Tensile Strain Rate Effect in Mechanical Properties of Dummy HTPB Propellants

H. L. CHUNG,* K. KAWATA, and M. ITABASHI

Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278, Japan

SYNOPSIS

The tensile strain rate effect in tensile strength and elongation at break for a series of filled dummy hydroxy-terminated polybutadiene (HTPB) propellant binders was studied. The data were obtained at various tensile strain rates from 10^{-4} to 10^{-1} s⁻¹ on two types of specimens at room temperature. The "high velocity ductility" behavior, which is qualitatively similar to those of unfilled elastomers, was revealed. This means that the breaking strain increases markedly at elevated strain rates. For "Bukkon-type" and rod-shaped specimens, test results are consistent with each other. The fact that the increased filled solids level leads to a decreased breaking elongation capability and an increased tensile strength was obviously found. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Solid composite propellants are the prime component of solid rocket motors, and the performance of such motors is influenced largely by the mechanical properties of propellant grains. In the design of rocket motors, great importance is attached to the mechanical behavior of solid propellant grains. This is because the presence or occurrence of cracks in the propellant during the ignition stage may lead to irregularities in the burning process and to malfunction of the rocket motor. Stress cracking in the propellant may occur either during the storage period, as a result of shrinkage or of thermal stresses, or during the ignition period, in which the pressure in the motor chamber increases rapidly to its equilibrium or operating value that depends upon ballistic property requirements, or during the combustion period due to the action of the combustion pressure or that of the acceleration forces. For casebonded grains, the most important mechanical property required for propellants is a relatively large ultimate elongation over a range of temperature and strain rate during motor storage, thermal cycling, and firing.¹

For the proper understanding of the mechanical behavior of composite solid propellants, detailed knowledge of the properties from uniaxial tensile tests of highly filled elastomers is essential. Composite propellants consist of a soft polymeric binder filled with a high amount of hard inorganic oxidizer (typically, aluminum and ammonium perchlorate) to provide the required performance. In this study, the hydroxy-terminated polybutadiene (HTPB) binder system, which is a widely used binder in solid composite propellant for large, high-performance rocket motors,^{2,3} filled with a quite high levels of solids particles of glass and plastic beads, instead of the real oxidizer, was adopted. Two kinds of simulated HTPB propellants were formulated.

Because of the viscoelastic nature of the binder, the modulus and ultimate mechanical properties of propellants depend markedly on temperature and strain rate.^{4,5} Studies were made previously on the dependence of the tensile strength and ultimate elongation of some elastomers for instance, an unfilled SBR rubber,^{6–9} on temperature and strain rate. The ultimate elongation may either increase or decrease with increasing strain rate, depending on the temperature and the range of strain rate covered. However, the effect of tensile strain rate to assess mechanical properties and fracture characteristics of filled HTPB composite propellants has not been investigated. The present study was focused on the

^{*} To whom correspondence should be addressed. Journal of Applied Polymer Science, Vol. 50, 57–66 (1993) © 1993 John Wiley & Sons, Inc. CCC 0021-8995/93/010057-10

evaluation of the strain rate effect in stress-strain relations up to breaking at room temperature for filled HTPB composite propellants not yet investigated. Breaking stress, breaking strain, and absorbing energy derived from the stress-strain curves are the principal propellant responses from which failure properties are obtained, and as the origin of "high velocity ductility" of this material is an interesting item, it will be studied in the next step.

Furthermore, the behavior of two types of HTPB propellants were compared to determine the effects of solid levels on mechanical properties. Also, for the purpose of future impact tensile tests, a designed rod-shaped specimen that has shorter gauge length than that of the standard tensile sample were tested at the same test conditions to evaluate the consistency of results with the "Bukkon-type" specimen. The configuration of the Bukkon-type specimen is subjected to the standard of the Property of Composite Propellant Committee of Japan¹⁰ and is a revised type of JANAF tensile sample.

EXPERIMENTAL

Materials

Two types of propellants composed of HTPB binder as the polymer matrix, filled with a large percentage of simulated oxidizer solids of glass and plastic beads (called dummy HTPB, hereafter), were adopted for various tensile tests in the present study. Table I gives the composition of two types of dummy HTPB propellants. In Table I, aluminum is the metal often added to solid propellants to increase their performance. Iron oxide added by 0.3 wt % in exterior percentage was selected as the burning rate additive in the HTPB propellants developed on this composition.

Two types of uniaxial tensile specimen—Bukkon and rod-shaped tensile specimens shown schemat-

Table IConstituents of Dummy HTPBPropellants

	Prope	llants
Composition (Wt %)	PB14	PB15
HTPB binder	14.0	15.0
Glass beads	50.0	49.0
Plastic beads	18.0	18.0
Aluminum	18.0	18.0
Iron oxide ^a	0.3	0.3

* Exterior percentage.



Figure 1 Dimensions and geometry of Bukkon-type specimens (dimensions in mm, designated by the symbol D in material types).

ically in Figures 1 and 2—were prepared from the bulk propellant of the same batch produced by Nippon Oil & Fats Co. The configuration of Bukkontype samples were die-stamped from the propellant sheets, with dimensions 50 mm in gauge length, 10 mm in width, and 10 mm in thickness, and as shown in Figure 1, slant line parts of the samples were clamped by grips with 80 mm in grip length.

On the other hand, rod-shaped samples were obtained by casting at the same batch with Bukkontype specimens. As shown in Figure 2, the rodshaped specimens were 12 mm in diameter and 10 mm in gauge length. They were bonded to the jigs with epoxy resin adhesive (Cemedine EP001). Prior to testing, some bench marks 1 cm apart in the specimen gauge length area of Bukkon-type samples were drawn for strain measurement reference.

Measurements

The tensile tests were carried out at various uniaxial constant crosshead rates of 0.5, 5, 50, and 500 mm/min and a temperature of $20 \pm 2^{\circ}$ C, by a universal material testing machine (Shimadzu, Autograph AGS-500A, loading capacity 0.5 ton). By these con-



Figure 2 Dimensions of rod-shaped specimens and an assembly drawing (dimensions in mm).

stant crosshead speed testings, the stress-strain behavior of dummy HTPB propellants up to rupture was measured at strain rate range from 10^{-4} to 10^{-1} s⁻¹.

In addition to the standard autograph recorder load-displacement trace, specimen elongation was recorded and assessed through the use of camera film at a framing rate of one frame per 4 min and 20 s at tensile crosshead speeds of 0.5 and 5 mm/ min, respectively. The time from the start of the test to the specimen rupture were cross-checked from load-displacement trace and record.

For Bukkon-type specimens, elongations between the bench marks of gauge length were measured from the film record at various strain levels to determine the corresponding effective gauge length factor α ,¹⁰ which can be calculated from the simple equation

$$\varepsilon_c = \Delta l_c / l_g \tag{1}$$

$$\varepsilon_g = \Delta l_g / l_g \tag{2}$$

$$\alpha = \Delta l_c / \Delta l_g = \varepsilon_c / \varepsilon_g \tag{3}$$

where ε_c is the strain in grip length; ε_g , the strain in gauge length (real strain); l_c , the grip length; l_g , the gauge length; Δl_c , the elongation in grip length; and Δl_g , the elongation in gauge length.

For Bukkon-type specimens, the stress-strain relations were determined directly from the autograph recorder load trace and elongation in grip length. By using the effective gauge length factor α at various strain levels, the measured elongation in grip length can be modified to real strain in gauge length. Thus, mechanical properties of dummy HTPB propellants are acquired.

RESULTS AND DISCUSSION

Effect of Tensile Strain Rate on Failure Properties

Figures 3 and 4 show the states of tensile tests using typical Bukkon-type and rod-shaped specimens, corresponding to unloaded and just before rupture, at a strain rate of 10^{-3} s⁻¹. As shown in Figures 3 and 4, all test specimens of Bukkon-type and rod-



Figure 3 The states of tensile tests for rod-shaped specimens: (a) unloaded; (b) just before rupture.



Figure 4 The states of tensile tests for typical Bukkon-type specimens: (a) unloaded; (b) just before rupture.

shaped were stretched uniformly without necking through the gauge length up to the occurrence of the crack. Several visible cracks occurring in the



Figure 5 Typical stress-strain curves for Bukkon-type specimens at various tensile strain rates.

surface of the specimens could be observed and then they proceeded to rupture progressively. Moreover, all test specimens failed within the gauge length with



Figure 6 Typical stress-strain curves for rod-shaped specimens.

a small dispersion of breaking elongation, indicating good consistency.

The typical stress-strain behavior of dummy HTPB propellants at various tensile strain rates at room temperature, 21°C, is shown in Figures 5 and 6. The curves in the figures show that the tensile strength σ_p (maximum stress supported by the specimen), strain at tensile strength c_p , and total strain c_T (breaking strain) increase with increasing strain rate. For Bukkon-type specimens, the initial slope of the curves increases slightly with increasing strain rate, but for rod-shaped specimens, it does



Figure 7 Effect of strain rate on mechanical properties of dummy HTPB propellants: (a) tensile strength σ_p ; (b) total strain ϵ_T ; (c) absorbed energy per unit volume E_{ab} .

not increase significantly with increasing strain rate. Also, in both cases, after a rather straight initial part, the shape of the stress-strain curves shows a sharp bend; thereafter, the tensile force remains approximately constant, whereas the overall strain still increases considerably before rupture finally occurs. For all the curves, the behavior of the sharp yield point does not exist in contrast with glassy polymers such as epoxy resins in room temperature.¹¹

On the basis of the results of experiments, the effect of tensile strain rate $\dot{\epsilon}$ on the tensile strength σ_{p} , the total strain at fracture ε_{T} , and the absorbed energy per unit volume in fractured specimen E_{ab} are clear, as shown in Figure 7. For filled dummy HTPB propellants, all σ_p , ε_T , and E_{ab} increase remarkably with increasing strain rates. Especially for a high strain rate up to 10^{-1} s⁻¹, obvious behavior of high velocity ductility is exhibited. These behaviors are consistent with the unfilled HTPB binder that has been examined,¹² and this is because the mechanical properties of composite solid propellants depend on the binder that is chosen. From these results, the HTPB propellant system is considered to have a suitable impact-absorbing ability and relatively large ultimate elongation capability at high strain rates. These are the most important mechanical properties required with propellant grains for case-bonded motor design.

Effect of Configuration of Specimen on Failure Properties

The effective gauge length factor vs. strain measured between the bench marks for Bukkon-type specimens is presented in Figure 8. For PB14D and PB15D, test results show that α (= $\Delta l_c / \Delta l_g = 1.42$ -1.27) is a function of strain, decreasing with increasing strain. In accordance with the measured effective gauge length factor α , the measured stressstrain curves, derived from grip distance, can be modified to the stress-strain curves based on gauge length. The comparison of these stress-strain curves is also shown in Figure 8.

Measured mechanical characteristic values of filled dummy HTPB propellants are summarized in Table II. As for Bukkon-type specimens, data pertaining to strain that are listed in Table II have been modified by the effective gauge length factor, and the effect of strain rate on the modified mechanical properties is shown in Figure 9. Comparison with the results of rod-shaped specimens is shown. From these data, the effect of tensile strain rate $\dot{\epsilon}$ on mechanical properties is also obvious. They increase



Figure 8 Typical curves of stress vs. strain in grip and gauge length, respectively, and effective gauge length factor vs. strain in gauge length: (a) PB14D; (b) PB15D.

noticeably with increasing strain rates, as summarized in the previous discussions.

The comparison of the mechanical properties for the rod-shaped and Bukkon-type tensile specimens is also shown in Table II and Figure 9. Within the range of the same tensile strain rate level, it is interesting to note that the mechanical properties (σ_p , ε_T , E_{ab}) have a slight difference for these two types. This indicates that the rod-shaped specimens can be used as a good tensile specimen.

In Table II, α_p is the effective gauge length factor at tensile strength, E is the Young's modulus, and ε_L is defined here as the ratio of the nominal maximum stress, σ_p , to the Young's modulus E. The definitions of these mechanical characteristic values in the stress-strain curve are illustrated in Figure 10, where the Young's modulus E, defined here as the slope between the origin (except the toe) and the point of $\sigma_p/2$ in the curve, and ε_L , ε_p , and ε_T are the Table II Summary of Experimental Results of Dummy HTPB Propellants at Various Strain Rates

	Strain	No.	Ten Streng (kP	sile ¢th o _p `a)	Strai Ten Stren	n at sile sth ε_p	Total { e_r ('	Strain %)	$egin{array}{c} Abso \\ Ene \\ per 1 \\ per 1 \\ Volt \\ E_{ab} (kc) \end{array}$	rtbed rrgy Unit J/m ³)	(Ino Modul Modul	ng's lus <i>E</i> 2a)	Lan Strain (%	del n ɛ _L ª .)	Effec Gau Leng Factor	tive gth rα _b t
Propellants	Rate $\dot{\varepsilon}$ (s ⁻¹)	Specimens N	M°	SD^d	M	SD	M	SD	M	SD	W	SD	W	SD	W	SD
PB15D	$1.28 imes10^{-4}$	ę	731	13.6	36.9	1.70	40.8	0.71	198	13.4	4.5	0.71	16.7	2.61	1.3	0.06
	$1.28 imes 10^{-3}$	H	800	1	46.7	I	52.1	ł	307	I	4.7	ļ	16.9	Ι	1.2	ļ
PB14D	$1.28 imes10^{-4}$	2	746	39.1	35.8	1.15	38.7	0.85	198	3.6	3.9	0.28	19.1	0.37	1.3	0.01
	$1.28 imes10^{-3}$	2	848	44.2	40.9	0.69	43.6	0.14	254	15.4	6.2	0.06	13.7	0.84	1.3	0.01
PB15	$0.72 imes10^{-3}$	က	849	35.6	31.4	2.54	45.3	5.00	269	4.4	7.0	0.69	12.3	1.39	1	ł
	$0.74 imes10^{-2}$	2	976	4.5	42.0	0.39	58.6	2.01	459	1.6	7.7	0.68	12.8	1.06	ł	ł
PB14	$0.70 imes10^{-3}$	ç	868	8.8	27.0	0.97	41.1	2.18	276	17.3	7.9	0.73	11.5	0.98	ł	I
	$0.79 imes10^{-2}$	2	1019	18.9	36.9	4.84	58.7	6.63	470	55.7	7.5	0.90	13.8	1.41	1	ļ

• $e_{L} = \sigma_p/E$ defined by Landel.¹³ ^b Effective gauge length factor at tensile strength. ^c M = mean. ^d SD = standard deviation.

TENSILE STRAIN RATE EFFECT IN HTPB PROPELLANTS 63



Figure 9 Effect of strain rate on the modified mechanical properties of dummy HTPB propellants: (a) total strain ϵ_T ; (b) absorbed energy per unit volume E_{ab} .

derived parameters from the stress-strain curves of tensile specimens. According to the measured data in this study, the dispersion of e_L is smaller compared with e_p and e_T at room temperature. This is the reason why e_L has been proposed as a favorable defined indicator of the uniaxial tensile failure criterion of solid propellants, although there have been many



Figure 10 Definition of some characteristic values in stress-strain curve (three different characteristic strains are defined).

other failure criteria previously proposed by several investigators. 13,14

Effect of Solids Content on Failure Properties

The engineering stress-strain curves for the filled propellants, the PB14 and PB15 dummy propellants at $T = 21^{\circ}$ C and $\dot{\epsilon} \simeq 10^{-3}$ s⁻¹, are shown in Figure 11. The figure reveals that the larger the value of wt % of solids loading, the higher the initial slope of PB14 composites with 50 wt % glass beads and 18 wt % plastic beads filler. This is due to the fact that the modulus of an elastomer is increased by the addition of rigid filler particles, provided the elastomer



Figure 11 Stress-strain curves for dummy HTPB propellant at tensile strain rate 10^{-3} s⁻¹.

wets or adheres to the filler, and several modulus equations of filled elastomers have been proposed previously.⁴

Figure 12 shows the effect of filler level on the tensile strength and total strain of samples. The results were also shown in Figure 11 and Table II and reveal that the tensile strength is increased, while the breaking elongation is decreased, with somewhat increasing filler content. In general, to provide a worthwhile increase in ballistic performance for the case-bonded grains, solid composite propellants are tailored so that the filler content becomes as high as possible, for instance, 85-90 wt %. Thus, in the present investigation, high filler contents of 85 and 86 wt % dummy propellants were selected for evaluation. Assuming that the average specific gravity of the filler, HTPB binder, and propellants are 2.11, 0.91, and 1.78, respectively, the weight percent of 85 and 86 fillers corresponds to about 71.0 and 72.6%by volume; thus, the volume fraction of the binder is 29.0 and 27.4%, respectively. This indicates 5.5%of the volume decreases in the binder for the material of 86 wt % fillers. Also, because the closest possible packing of the uniform sphere is about 74% by volume, the ratio of the spacing between adjacent uniform filler particles to the particle diameter is 1.41%for the material of 85 wt % fillers and 0.66% for the 86 wt % fillers. Thus, an estimate can be obtained of the decrement in the spacing between the adjacent uniform filler particles of about 53.2%. It is probably



Figure 12 Effect of filler level on the tensile strength and total strain of dummy HTPB propellants.

induced because the viscosity resistance is increased by the restricted motion of the HTPB binder with increasing filler content and results in a decreased breaking elongation capability and an increase in the tensile strength.

On the other hand, the yield strain at which dewetting occurs, of the filled elastomers, can be related to the volume fraction of the filler by an equation based on certain simplifying assumptions, which is given by Smith¹⁵ as follows:

$$\varepsilon_c = \varepsilon_r (1 - 1.105 V_f^{\frac{1}{3}}) \tag{4}$$

where V_f is the volume fraction of the filler; ε_r , the strain in the binder between adjacent spheres; and ε_c , the strain imposed on the composite. When the volume fraction of the filler in the closest packing array, V_t , equals 0.74, the equation shows that ε_c = 0. These results, in accordance with microscopic character of the propellant rupture that was studied previously on the dewetting processes around the filler particles, ^{16,17} apparently increases the propagation of the dewetting effect to neighboring particles with the filler content under strain. Thus, the higher solids level for PB14 propellants, which in essence reduces the amount of binder and leads to higher tensile strength and initial slope values, is due to better solids reinforcement of the HTPB binder by an increasing amount of fillers. On the basis of the results of these experiments, it is evident that the level of filler is a primary factor governing mechanical properties' levels.

CONCLUSIONS

- 1. For filled dummy HTPB propellants, the mechanical properties (σ_p , ε_p , ε_T , and E_{ab}) increase noticeably with increasing strain rate in the strain rate range from 10^{-4} to 10^{-1} s⁻¹ at room temperature. "high velocity ductility" behavior is exhibited.
- 2. The mechanical behavior of dummy HTPB propellants is contrary to that of glassy polymers; high strain rates tended to an improvement in tensile strength and breaking strain.
- 3. The dummy HTPB propellants have an excellent impact-absorbing ability and relatively large breaking elongation capability at high strain rates. It is a suitable character in propellant grains for case-bonded motors.
- 4. The effective gauge length factor α of Bukkon uniaxial tensile specimens was studied experimentally. Test results show that α is re-

lated to the strain. The results of mechanical properties obtained by Bukkon-type specimens and modified using this α are consistent with the data obtained by rod-shaped specimens.

5. The wt % of solids loading in HTPB propellants has a profound effect on the mechanical properties. Increased solids level results in a decreased breaking elongation capability and an increase in tensile strength.

The authors wish to acknowledge Nippon Oil & Fats Co. Ltd. for their manufacturing and supplying the dummy HTPB propellant specimens and Mr. O. Matsumoto for his eager assistance in the experiments.

REFERENCES

- 1. T. L. Smith, Ind. Eng. Chem., 52, 776 (1960).
- P. L. Smith and H. Bankaitis, AIAA Paper No. 71-708, June, 1971.
- R. Nagappa and M. Kurup, AIAA Paper No. 90-2331, July, 1990.
- 4. R. F. Landel and T. L. Smith, ARS J., 31, 599 (1961).
- M. Rajan and C. V. Mohandas, AIAA Paper No. 75-1344, Sept., 1975.

- T. L. Smith and P. J. Stedry, J. Appl. Phys., 31, 1892 (1960).
- 7. T. L. Smith, J. Polym. Sci., 32, 99 (1958).
- 8. T. L. Smith, J. Polym. Sci. Part A, 1, 3597 (1963).
- 9. T. L. Smith, J. Appl. Phys., 35, 27 (1964).
- K. Kawata, M. Ida, and A. Hondo, Bull. Instit. Space Aeronautical Sci. (University of Tokyo), 5(4), 506 (1969) (in Japanese).
- K. Kawata, S. Ninomiya, and S. Fujitsuka, in Proceedings of 19th Aircraft/Aerospace Materials Symposium, University of Tokyo, March 13, 1989, p. 51 (in Japanese).
- K. Kawata, H. L. Chung, and M. Itabashi, in Proceedings of 6th Japan-U.S. Conference on Composite Materials, Orlando, FL, June 22-24, 1992, Technomic Publishing, 771 (1993).
- 13. R. F. Landel, CBS No. 66, Jet Propulsion Laboratory, CIT, August, 1958.
- W. T. Milloway and J. H. Wiegand, J. Appl. Polym. Sci., 7, 1325 (1963).
- 15. T. L. Smith, Trans. Soc. Rheol., 3, 113 (1959).
- K. W. Bills, Jr. and J. H. Wiegand, AIAA J., 1(9), 2116 (1963).
- K. Kawata, M. Ida, and A. Hondo, Bull. Instit. Space Aeronautical Sci. (University of Tokyo) 5(4), 521 (1969) (in Japanese).

Received August 13, 1992 Accepted January 29, 1993