

Fracture Energies of Composite Propellants

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Synopsis

Three types of fracture energies, i.e., for initiation, propagation, and the work of fracture, were measured for an ammonium perchlorate/polybutadiene composite propellant. The testing employed the "trouser leg" specimen configuration. The effect of an accelerated aging process on these energy values was also investigated, showing that such a process ultimately results in a reduction in the fracture energies.

INTRODUCTION

One of the most important problems concerning a solid propellant is its aging which will ultimately limit the useful service life of the motor. A composite propellant consists of a mixture of oxidizer and fuel. The oxidizer (e.g., ammonium perchlorate) is embedded in the fuel matrix which is normally an elastomer. This highly filled elastomer is bonded to a metal or fiber glass case through liner and insulation materials. This complex structure provides many sources of aging processes enhanced by the various storage conditions of the operational motor. One of these aging processes is, for example, a continuous oxidation of the matrix by the filler during storage, leading gradually to structural failure of the propellant and malfunctioning of the motor (see, for example, ref. 1).

Most of the common methods for assessing motor service life are based on measuring mechanical properties such as modulus and ultimate strength as functions of accelerated aging conditions.² Such mechanical properties, however, are less sensitive than the fracture energy to internal changes in the material. Also, the fracture energy is independent of test configurations and specimen geometries, and, being a characteristic of the material, it is a more fundamental measure of strength than the ultimate strength.

Thus, the present study has been undertaken to measure various types of fracture energy of an ammonium perchlorate/polybutadiene propellant under accelerated aging conditions.

FRACTURE ENERGIES

A commonly used test specimen in tear tests for the determination of the fracture surface energy, γ (γ is related to the tear energy T by $T = 2\gamma$), is the "trouser leg" specimen used in the present work and described in Figure 1 (see,

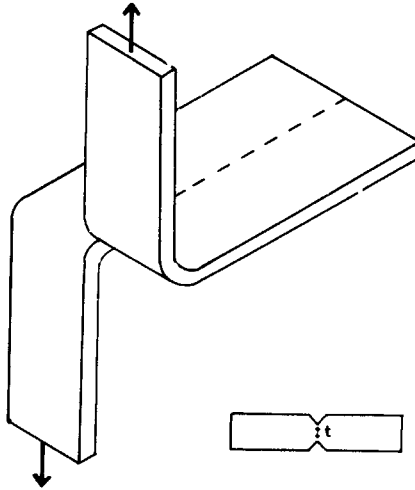


Fig. 1. "Trousler leg" specimen used for determination of fracture energies.

for example, ref. 3-6). By application of the Griffith criterion to this test configuration, Rivlin and Thomas³ have arrived at eq. (1), which gives γ in terms of the measured force f to produce tearing, the measured extension ratio λ , and W_λ , the stored energy per unit volume corresponding to an extension ratio λ :

$$\gamma = \lambda f / t - W_\lambda A_0 / 2t \quad (1)$$

where A_0 and t are the cross-sectional area and the thickness of the specimen, respectively.

Anderton and Treloar,⁴ who arrived at the same result from considerations avoiding the direct use of the Griffith criterion, show that for certain materials

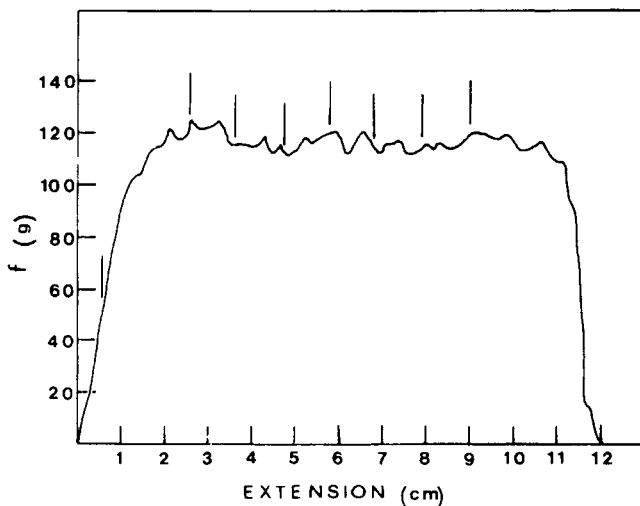


Fig. 2. Typical force-extension curve with markings of tear initiation and of intervals of tear propagation.

or under certain experimental conditions $W_\lambda A_0/2t$ is negligible compared with $\lambda f/t$, and $\lambda \simeq 1$. Thus, in these cases, eq. (1) reduces to

$$\gamma \simeq f/t \quad (2)$$

Figure 2 presents a typical force-extension trace obtained for the composite propellants tested in this work. Such a trace enables us to calculate three different values of γ as follows: (i) the fracture surface energy for initiation γ_I , obtained by taking the value of f required to initiate fracture; (ii) the fracture energy for propagation γ_P , obtained by taking the average value of f during the stage of stable crack propagation; (iii) the work of fracture γ_F , derived from the ratio of the total energy required to completely tear the specimen and the newly formed fracture surface.

EXPERIMENTAL

The propellants were composed of ~60% ammonium perchlorate particles (10–14 μm) and ~15% aluminum particles (14 μm) as solid fillers, and of a terpolymer of butadiene, acrylic acid, and acrylonitrile (PBAN) as a polymeric matrix. Test specimen of $0.2 \times 2.0 \times 7.0 \text{ cm}^3$ of the configuration shown in Figure 1 were sliced off the propellant block by a guillotine. An initial cut of length about 2.0 cm was inserted along the center line of the specimen by means of a razor blade. Two razor blade slots were inserted on both sides of the specimen along its center line starting from the tip of the initial cut, so that about 75% of the thickness remained to be torn through. The exact depth of each of these slots for every specimen was determined after it was torn by means of a stereomicroscope, so that the exact value of t could be determined. Pen marks at distances of 0.5 cm were made across each specimen to enable the calculation of the extension ratio as described below. At least 25 specimens were tested for each type of material.

Testing was carried out on an Instron machine as a cross-head speed of 5.0 cm/min. A pip marker was used to mark the point of fracture initiation and also to mark stages in fracture propagation corresponding to the pen marks on the specimen. A typical Instron curve showing these marks is shown in Figure 2. The average value of λ , which is the ratio of the strained length to the unstrained length, was determined from the ratio of the distance measured on the chart to twice the corresponding distance marked on the specimen.

The value of the stored energy function can be shown to be given by eq. (3) as follows:

$$W_\lambda = E(\lambda - 1)^2/2 \quad (3)$$

were E is Young's modulus of the material. The modulus was determined with dumbbell-shaped specimens using a strain gauge extensometer at a cross-head speed of 0.5 cm/min. For determining an average value for each material, three specimens were tested.

Accelerated aging was carried out at a constant temperature of 60°C, thought to enhance the oxidation interaction between the ammonium perchlorate and the organic matrix.

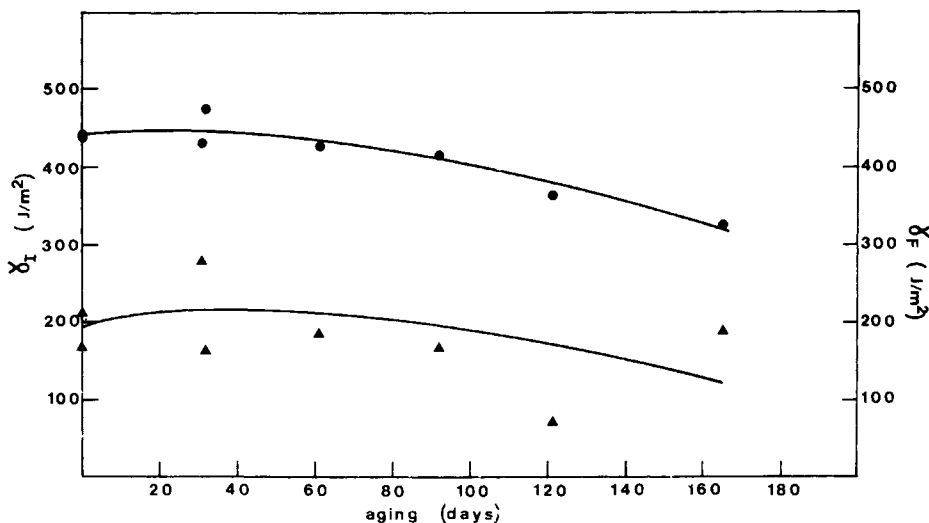


Fig. 3. Values of fracture energy for initiation (▲) and of work of fracture (●) as functions of aging period.

RESULTS AND DISCUSSION

In a preliminary investigation, we discovered that the specimen dimensions do not affect the average value of either one of the energy values measured. In this investigation, the length of the specimens was varied in the range of 5.0–12.0 cm, the width in the range of 0.9–2.0 cm, and the thickness in the range of 0.05–0.3 cm. Also, stereomicroscope investigations of the fracture surfaces showed that the tear path did not follow a zigzag cross section reported for other elastomers in reference 6. Thus, in our calculation of the energy values, t was not multiplied by $\sqrt{2}$ as proposed.

Figure 3 presents the results of the fracture surface energy for initiation (γ_I) and of the work of fracture (γ_F) as functions of the aging period. The former was calculated according to eq. (1). It is seen that after about 40 aging days, both γ_F and γ_I slightly surpass the original values for the unaged material; thereafter, γ_F exhibits a consistent decrease with the aging period, while γ_I exhibits a very big scatter with less consistent trend. This scatter results from the difficulty in determining accurately the instant of fracture initiation. Figure 4 presents the results of fracture energy for tear propagation. Here, two values of γ_P are given: the first, γ_{P1} , calculated according to eq. (1), and the second, γ_{P2} , calculated according to eq. (2). In both cases, γ_P reaches a maximum value after about 30 aging days; thereafter, it decreases gradually to about 70% of the original value after 165 days.

Since the tear energy of the pure matrix material is directly proportional to the molecular weight between crosslinks,⁵ and since aging results in degradation of polymer chains, the tear energy of the matrix material is thus expected to decrease with the aging process. Hence, the trends of the tear energy results which exhibit maxima may be understood as follows. An aging process such as used in the present study is expected to increase the rate of oxidation reaction expected to occur between the filler and the matrix, and to destroy the adhesion

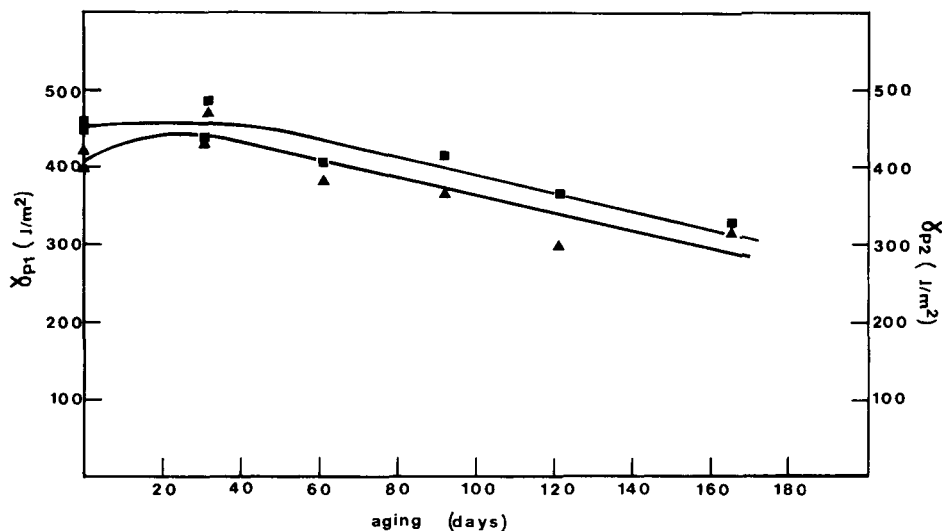


Fig. 4. Values of fracture energy for propagation calculated by eq. (1) (▲) and by eq. (2) (■) as functions of aging period.

between them. It has been shown for other particulate composites such as glass bead-filled epoxies or poly(phenylene oxides) that a reduction in the filler-matrix bond strength results in increasing the fracture energy.^{7,8} This is so because strong bonding yields subsurface cracking away from the filler particles, thus eliminating the energy dissipating crack-front bowing mechanism acting when an interaction of the crack front with the particles is feasible.⁹ It is, therefore, suggested that the initial increase in the values of γ results from a corresponding drop in the ammonium perchlorate-polybutadiene bond strength due to accelerated oxidation reaction between these components. However, as the oxidation reaction proceeds with the aging process, damage spreads from the interface into the matrix. A possible reason for such internal damage may be internal gas pressure built up by the gases evolved during oxidation.¹ Such matrix damage may be responsible for the reduction in values of γ .

Examination of Figure 4 also reveals that the differences between γ_{P1} and γ_{P2} are insignificant. This suggests that in the case of the above materials and specimen dimensions, the contribution of the term $W_\lambda A_0/2t$ is, in fact, negligible. Table I displays the average values of E , λ , and W_λ obtained for each of the tested sets. It is seen that the value of λ is reasonably constant with the aging period while the modulus decreases gradually. W_λ , which is directly proportional to $(\lambda - 1)^2$, is, therefore, very sensitive to minor changes in λ and thus exhibits a very inconsistent trend.

TABLE I
Effect of Aging on Modulus, Extension Ratio, and on Stored Energy Function

| | Aging 0 days | 0 days | 31 days | 32 days | 61 days | 92 days | 121 days | 165 days |
|---------------------------------|--------------|--------|---------|---------|---------|---------|----------|----------|
| E , MN/m ² | 5.86 | 5.86 | 5.36 | 5.06 | 5.64 | 5.01 | 4.55 | 4.77 |
| λ | 1.053 | 1.055 | 1.055 | 1.032 | 1.060 | 1.075 | 1.080 | 1.044 |
| W_λ , kN/m ² | 8.3 | 8.9 | 8.1 | 2.6 | 10.2 | 14.1 | 14.6 | 4.3 |

CONCLUSIONS

The trend of the values of the fracture surface energies measured in this study as a function of the aging period suggests that these physical properties are sensitive to internal changes suspected to be induced by filler-matrix oxidation interaction. It is thought that the trend of these energy values reflects initially the destruction of the bonding between ammonium perchlorate and the polybutadiene matrix, and later on it reflects the spread of the damage from the interfacial zone into the matrix. Of the three energy values examined, γ_P and γ_F seem to be more reliable than γ_I due to a larger scatter of the results of the latter.

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