Mechanical and Burning Properties of Highly Loaded Composite Propellants

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ABSTRACT: An improvement in the performance of solid rocket motors was achieved by increasing the oxidizer content of HTPB-based solid propellants. To minimize the adverse changes in the mechanical and rheological properties due to the increased amount of hard solid particles in the soft polymeric binder matrix, the optimum combination of the particle sizes and volume fractions of the bimodal ammonium perchlorate and the aluminum powder in the solid load was obtained from the results of testing a series of propellant samples prepared by using ammonium perchlorate in four different average particle sizes, 9.22, 31.4, 171, and 323 μm. The maximum packing density of solids in the binder matrix was determined by changing the sizes and the volume fractions of fine and coarse ammonium perchlorate at constant solid loading. The average size (10.4 μm) and concentration of aluminum powder used as metallic fuel were maintained constant for ballistic requirements. Optimum sizes and fine-to-coarse ratio of ammonium perchlorate particles were determined to be at mean diameters of 31.4 and 323 μm and fine-to-coarse ratio of 35/65. Solid content of the propellant was then increased from 75 to 85.6% by volume by using the predetermined optimum sizes and fine to coarse ratio of ammonium perchlorate. Mechanical properties of the propellant samples were measured by using an Instron tester with a crosshead speed of 50 mm/min at 25°C. The effect of oxidizer content and fine-to-coarse ratio of oxidizer on the burning rate of the propellant was also investigated by using a strand burner at various pressures. From experiments in which the size and the fine-to-coarse ratio of ammonium perchlorate were changed at constant solid loading, a minimum value of initial modulus was obtained for each fine-to-coarse ratio, indicating that the solids packing fraction is maximum at this ratio. The tensile strength and the burning rate increase, while the elongation at maximum stress decreases with increasing fine-to-coarse ratio of ammonium perchlorate. Experiments in which the total solid loading was increased at constant fine-to-coarse ratio of ammonium perchlorate show that the modulus, the tensile strength and the burning rate increase, while the elongation at maximum stress decreases with increasing solid loading. Propellants having solid loading of up to 82% exhibit acceptable mechanical properties and improved burning properties suitable for rocket applications. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1457–1464, 1998

Key words: composite; propellant; packing; mechanical properties; burning rate; HTPB; ammonium perchlorate; aluminum

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INTRODUCTION

Composite solid propellant, which is mainly composed of a polymeric binder, an inorganic oxidizer, and a metallic fuel, is the source of the propulsive energy of solid rocket motors. Solid propellants having high levels of density and specific impulse have been desired in the solid rocket technology for years. In the past, to satisfy these ballistic requirements, investigations were performed by using some energetic materials like nitronium perchlorate as an oxidizer and beryllium as metallic fuel, but desired results were not obtained due to the problems caused by high toxicity, hazardous behavior, and instability of energetic materials used.[1] A better way of improving the specific impulse of a propellant is to increase the percentage of solid ingredients in the binder matrix as much as possible. Remarkable enhancement in the specific impulse has already been achieved by increasing the percentage of ammonium perchlorate in the composite propellant.[2,3] Increasing the total amount of solids, however, deteriorates the mechanical and rheological properties and changes the other ballistic properties such as the burning rate of composite solid propellants.

Higher solid content can be incorporated to the binder matrix with changes in the mechanical and ballistic properties within the acceptable limits. Highest solid content is obtained when the mixture of solid ingredients reaches maximum packing density and the voids between the solid particles is minimum. In essence, the maximum packing requires the small particles to occupy the voids produced by larger particles in a successive way. Packing density of particles is controlled by a combination of parameters such as the particle size and size distribution, number of component sizes (modality), volume fraction of components, and the shape and surface characteristics of particles.

EXPERIMENTAL

Materials

HTPB (R-45M, number average molecular weight of 2700 g/mol, functionality of 1.93, ARCO Chemical Company, Philadelphia, PA), Isophoron diisocyanate, IPDI, (Fluka AG, Leverkusen, Germany), crystalline ammonium perchlorate, AP, (average particle sizes of 9.22, 31.4, 171, and 323 μm SNPE, France), Aluminum powder (average particle size of 10.4 μm, ALCAN TOYO), dioctyladipate (DOA, Kimtaş, Istanbul, Turkey), Triethanol amine, TEA, (Merck, Darmstadt, Germany), Tepanol (Dynamar HX-878, 3M, MN), were used as purchased. Ammonium perchlorate with the average particle size of 9.22 μm was produced by grinding the coarse ammonium perchlorate of 171 μm size in a laboratory mill (Alpine, Type 160 Z).

Preparation of Propellant Samples

For all the propellant samples, NCO/OH and triol/diol ratios of the polyurethane binder were kept constant at 0.94 and 0.09, respectively. The aluminum content was also maintained constant at 16% by weight. No burning-rate modifier was used to avoid complication in evaluating the effect of solid loading on the ballistic properties of the propellant. The total solid content in the propellant was changed in the second part of the experiments by increasing the amount of ammonium perchlorate. All the ingredients except the curing agent were blended thoroughly in a vertical mixer for about 10 min at 65°C. The mixing was then continued under vacuum for about 3 h. After addition of curing agent to the slurry, the mixture was blended for another 15 min. Freshly prepared matrix was cast into preheated, Teflon-coated molds in vacuum. The molds were cured for 7 days at 65°C.

Methods of Testing

Tensile tests of the propellants were carried out by using a conventional uniaxial testing system (Hewlett Packard, 1185 type INSTRON) according to JANAF procedure. Before tensile testing, specimens prepared were conditioned at 25°C for 24 h. The cured samples were tested for their mechanical properties (tensile strength, elongation at maximum stress) at room temperature and with a crosshead speed of 50 mm/min.

The burning rates of composite propellants were determined in a strand burner by using the standard procedure (MIL STD-286B). The size of specimens used in the tests was approximately 3 × 3 mm in cross section and 130 mm in length. Measurements were taken at various pressures in the range of 20–140 bar and at an initial temperature of 25°C for all the propellant samples.

The viscosity of uncured propellants were mea-

Table I Sizes and Volume Fractions of Ammonium Perchlorate (AP) in the Solid Part of Propellants

Set Number	AP (9.22 μm)	AP (31.4 μm)	AP (171 μm)	AP (323 μm)
1	0.05	0.81		
	0.10	0.76		
2	0.10		0.76	
	0.24		0.62	
	0.40		0.46	
3	0.04			0.82
	0.15			0.71
	0.33			0.53
	0.50			0.36
4		0.10	0.76	
		0.26	0.60	
		0.38	0.48	
		0.49	0.37	
5		0.15		0.71
		0.30		0.56
		0.40		0.46
		0.55		0.31
6			0.15	0.71

The volume fraction of aluminum in the solid part is 0.14 for all the propellants.

sured on a Brookfield viscometer HBTDV-II at 65°C by using a T-spindle with 2.5 rpm according to the ASTM D2196-81.

RESULTS AND DISCUSSION

Effect of Volume Fraction of Components on Mechanical Properties

Propellants were prepared by using three solid components (trimodal solid content) consisting of two ammonium perchlorate particles in different sizes and the aluminum powder. To investigate the dependence of packing density on the particle size and size distribution, propellant samples of six different sets were prepared by using all the possible combination of pairs of four ammonium perchlorate particles in different sizes while keeping the total solid content constant at a level of 75% by volume. According to the packing theory, the amount of fine particles must be less than that of coarse particles to obtain the maximum packing density.[4] This fact was taken into account in the selection of concentrations of the fine and coarse ammonium perchlorate particles of the propellant samples in each set, as shown in Table I. The propellants of sets 1 and 6 (Table I) exhibited very high viscosities, which prevented mixing. Therefore, they were not tested for mechanical properties. The propellant samples of sets 2–5 could be prepared and tested for their mechanical properties.

Figure 1 shows the variations in the initial modulus of the composite propellants of each set as a function of volume fraction of fine AP in the solid part of the propellant. For all the propellant samples, the initial modulus decreases first, reaching a minimum at a particular value of volume fraction of fine AP, and then starts to increase. This behavior of the initial modulus can

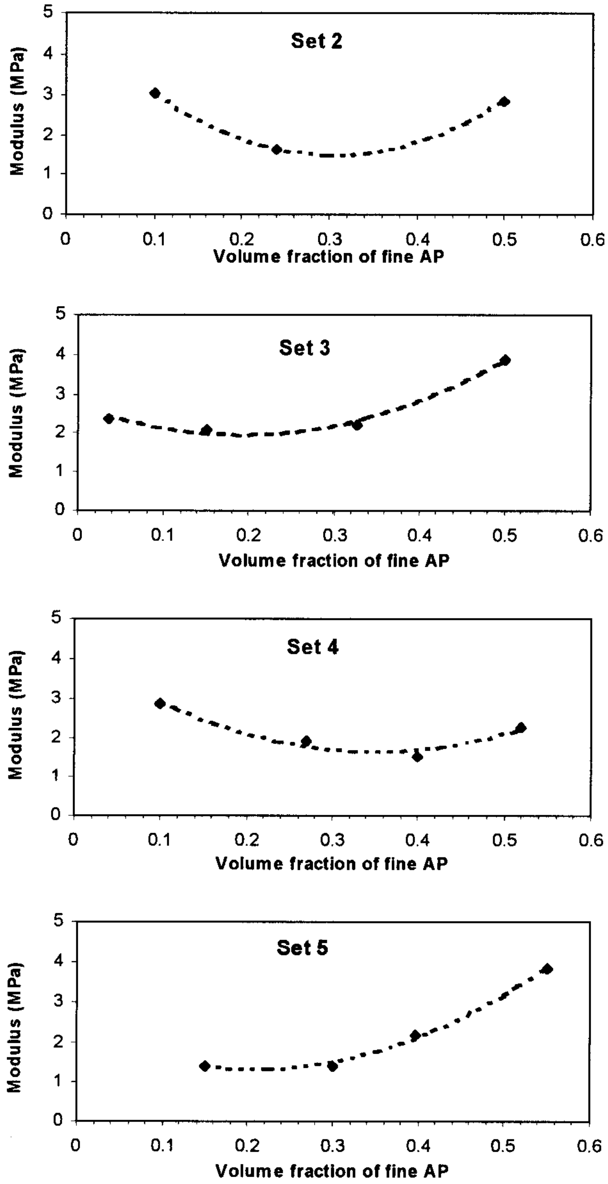

Figure 1 The initial modulus of the composite propellants of each set as a function of the volume fraction of fine AP in the solid part of the propellant.

be explained by the Eilers and Van Dyck equation that relates filler concentration and packing fraction of particles to the modulus of composite materials[5]:

$$E = E_o \left(1 + \frac{1.25\phi}{1 - \frac{\phi}{\phi_P}} \right)^2 \tag{1}$$

where E and E_o are the initial modulus of the propellant and the unfilled binder system, respectively; ϕ is the volume fraction of fillers (solid loading); and ϕ_p is the packing fraction of fillers for a given composition. The latter mainly depends on the number of components (modality), volume fraction of each component, particle size, and particle size distribution of components. Equation (1) shows that the initial modulus of a composite material depends on the modulus of the unfilled binder matrix, the solid loading, and packing fraction of solid particles. Because the NCO/OH and triol/diol ratios, the parameters that determine the physical and chemical characteristics of polyurethane binder, are maintained constant throughout the study, the initial modulus of unfilled binder, E_o, is constant. As the solid loading, ϕ, is kept constant at 75% by volume in this part of the study, the only parameter affecting the initial modulus of composite propellants is the packing fraction of solid particles, ϕ_p. Equation (1) shows that the initial modulus decreases with the increasing packing fraction of solid particles, ϕ_p, and reaches the minimum value when ϕ_p gets its maximum value, $\phi_{\max}$.

Figure 1 shows the variations in the initial modulus of the propellant samples in four sets 2–5 with the volume fraction of fine ammonium perchlorate in the solid part of the propellant. Variation in the packing fraction of fillers was achieved by changing the oxidizer fine-to-coarse ratio; however, the other parameters that may affect the packing fraction such as modality, particle size, and size distribution of solid components were maintained constant. The initial modulus reaches its minimum values of 1.5, 1.9, 1.6, and 1.3 MPa at 0.3, 0.2, 0.4, and 0.3 volume fraction of fine AP in the propellant sets 2–5, respectively. Because the voids between the coarse AP particles are occupied by the fine AP particles as efficient as possible, the packing fraction ϕ_p reaches its maximum value $\phi_{\max}$, and the initial modulus reaches its minimum value at the given volume fraction of fine AP in each propellant set. A brief inspection of the experimental data shows that the minimum value of initial modulus in all the propellant sets is obtained for the propellant compositions having the amount of fine AP particles less than that of coarse AP as predicted by the Packing Theory.[4]

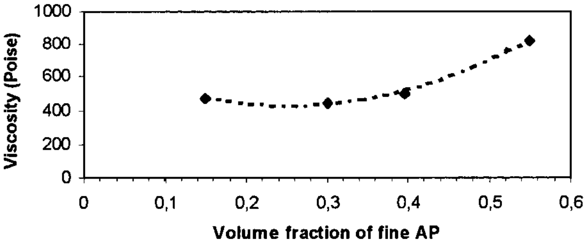

Figure 2 Variation in viscosity of the uncured propellant in set 5 with the volume fraction of fine AP.

The viscosity of uncured propellants is also affected by the variation of packing density and can be used to determine the maximum packing density. Figure 2 illustrates the determination of the composition giving the maximum packing density from the variation in viscosity with the volume fraction of fine AP in the propellant set 5, as an example. The volume fraction giving the minimum viscosity is found to be 0.3, the same value obtained from the measurements of initial modulus. Both the minimum viscosity and the minimum initial modulus are obtained at the same value of volume fraction of fine AP particles giving the maximum packing of propellants while keeping all the other parameters constant. As a result of both types of measurements, the propellant composition with 0.3 volume fraction of fine AP (fine-to-coarse ratio is 35/65) was selected for further investigation of increasing the total solid content of the composite propellants.

Figure 3 shows the variation in the ultimate tensile strength of propellants with the volume fraction of fine AP. The tensile strength of the propellants increases with the increasing volume fraction of fine AP. This trend is observed in all of the four systems having different size and size distribution of fillers. When the samples of the filled polymers are subjected to a stress, a polymer system filled with coarse particles starts dewetting at a smaller stress compared to a system containing fine particles. The reason for this is the stress concentration effect.[6,7] Thus, the ultimate strength increases with the increasing content of fine particles in the solid part of the system.

The changes in elongation at maximum stress are plotted against the volume fraction of fine AP for each propellant system in Figure 4. It is observed that the increasing volume fraction of fine filler reduces the elongation capability of the composite propellant. This behavior in the elongation is also caused by different dewetting nature of large and small particles. Vacuoles occur between solid particle and binder phase when the propellant sample dewets. If the load on the sample is maintained, vacuoles enlarge and eventually combine with each other. The volume of the propellant sample increases during tensile testing due to presence of vacuoles.[8,9] This means that these vacuoles contribute to the total elongation after dewetting occurs. Formation of vacuoles in the propellants containing a larger quantity of fine AP is less than that in propellants containing coarse particles. Thus, the increasing fine-AP fraction decreases the elongation at maximum stress, as observed in Figure 4.

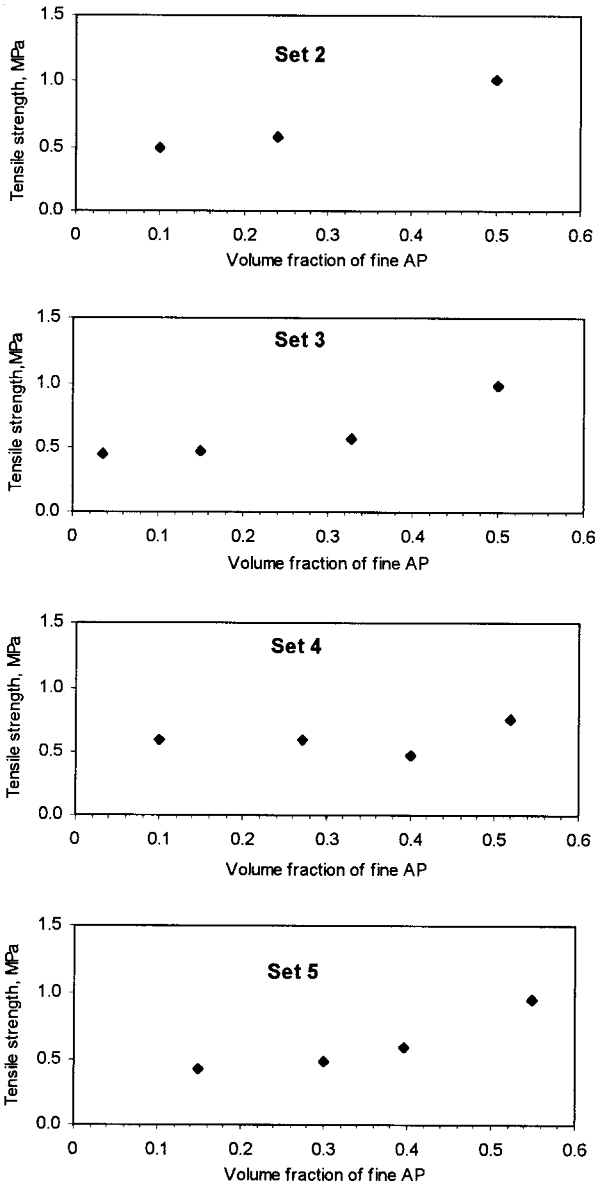

Figure 3 Effect of volume fraction of fine AP on the tensile strength of the propellant.

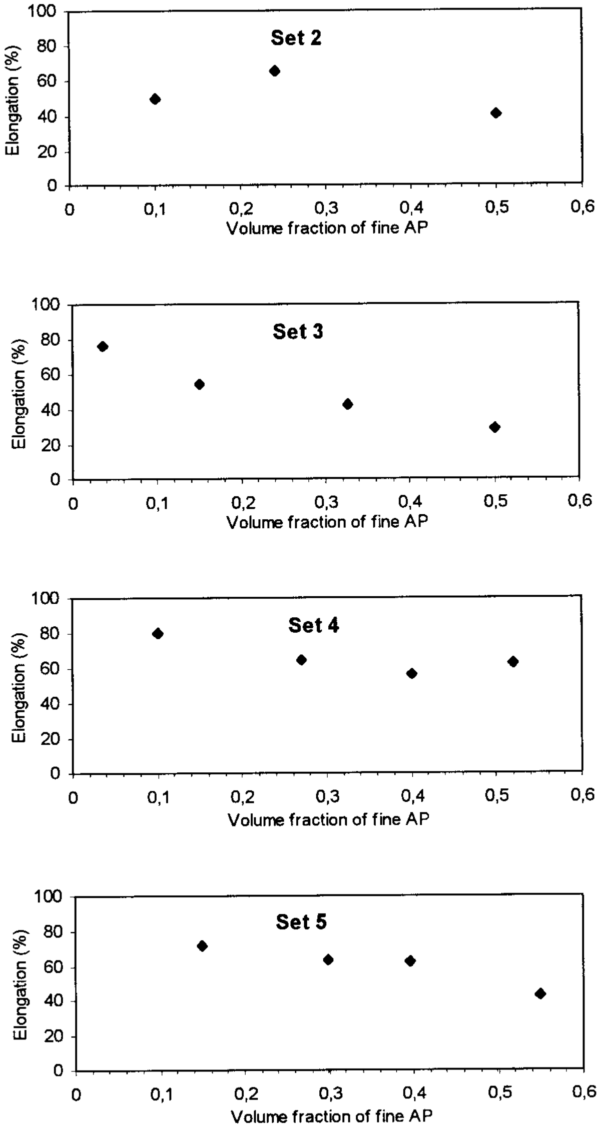

Figure 4 Effect of volume fraction of fine AP on the elongation at maximum stress.

Effect of Solid Loading on Mechanical Properties

In the previous section, the solid composition of propellant giving the maximum packing density was determined by changing the mean particle size and volume fraction of fine and coarse AP particles at a constant solid loading. In this part of the study, the solid loding of the propellant was varied to investigate its effect on the mechanical properties of the propellant. Propellant samples were prepared at solid loadings of 75%, 78.4%,

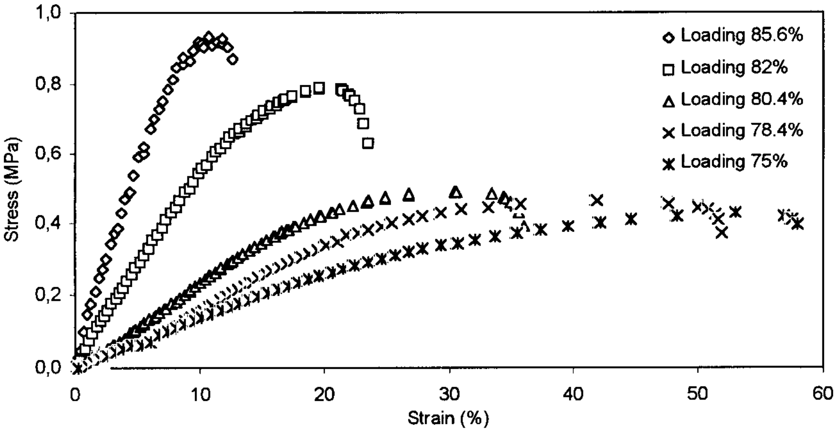

Figure 5 Stress–strain curves for propellants with varying solid loading.

80.4%, 82%, and 85.6% by volume, keeping the component sizes and fine to coarse ratio of AP constant. Sizes of aluminum, fine and coarse AP particles were 10.4, 31.4, and 323 μm, respectively. The volume fractions of these solid components with respect to the total solid content were 0.14, 0.30, and 0.56, respectively. Thus, the value of 0.3 obtained for the volume fraction of fine AP in set 5 was used in this part of the study.

A typical uniaxial stress–strain behavior of HTPB composite propellants with varying solid loading measured at room temperature is shown in Figure 5. At first glance it is seen that the stress–strain behavior of the HTPB-based propellant is strongly affected by the solid loading. The important mechanical characteristics determined from these stress–strain curves are listed in Table II. The experimental values of mechanical properties given in Table II were determined from the averages of nine specimens.

For understanding the influence of solid loading on mechanical properties of composite propellants, the initial modulus, tensile strength, and elongation at maximum stress are evaluated as a function of solid loading separately. The inspection of the data given in Table II reveals that initial modulus increases with increasing solid loading. It is interesting to note that the modulus shows a significantly rapid increase especially after 78.4% volume fraction of the total solid loading. This result is in agreement with the equation proposed by Eiler and Van Dyck,[5] the same equation as eq. (1), except ϕ_p is replaced by $\phi_{\max}$, the maximum packing fraction of solid particles. The value of $\phi_{\max}$ should be approximately the same for all the propellants studied in this part, because the sizes and relative volume fractions of the solid components were maintained constant. Thus, in this case, the modulus of propellants depends only on the solid concentration, ϕ, and increases with the increasing total solid content.

The tensile strength of HTPB composite propellants increases with increasing filler concentration as seen from the Table II. The only deviation from the general trend was obtained for the tensile strength of the propellant with 78.4% solid content. This result appears to be in agreement with a hypothesis assuming that the solid particles are sharing a disproportionately larger portion of the load than the comparatively soft matrix.[10] The other possible effect to increase the tensile strength with the increasing solid loading may be the formation of additional crosslinks between the solid particles and the network chains of the binder matrix.

Table II Mechanical Properties of Propellants with Varying Solid Loading

Solid Loading (vol %)	Initial Modulus (MPa)	Tensile Strength (MPa)	Elongation at Max. Stress	Viscosity of Uncured Propellant (poise)
75	1.44	0.487	63.6	448
78.4	2.05	0.455	41.88	852
80.4	2.40	0.578	31.53	1520
82	4.58	0.756	19.93	2690
85.6	9.22	0.863	10.75	8080

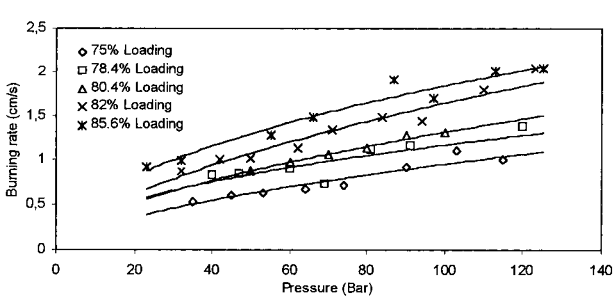

Figure 6 Burning rate–pressure curves for the propellants with varying solid loading. The solid curves indicate the best fits of $r = aP^n$.

The elongation at maximum stress of the propellant shows a dependence on the solid loading (Table II). In all cases, the elongation of HTPB composite propellant decreases with increasing solid loading. The decrease in the elongation at maximum stress may arise from the reduced volume fraction of the binder matrix due to the increasing volume fraction of solid particles. When the sample of composite propellant is subjected to uniaxial tensile stress, the total deformation is accommodated only by the binder matrix, because aluminum and ammonium perchlorate particles are hard and possess very high elastic modulus compared to the binder matrix.

Effect of Solid Loading on the Burning Rate of Propellant

The results of burning rate measurements at various pressures in the range of 23–125 bar are given as a function of solid loading between 75–85.6% by volume in Figure 6. It reveals that for all the propellants the dependence of the burning rate on the pressure obeys the Vielle equation, $r = aP^n$, where r is the burning rate in cm/s, P is the pressure (bar), a is the pressure constant, and n is the pressure exponent. Furthermore, the burning rate expectedly increases in the entire pressure range with the increasing solid loading. The a and n values of the propellant were determined from the best curve fitting of the burning rates vs. pressure data in Figure 6 and given in Table III. To see the effect of solid content clearly, the burning rates at a pressure of 100 bars are plotted against solid loading in Figure 7. In general, burning rate increases with the increasing total solid content. An important reason for the increase in the burning rate with the oxidizer content is the increasing flame temperature of the burning propellant. This temperature increase is caused by an increase in the oxygen content of the propellant (by the augmentation in the amount of ammonium perchlorate). As a result, some reactions during the combustion will be faster, and the heat transfer back to the burning surface will increase.[11]

Table III The *a* and *n* Values of Propellants with Varying Solid Loading

Solid Loading (%)	a (cm/s)	n
75	0.059	0.605
78.4	0.130	0.477
80.4	0.089	0.584
82	0.099	0.611
85.6	0.179	0.506

Effect of Volume Fraction of Components on the Burning Rate

Propellants in set 5 containing fine (average particle size 31.4 μm) and coarse (average particle size 323 μm) ammonium perchlorate were selected for the investigation of the particle size effect on the burning rate of the composite solid propellant. The burning rates of propellants with volume fractions of fine ammonium perchlorate at 0.15, 0.30, 0.40, and 0.55 were measured under various pressures in the range of 40–100 bar. The results of these measurements are illustrated in Figures 8 and 9. The burning rate of the propellant expectedly increases with the increasing volume fraction of the fine ammonium perchlorate. This can be readily attributed to the large surface area of fine AP (0.325 m^2/g) compared to the coarse AP (0.026 m^2/g) as determined on a Malvern particle size analyzer.

CONCLUSIONS

The results of testing six sets of propellant samples prepared by using ammonium perchlorate in

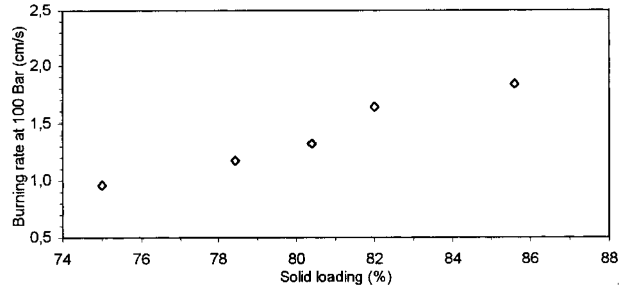

Figure 7 Variation in the burning rate of the propellant with the solid loading at 100 bar.

four different average particle sizes were collected to evaluate the effects of fine to coarse AP ratio and their sizes on the mechanical and ballistic properties of HTPB-based solid composite propellants at constant total solid content. The initial modulus shows a minimum in each set of propellant samples indicating the best fine-to-coarse AP ratio to be used. These minima correspond to the maximum packing fraction in each set. The tensile strength increases and elongation at maximum stress decreases with the increasing fine to coarse ratio of ammonium perchlorate particles. One also observes an increase in the burning rate of the propellant with the increasing amount of fine ammonium perchlorate. Among the propellants studied, samples of set 5 consisting of Al (size 10.4 μm), fine AP (size 31.4 μm), and coarse AP (size 323 μm) give the lowest values for the initial modulus and viscosity at volume fractions of 0.14, 0.30, and 0.56, respectively. This corresponds to the highest maximum packing in this study. This composition was used to increase the total solid content of the propellant. The initial modulus, tensile strength, and burning rate increase, while the elongation at maximum stress decreases, with the increasing total solid content of the propellant in the range of 75 to 85.6% by volume.

The propellants up to the solid loading level of 82% by volume have sufficient mechanical properties to be used in rockets. However, at loading levels higher than 85.6% the propellants with the binder characteristics used in this study become brittle. Propellants with solid contents higher than 85.6% do not have enough elongation to withstand the thermal and mechanical stresses that occur during storage and firing period of a rocket.

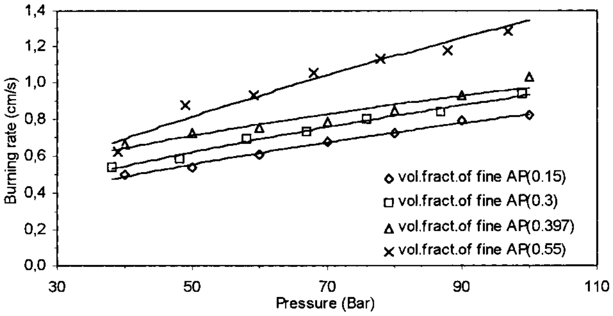

Figure 8 Effect of the volume fraction of fine AP on the burning rate of propellants in set 5.

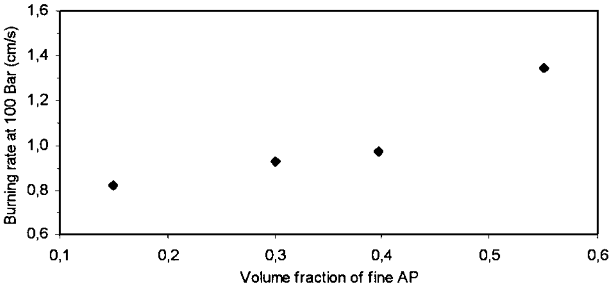

Figure 9 Variation in the burning rate of the propellant as a function of the volume fraction of fine AP at 100 bar.

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