delta E_D. \quad (4)$$

Equation (4) is applied to compute energy losses due to microstructural damage. This is an approximation, since other irreversible processes may be involved which are not readily measured or computed.

EXPERIMENTAL

The experimental procedures were derived from the requirements to measure fractional dissipated energies as a function of strain, temperature, and straining rate. Tensile cycling experiments in increasing strain steps were carried out on end-bonded, cylindrical propellant samples. The propellant contained 85% ammonium perchlorate and powdered aluminum as solid filler and 15% hydroxyl-terminated isocyanate-crosslinked polybutadiene as a polymeric binder.

The samples were strained with a rate (R) to predetermined strain levels (ϵ_i) and then immediately driven back to the initial length of the specimen. Each sample was allowed to recover without applied tensile stress for 60 min before the next increasing strain step was applied. The test temperature was held constant during the entire experiment.

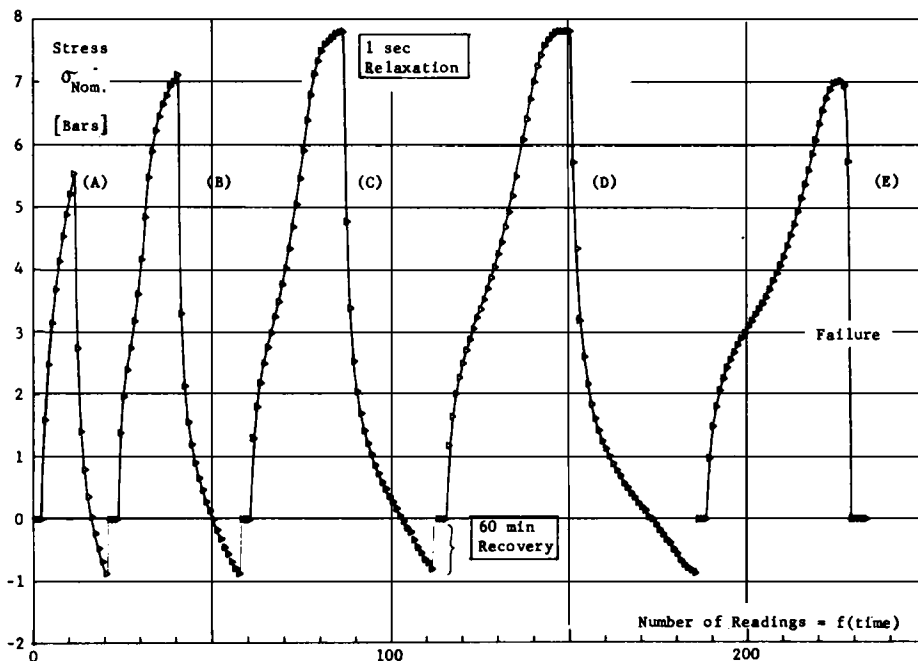


Fig. 1. Tension cycling test on HTPB propellant. Straining rate = 5.0 cm/min, $T = 0^{\circ}\text{C}$, and time between readings = 0.980 sec.

The following parameters were chosen for cycling experiments: Straining rates (R) from 0.05 to 5.0 cm/min and six different temperatures (T) from 23° to -30°C . The tension cycling steps were increased in 10% strain intervals or steps. Stepwise stress-strain curves with 60 min recovery time were obtained via an Instron tester. The test runs were controlled by an automatic timing device. A typical test run with stress recordings for cycles A to E versus time is shown in Figure 1.

TEST EVALUATION

The input energies as function of strain were computed from the areas under the stress-strain curves by stepwise numerical summation. Figure 2 shows an example of stepwise experimental stress-strain curves of a cycling test and the obtained integral curves.

The fractional damage energies between cycles were calculated as differences in strain energies of sequential cycles. An example of dissipated fractional damage energies of a cycling experiment is plotted in Figure 3. The total damage energies as a function of strain were calculated by adding the fractional damage energies ΔE_D in 10% strain increments.

In this manner, the damage energies as a function of strain were obtained for six different temperatures and three straining rates, covering three logarithmic decades.

Figure 4 shows a three-dimensional stereo plot of the damage energies versus temperature and straining rate with strain as a parameter. The figure indicates that shift procedures⁶ can be applied to the experimental results, in

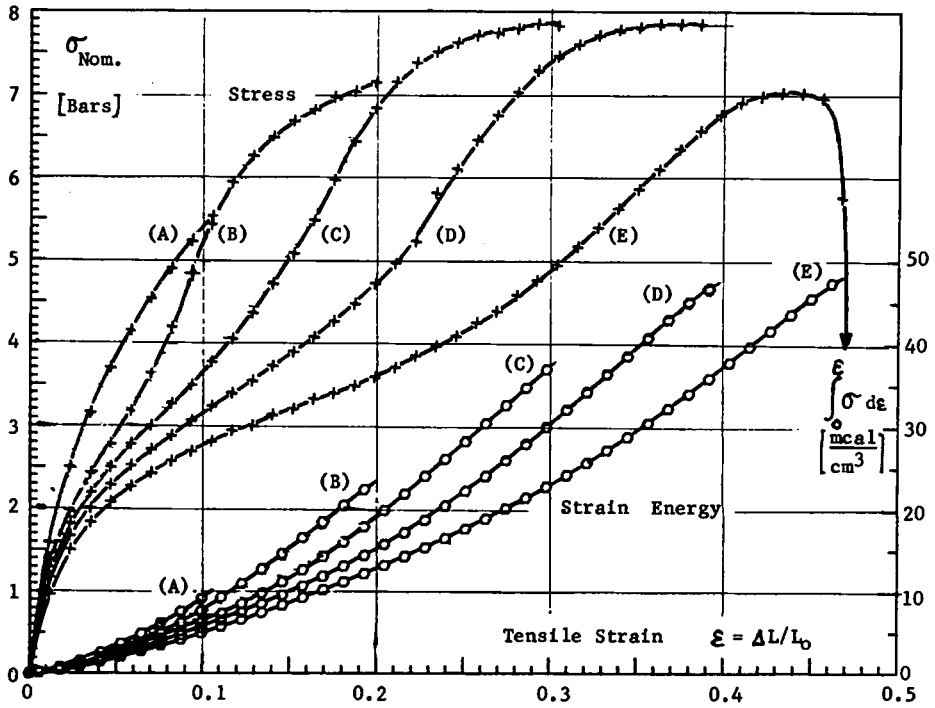


Fig. 2. Tension cycling test, stresses and energies vs. strain. Straining rate = 5.0 cm/min, $T = 0^{\circ}\text{C}$, recovery time between cycles = 60 min.

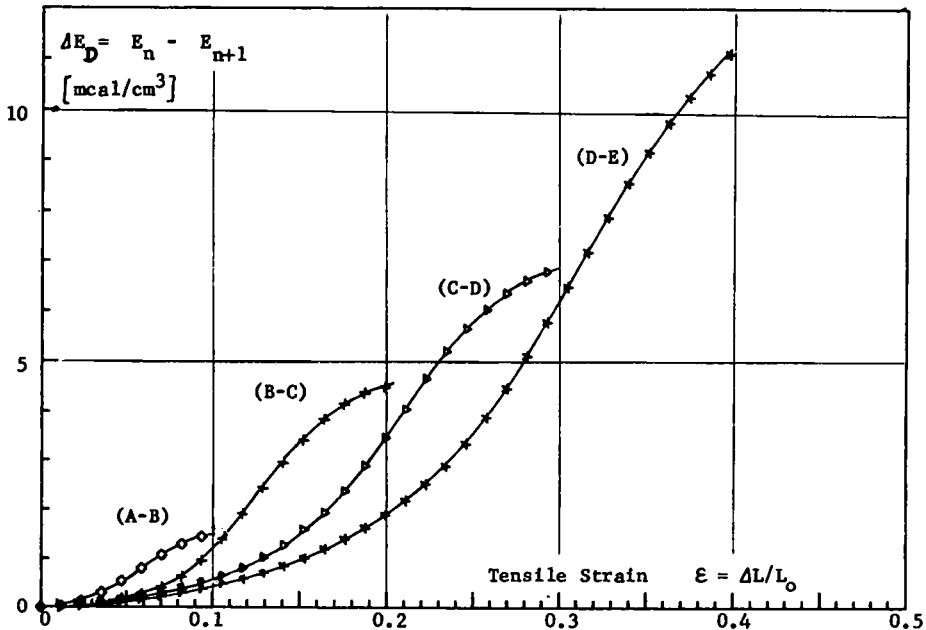


Fig. 3. Damage energies during cycling test vs. strain. $T = 0^{\circ}\text{C}$, $R = 5.0$ cm/min, recovery time between cycles = 60 min.

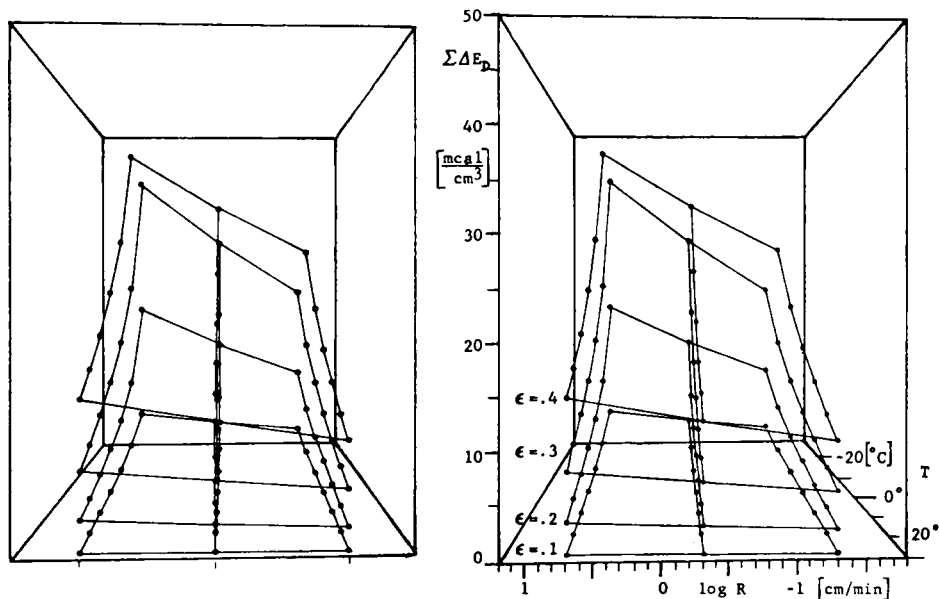
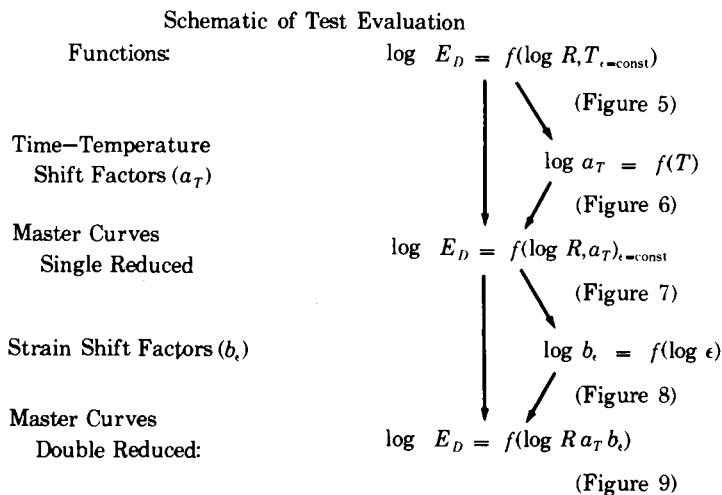


Fig. 4. Effect of temperature, strain, and straining rate on damage energies. $\Sigma \Delta E_D = f(T, R, \epsilon)$ with strain as parameter (stereo plot).

order to obtain a single reduced master curve. One of the possible double shifts was carried out and is explained in the following schematic with references to the corresponding figures:



The plots including shift factors obtained during the shift procedures are presented in Figures 5–9.

DISCUSSION

The damage energy as discussed in this paper is related to the difference in stress levels observed in a successive stretching experiment and is determined

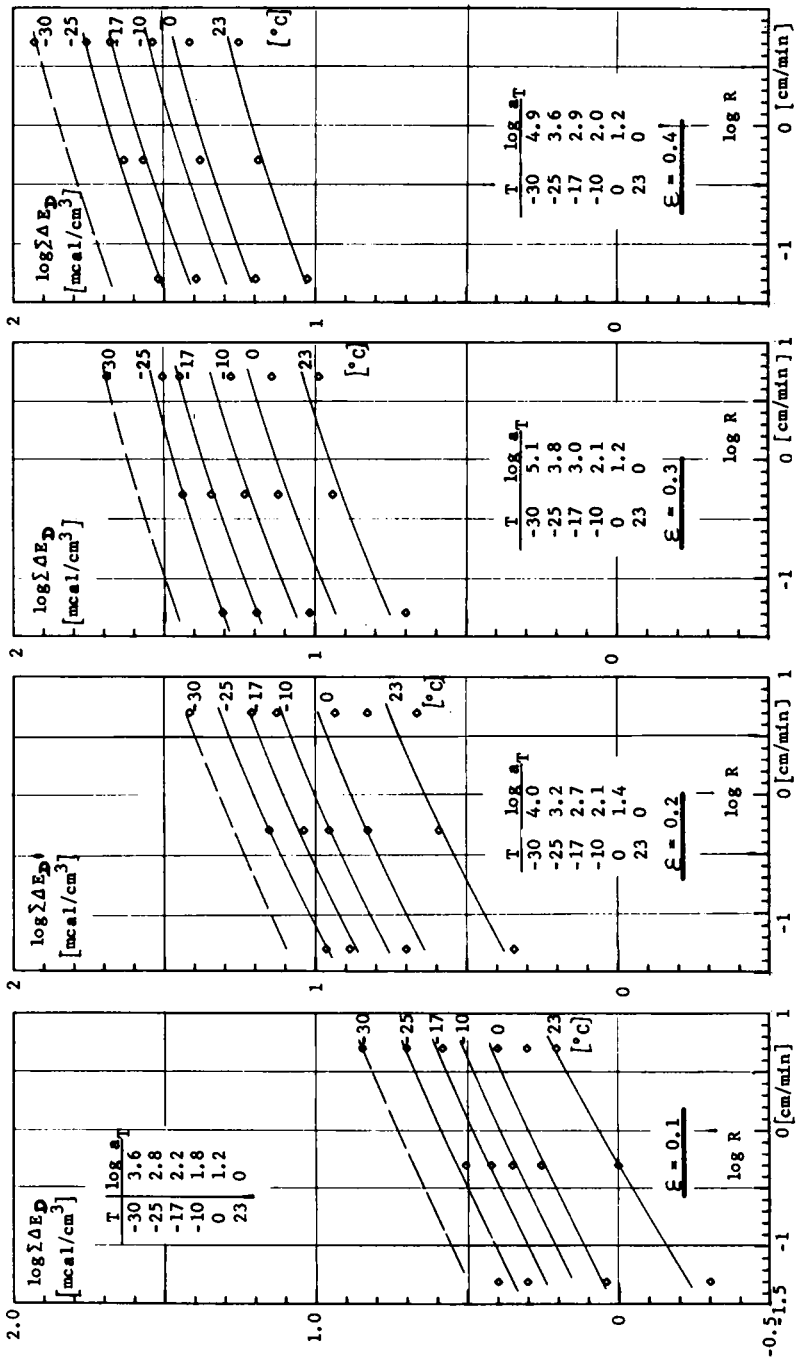


Fig. 5. Damage energies as a function of straining rate and temperature.

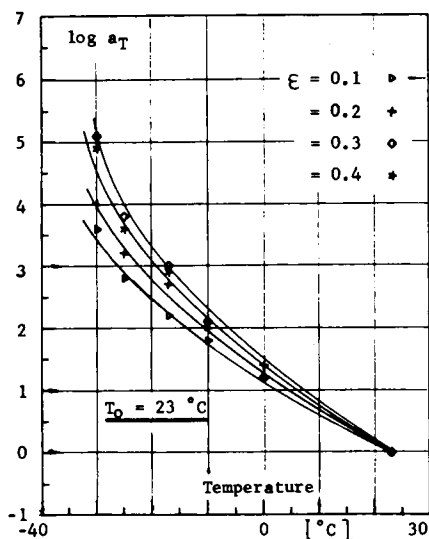


Fig. 6. Time-temperature shift factors vs. temperature.

from the stress-strain loops. The loop should not be interpreted as a hysteresis loop, since a recovery in stress and strain was permitted to occur between successive stretches.

It can be assumed that the damage energy includes all of the nonrecoverable, irreversible processes that are the primary microstructural damage effects occurring in the sample. In this experiment, the sample was driven back to its unstrained length rather than permit an increase of damage that might occur in the specimen during extensive stress relaxation at maximum

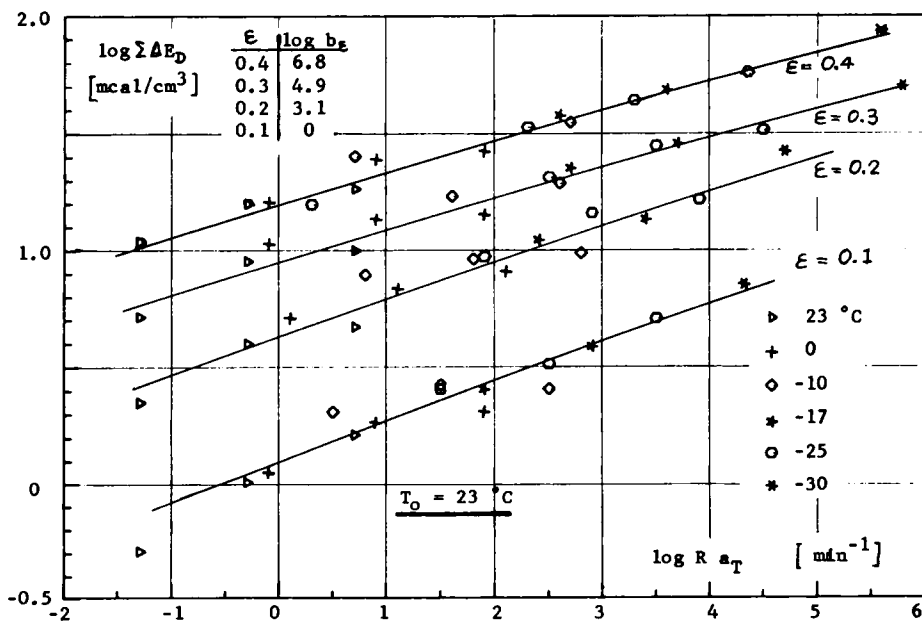


Fig. 7. Reduced master curves for damage energies at different tensile strains.

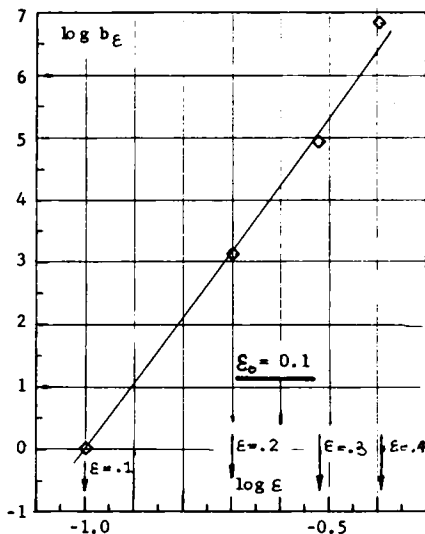


Fig. 8. Strain shift factors vs. log strain.

strain. A small increase in damage as a function of stress relaxation time at maximum strain was observed in earlier work.⁷

It was also of interest to examine the possible existence of a healing process occurring during the recovery period between successive strains. This was done by examining the damage as a function of time between successive stretches. The measured damage energies were the same after 30 to 50 min of recovery. The sample, however, was slightly in compression (Fig. 1), and the compressive load diminished to nearly zero after 60 min. Other investigators reported propellant volume expansions of approximately 10% at fail-

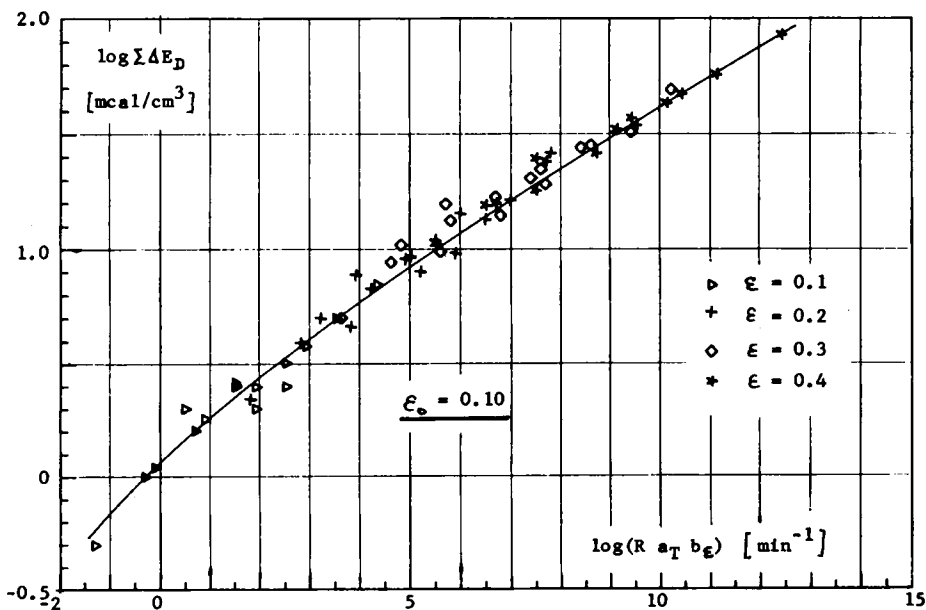


Fig. 9. Master curve for damage energies, reduced by two shift factors, $\log a_T$ and $\log b_\epsilon$.

ure strains.^{8,9} After releasing the strained sample to its original length, an exponential decrease in volume with time was measured. The volume contraction came nearly to a stop after 30 to 60 min of recovery time, and a permanent volume increase was observed after 24 hr. Based upon these experiments, a recovery time of 60 min between successive stretches appeared to be adequate.

Examination of the repeated interrupted stress-strain curves reveals that the envelope of the cycling curves to failure is similar to the uninterrupted stress-strain curve. The major difference is that the repeated interrupted stress-strain curves show slightly lower stress values than the uninterrupted curves during the last 10% strain before the failure. The difference does not appear to be overly significant and is ignored for the purpose of this paper. The interrupted stress-strain curves seen in Figure 2 show that in sequential stretches the damage to the sample increases only after the previous maximum strain level is reached. Holding the sample at the previous maximum strain level, the damage is only slightly increased. The master curve for the damage energies seen in Figure 9 is the result of two sequential shifts applied to the damage energies. The fact that the data can be shifted in this way to yield a master curve of simplicity is a reality, indicating that the extent of damage and propellant failure can be written as a function of three parameters: strain, temperature, and straining rate.

The strain dependence of the WLF time-temperature shift factors for the dynamic shear moduli was discussed in a previous publication.¹⁰ The dynamic moduli were determined from sinusoidal tensile oscillations superimposed to finite strains and were used to characterize the change in viscoelastic properties at each experimental strain plateau.

The effect of straining rate on damage properties discussed in this paper is then simply another experimental measure of the nonlinear viscoelastic behavior of a propellant. A propellant, unlike most elastomers, is a very complex system compared to conventional rubbers. In addition to the high volumetric loading with inorganic materials, the elastomer is usually undercured (80-90% extent of reaction) and contains many unreacted chain ends.

Polybutadiene has an entanglement molecular weight¹¹ of approximately 1500 g/mole, and the propellant binder has a crosslink density on the order of 10^{-5} to 10^{-6} moles/cm³. The observed straining rate effect on damage can, therefore, be a measure of the extent to which entanglements can disentangle versus the rate at which bonds can rupture.

It has been shown that the energy required to damage a propellant sample at 40% strain is of the order of 80 to 100 mcal/cm³ and is dependent upon temperature and the straining rate. A slight increase in damage energy with increasing rate of strain can be expected because of the viscoelastic nature of the matrix and the time required for stress relaxation around the particles. It has been evaluated elsewhere¹² that the primary damage mechanism contributor that can be invoked to account for the measured damage energy has to be scissions of primary bonds of crosslinked binder. For carbon-carbon bonds (82 kcal/mole), this amounts to 1.4×10^{-16} mcal per bond and 7×10^{17} scissions per cm³. Carbon-oxygen and carbon-nitrogen bonds would yield other values for bond scissions than those calculated for carbon-carbon bonds. Adhesive failure for realistic surface areas can only account for be-

tween 1% and 10% of the measured damage energies. One can visualize, in principle at least, that adhesive failure under vacuum is reversible, while bond scission is permanent and irreversible. Suitable annealing times should result in some partial healing of the sample if pure adhesive failure does occur to any extent in the propellant. Lack of significant rehealing reinforces the suggestion that the primary process involves primary bond scission.

CONCLUSIONS

The results of this investigation suggest that microstructural damage can be assessed and measured through the evaluation of differences in the stress-strain curves obtained in successive stretches of a sample. This difference in the measured energies required to strain the sample, called damage energy in the paper, seems to be a fundamental property involved in ultimate failure. The damage energy can be directly related to the bond scission occurring in the propellant, which accounts for the major portion of the dissipated or damage energy.

The damage energy appears to be a material property which can be treated in a fashion similar to other viscoelastic properties in that time-temperature and strain shift factors can be used to reduce the data to a single master curve.

Current experience indicates that the damage energy is a constant for the propellant and independent of the mechanical path. This permits the determination of extent of damage that a propellant has undergone during environmental exposure and the fraction of the failure life remaining in the propellant at time of testing. The propellant must have been previously calibrated.

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