Rheology of HTPB Propellant. I. Effect of Solid Loading, Oxidizer Particle Size, and Aluminum Content

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SYNOPSIS

Composite solid propellants based on hydroxyl-terminated polybutadiene (HTPB) have become the workhorse propellants in the present-day solid rocket motors. The other major ingredients of a composite propellant are the crystalline oxidizer and metallic fuel. As the solid loading of such propellants is as high as 86–90%, their rheological behavior is very complex. The propellant slurry needs to have reasonably low viscosity and a long pot life for better casting and, hence, for a defect-free rocket motor. The primary factors affecting the solid propellant viscosity are solid content, particle size, shape, and distribution. The present study concerns the variations of solid loading from 80 to 89% at constant aluminum content, variation of aluminum from 0 to 22% at constant solid loading, and the coarse-to-fine ratio of the oxidizer. The plots of yield stress, consistency index, pseudoplasticity index, and thixotropic index at different time intervals are drawn for all these parametric changes. Based on these rheological studies, the optimum ratio of oxidizer coarse-to-fine ratio, aluminum content, and level of solid loading have been determined.

INTRODUCTION

Composite solid propellant is a heterogeneous mixture of three major ingredients, viz. a polymeric fuel binder, a metal additive, and a solid oxidizer. The solid loading levels in modern systems go as high as 86–90% by weight in the liquid polymer, making its flow behavior very complex. The rheological behavior of the propellant slurry has been studied in detail by Klager et al.,[1] Osgood,[2] Killian,[3] Rumbel,[4] and Rajan et al.[5] in order to understand its processability, pot life, and flow characteristics to obtain a defect-free propellant grain.

During casting, the propellant must have rheological properties that permit flow into all parts of the motor case. If the flow is not adequate, voids or other defects develop, causing an increase in burning surface, which results in increased pressure and subsequent malfunctions of the motor; that is, the propellant slurry should have a reasonably low viscosity and long enough pot life to make it castable. The primary factors affecting composite solid propellant viscosity are type of solids, particle size, shape and size distributions, level of solid loading, packing fraction, and plasticizer.

Composite propellants based on hydroxyl-terminated polybutadiene (HTPB) have become the workhorse propellants[6] in the present-day solid rocket motors. Crystalline ammonium perchlorate (AP) and fine aluminum powder are used as oxidizer and metallic fuel, respectively, in the composite solid propellants. Although high-solid propellant manufactured from the single size fraction of the oxidizer is too viscous, a suitable bimodal distribution of the oxidizer gives good propellant unloading viscosity. The rheological properties of HTPB-based propellants have been studied by Sanden[7] and Rajan et al.[8] in order to optimize the casting conditions to produce defect-free grains. Chen and Hser[9] and Yang et al.[10] proposed a model to predict the viscosity of the HTPB propellant slurry when knowing the composition of the propellant.

As noted earlier, the solid loading, aluminum content, and particle-size distribution significantly contribute to the rheological properties of the pro-

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Journal of Applied Polymer Science, Vol. 44, 2043–2052 (1992)

CCC 0021-8995/92/112043-10$04.00

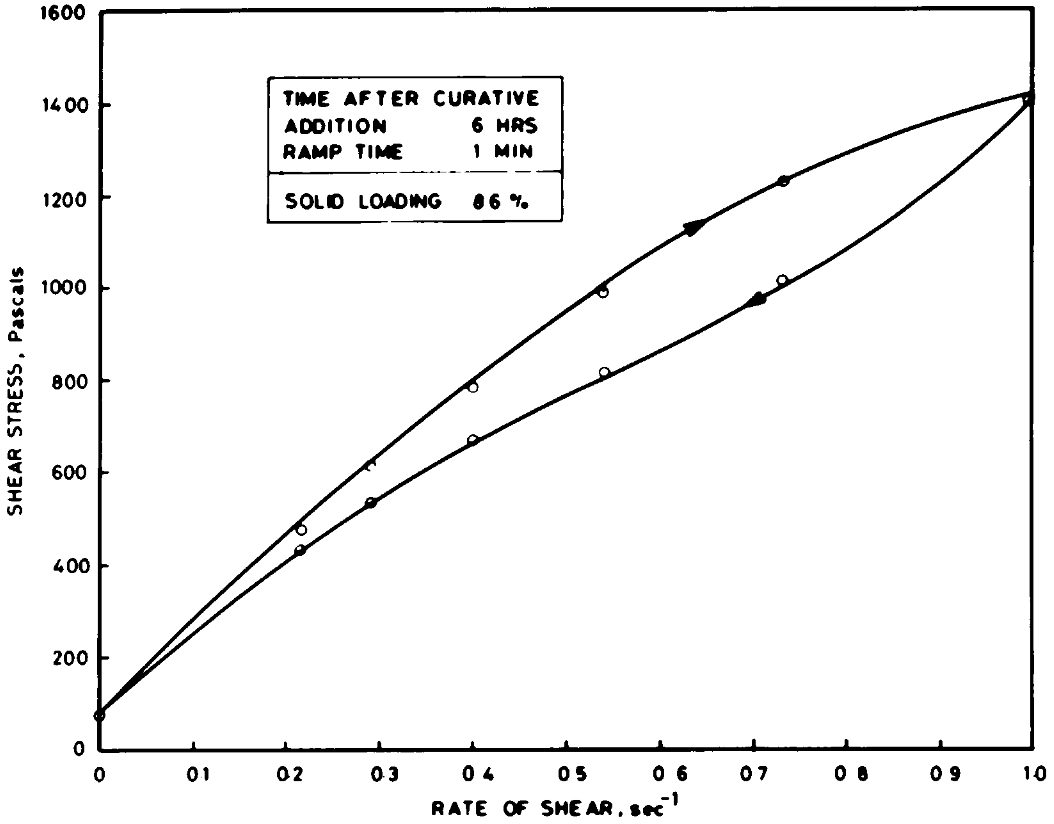

Figure 1 Typical rheogram.

pellant. The present study concerns the variations of (a) oxidizer loading from 80 to 89%, keeping the aluminum powder constant; (b) aluminum content, keeping the solid loading constant; and the (c) coarse-to-fine ratio of ammonium perchlorate at constant loading and aluminum content on the rheological behavior of HTPB-based propellant slurry.

EXPERIMENTAL

The solid propellant used in the present study is based on the HTPB prepolymer, supplied by the Propellant Fuel Complex, Vikram Sarabhai Space Centre; coarse ammonium perchlorate (300–320 microns average particle size) from the Ammonium Perchlorate Experimental Plant; and VSSC and aluminum powder (10–12 microns average particle size) from the Metal Powder Company, Madurai. Dioctyl adipate (DOA) and toluene diisocyanate (TDI) were procured from the trade and used as such. Trimethylolpropane (TMP) was from KEK, Japan, and used after drying to a moisture content of less than 0.1%. The fine ammonium perchlorate (40–45 microns average particle size) was obtained by grinding the coarse ammonium perchlorate in a pin mill grinder under nitrogen atmosphere.

The basic propellant formulation is the one chosen for the Polar Satellite Launch Vehicle's (PSLV) first stage and contained 68% ammonium perchlorate and 18% aluminum. All the propellant mixings were carried out in a 500 mL Guittard-make Sigma Mixer with blade speeds set at 25 and 18 rpm. A constant temperature of 50°C was maintained by circulating hot water in the mixer jacket. The mixing cycle of 120 min included 50 min under vacuum (10–15 Torr) after all the AP was added and 40 min after the curative addition.

Contraves Rheometer, Model Rheomat-30, was used for the rheological measurements. The instrument has both coaxial cylinders and a cone and plate measuring attachment. A provision for keeping the sample at constant temperature is built into the system. The rheometer is attached to a microprocessor so that the shear rates can be continuously varied from zero to any desired value. Since the average particle size of the solid oxidizer is around 300 mi-

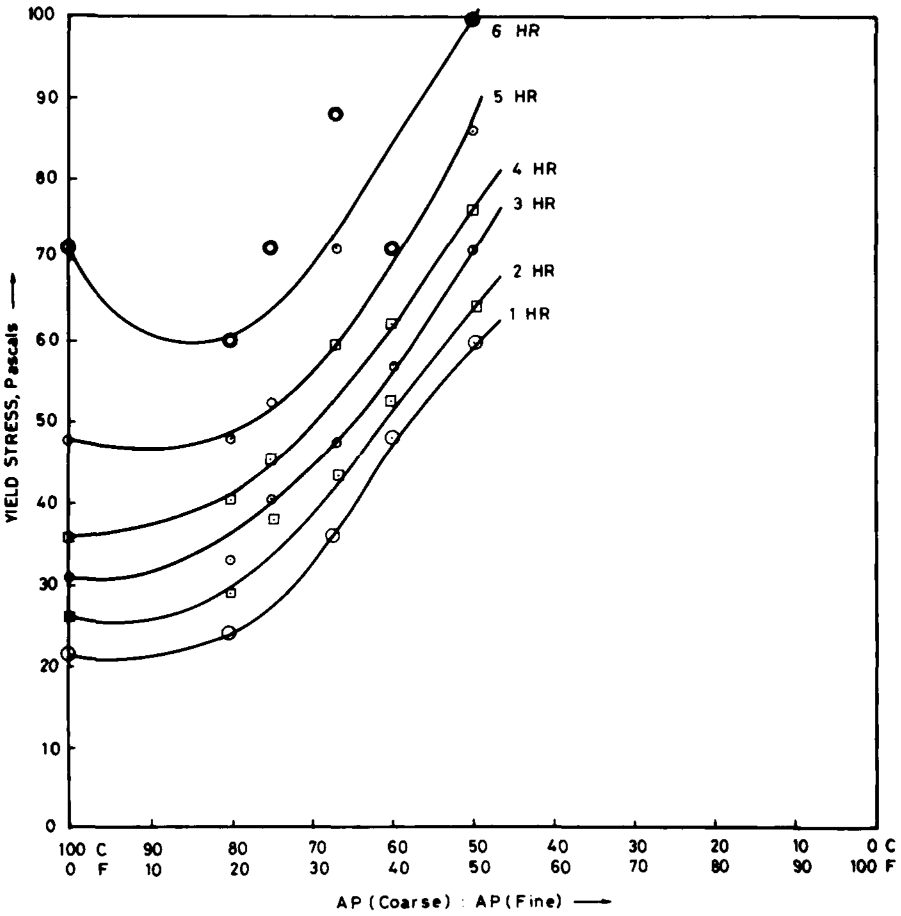

Figure 2 Effect of AP particle-size distribution.

crons, the coaxial cylinder measuring with an annular gap of 3.5 mm is used so to obtain a statistically reasonable average of the flow behavior.

As the method of filling the measuring system is found to affect the reproductibility of the results, propellant slurry is extruded into the cup for each measurement. The shear rate is varied from 0 to 0.997 per s in 1 min. The tests were conducted at 50°C. For characterising a propellant slurry, rheograms are obtained by plotting shear stress against rate of shear at different time intervals after curative addition. Each rheogram is analyzed for determining yield stress (T_0), viscosity index (k), and pseudoplasticity index (n). Additionally, the area enclosed by the hysteresis loop gives the energy for the destruction of the thixotropic structure and is known as an index of thixotropy. At the optimum process temperature, the propellant slurry will have minimum yield stress, maximum fluidity, minimum pseudoplasticity index, and minimum thixotropic index for a longer duration of time.

The following set of experiments were performed:

(a) Particle size of AP was varied by changing the coarse-to-fine ratio from complete coarse to a 1 : 1 coarse-to-fine ratio at a constant solid loading of 86%.

(b) Aluminum content was changed from 0 to 22%, while keeping the solid loading constant at 86%.

(c) Keeping the aluminum content constant at 18%, the total solid loading was varied from 80 to 89%.

RESULTS AND DISCUSSION

A typical rheogram obtained after 6 h of curative addition is given in Figure 1. As stated earlier, HTPB propellant slurry exhibited time-dependent flow behavior in addition to shear rate and temperature.

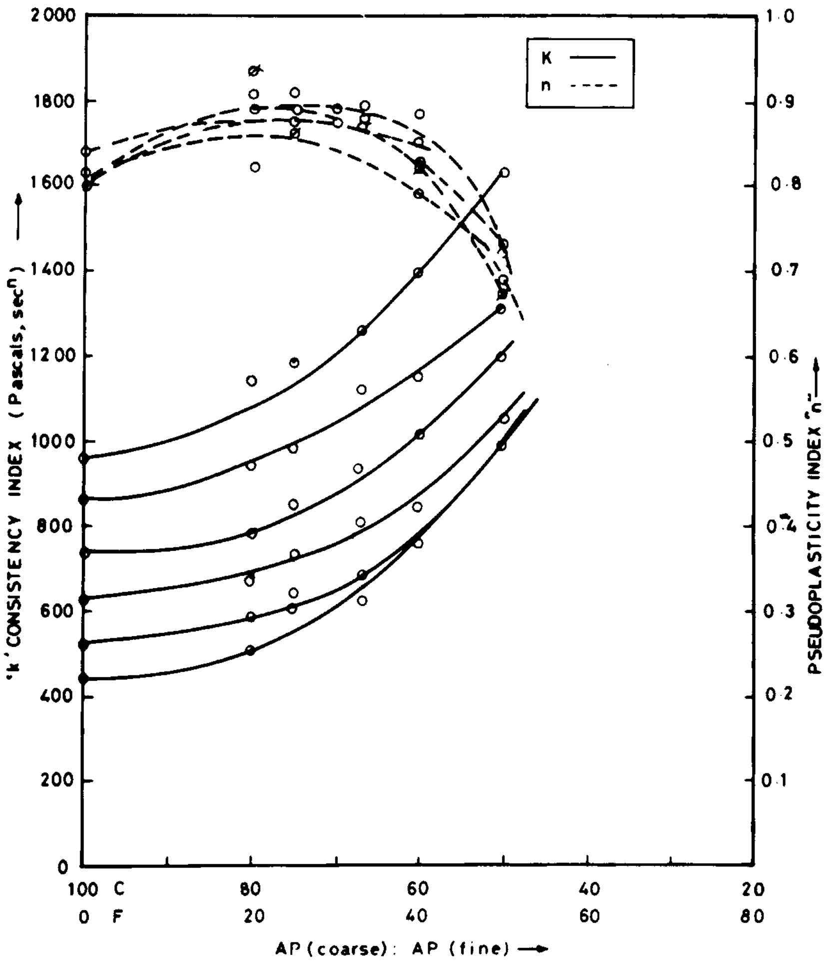

Figure 3 Effect of AP particle-size distribution.

The shear stress/shear rate curve can be represented by the equation

$$T - T_0 = kD^n$$

where T is the shear stress, T_0 is yield stress, D is the rate of shear, k is the consistency index, and n is the pseudoplasticity index. The up curve is plotted at increasing rates of shear, whereas the down curve is obtained at decreasing rates of shear. The area enclosed under this rheogram gives an idea of the extent of thixotropic breakdown and is called the thixotropic index.

The plots of yield stress, consistency index and pseudoplasticity index, and thixotropic index against AP particle-size distribution (in terms of coarse-to-fine ratio) at different time intervals after curative addition are given in Figures 2–4, respectively. For better processability, the propellant slurry should have a low viscosity that will allow it to flow readily for a sufficient length of time after mixing. A close scrutiny of the rheological parameters like yield stress, pseudoplasticity index, consistency index, and thixotropic index reveals that there is an optimum ratio of coarse to fine at which the propellant slurry remains castable for a longer time. It is seen that as the fine content is increased from 0 to 50% the yield stress increases exponentially up to a 3 : 1 ratio of coarse to fine. The yield stress variations are relatively small, indicating a rheologically better region for casting. The consistency index also shows similar variations up to a 3 : 1 ratio for coarse to fine, beyond which it changes with a relatively faster rate. Figure 3 also shows that the value of "n," i.e., the pseudoplasticity index, is maximum at around a 3 : 1 ratio of coarse-to-fine particle size, indicating that the shear effect is minimum. The shear thinning value is maximum at around a 3 : 1 ratio. The thixotropic index from Figure 4 is found to be minimum

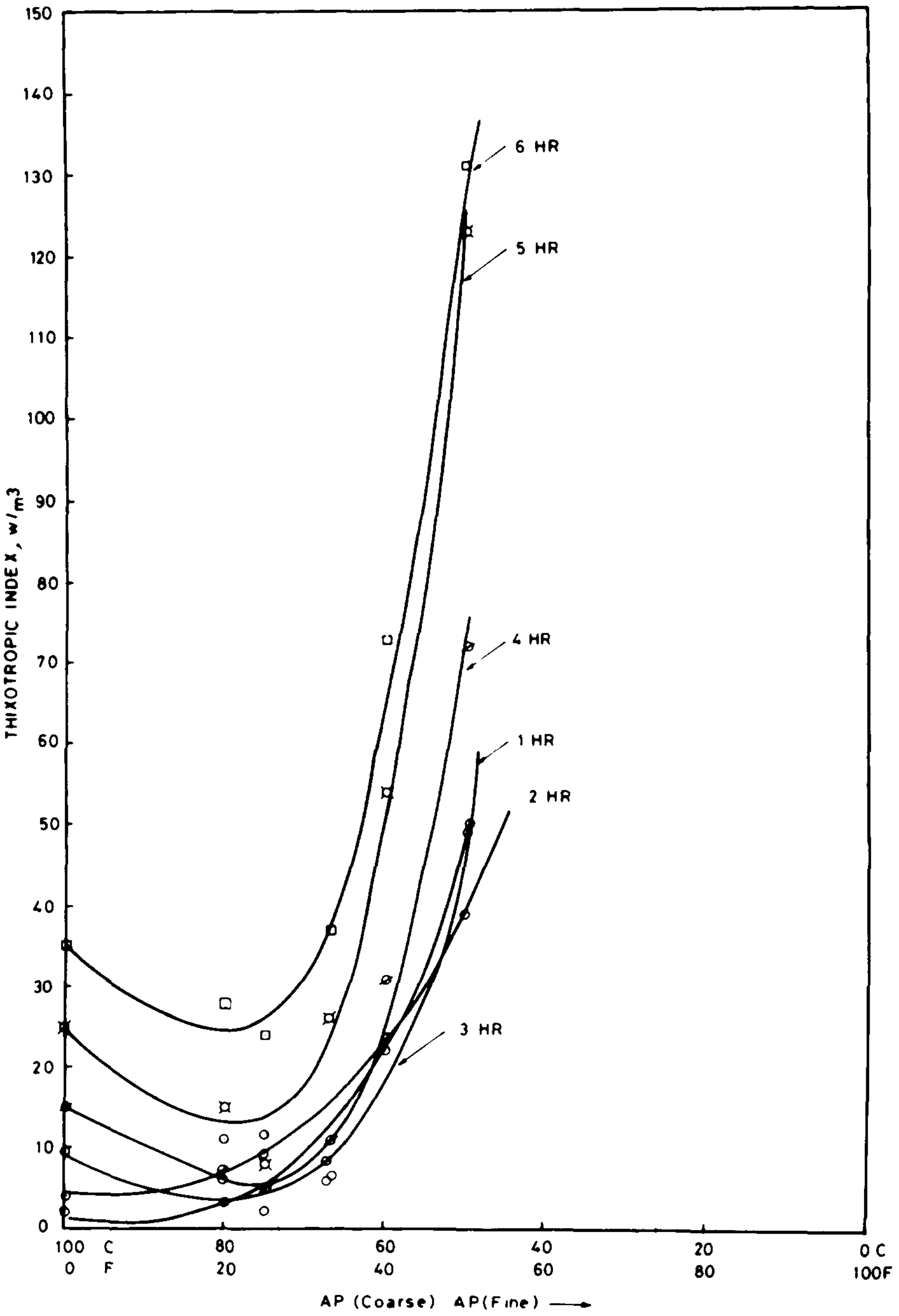

Figure 4 Effect of AP particle-size distribution.

at this ratio, showing that the irreversible energy losses are the least.

When a polymer system is subjected to deformation, the following processes take place simultaneously:

(a) Completely recoverable elastic response due to distortion of primary and secondary valence bonds.

(b) Time-dependent elastic deformation due to chain entanglements.

(c) Uncoiling of polymer chains.

(d) Unrecoverable viscous flow due to the slippage of polymer chains past each other.

In the viscous flow measurements, the pseudoplasticity of the propellant slurry is attributed to the

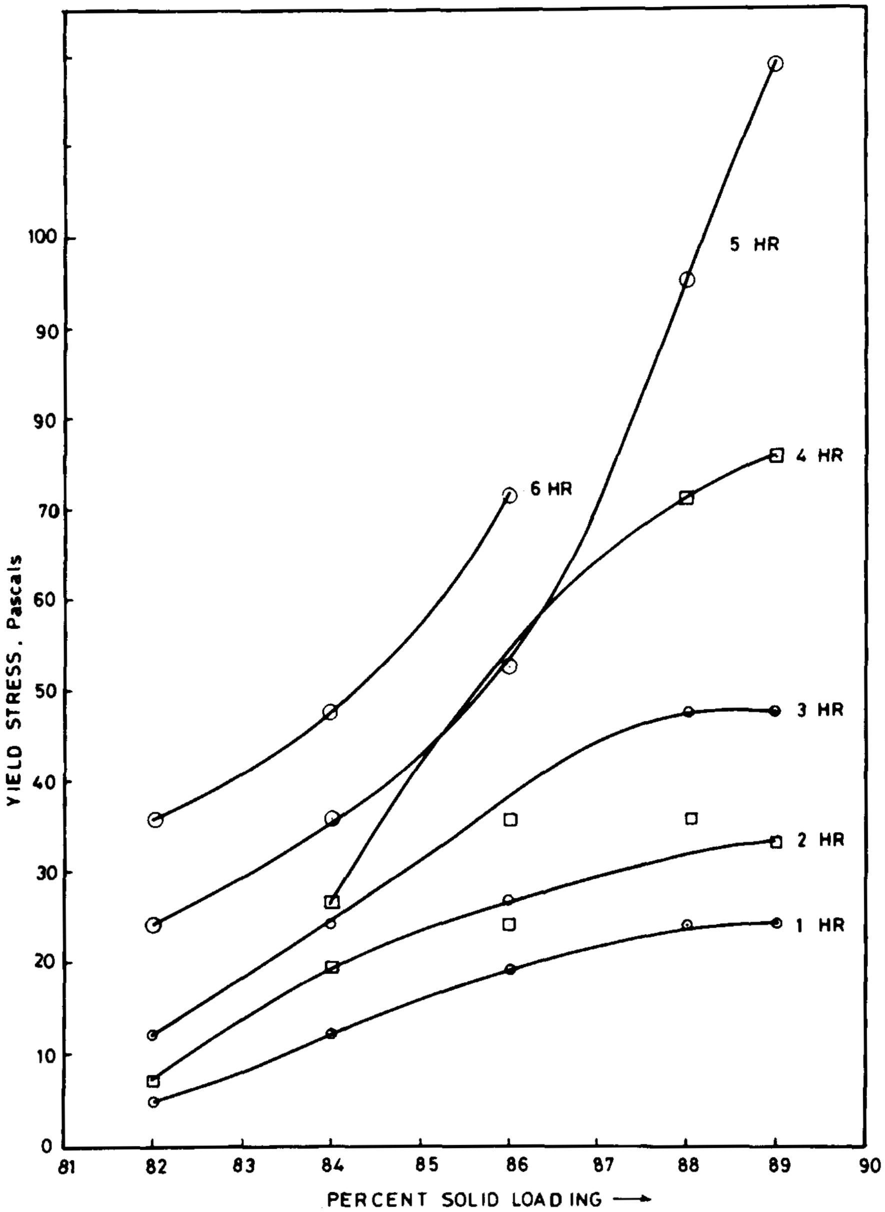

Figure 5 Effect of solid loading.

packing density of the filler and the molecular structure of the binder. While at rest, the particles are in a randomly intermingled state and the application of force aligns the particles and molecules, reducing thereby the resistance to slippage past one another. The high solid loading of slurries slows down the process of alignment of the particle, and as such, the propellant slurries exhibit thixotropic behavior. In a truly thixotropic material, it is possible to break down the structure completely to make it behave as true liquid at high shear rate and after a specified time.

At a particular temperature in presence of curing agents, the process of alignment of particles and long-chain molecules reduces the viscosity of the propellant slurry, whereas the curing reaction increases it because of molecular cross-linking. Initially, the rate of cure is slow; hence, the first process predominates, and later, the second process is controlling. This results in the viscosity going from a minimum value initially and then subsequently increasing.

The effect the relative size and number of large-to-small particles has on the viscosity of the pro-

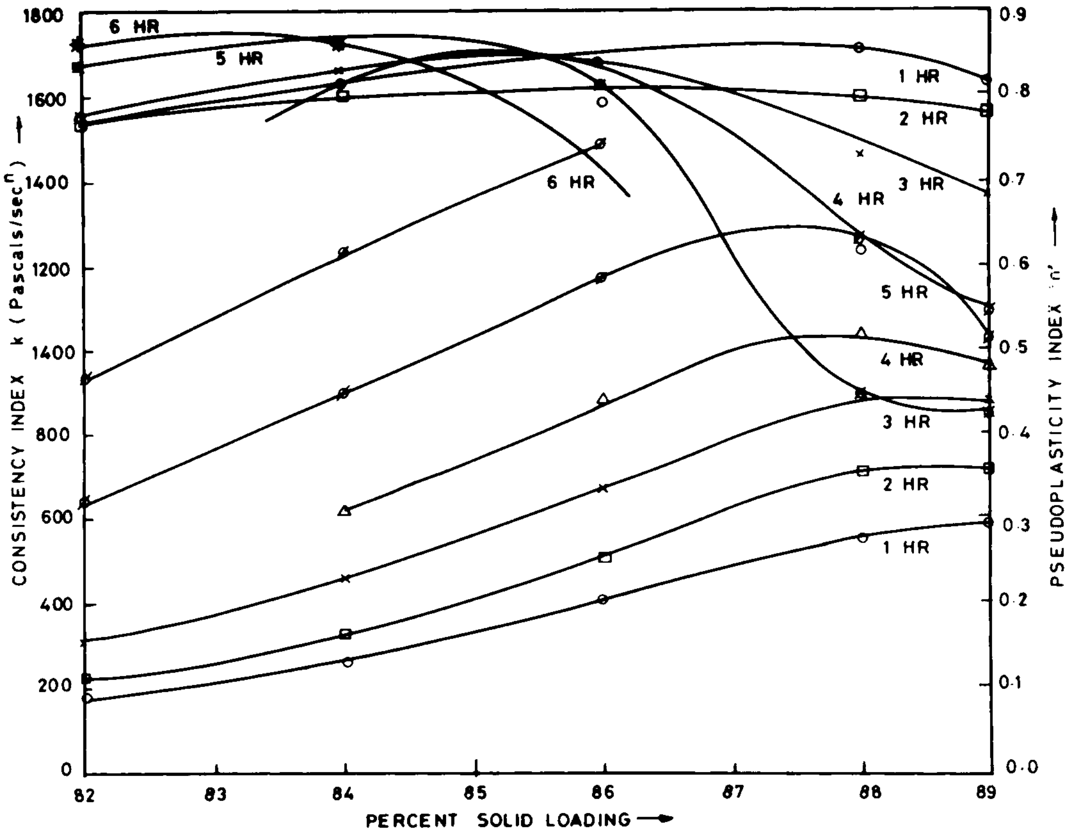

Figure 6 Effect of solid loading.

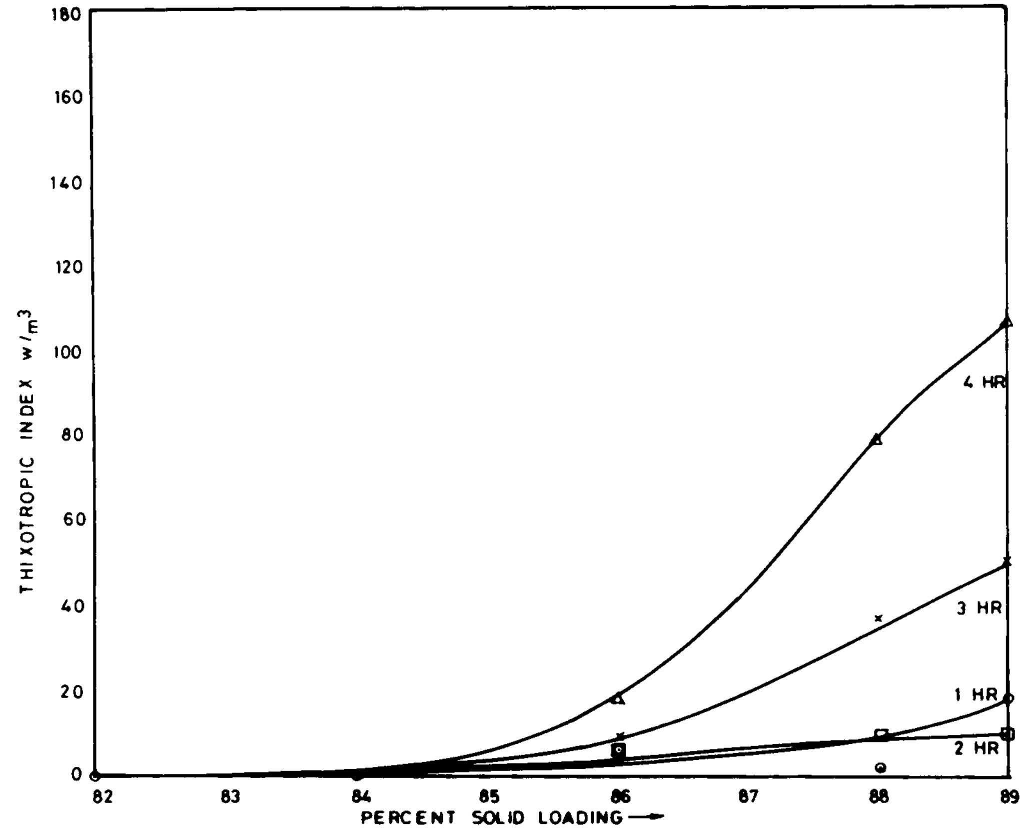

Figure 7 Effect of solid loading.

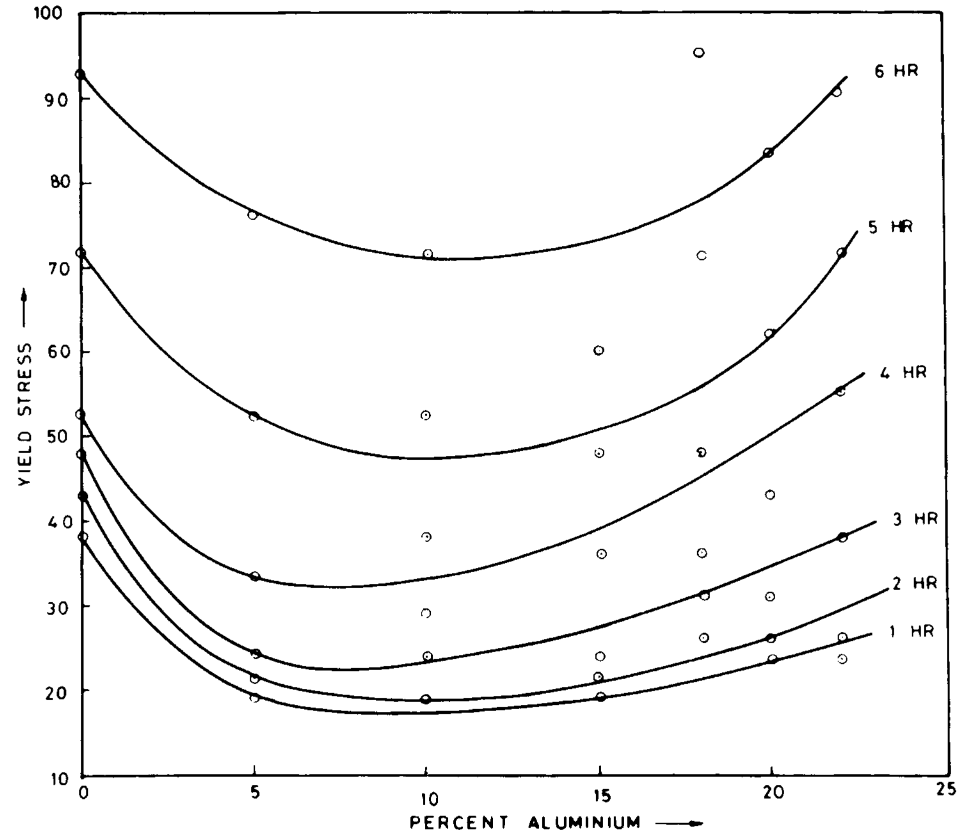

Figure 8 Effect of aluminum variation.

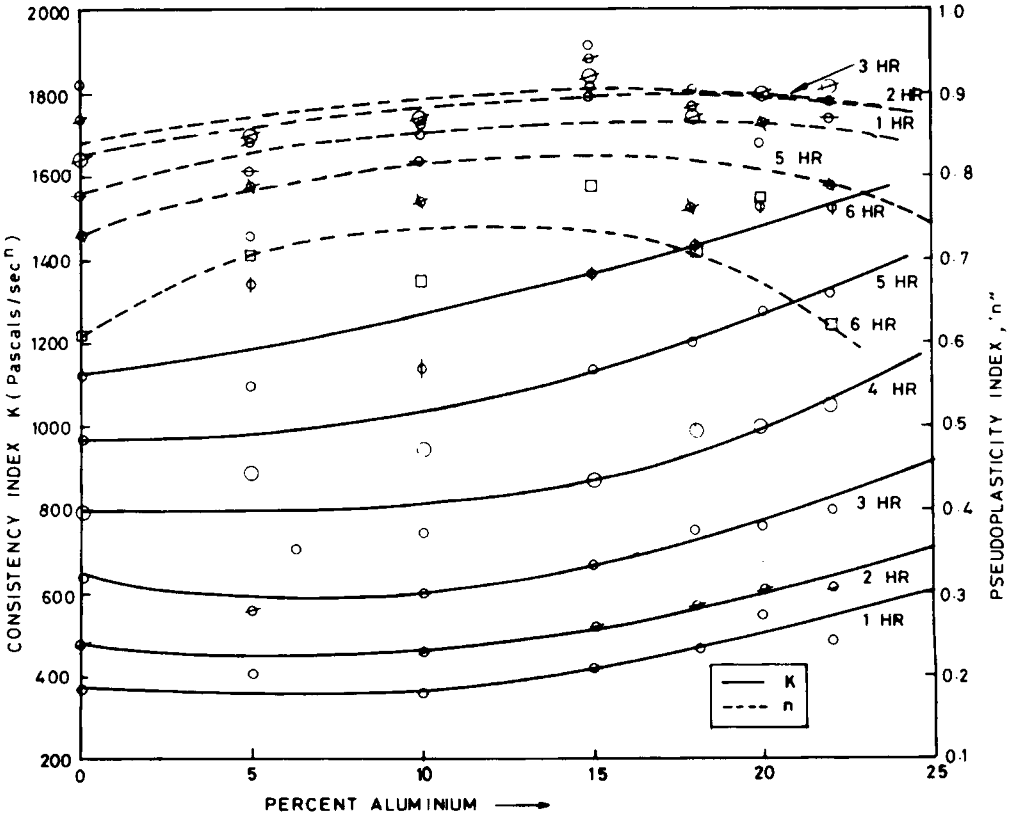

Figure 9 Effect of aluminum variation.

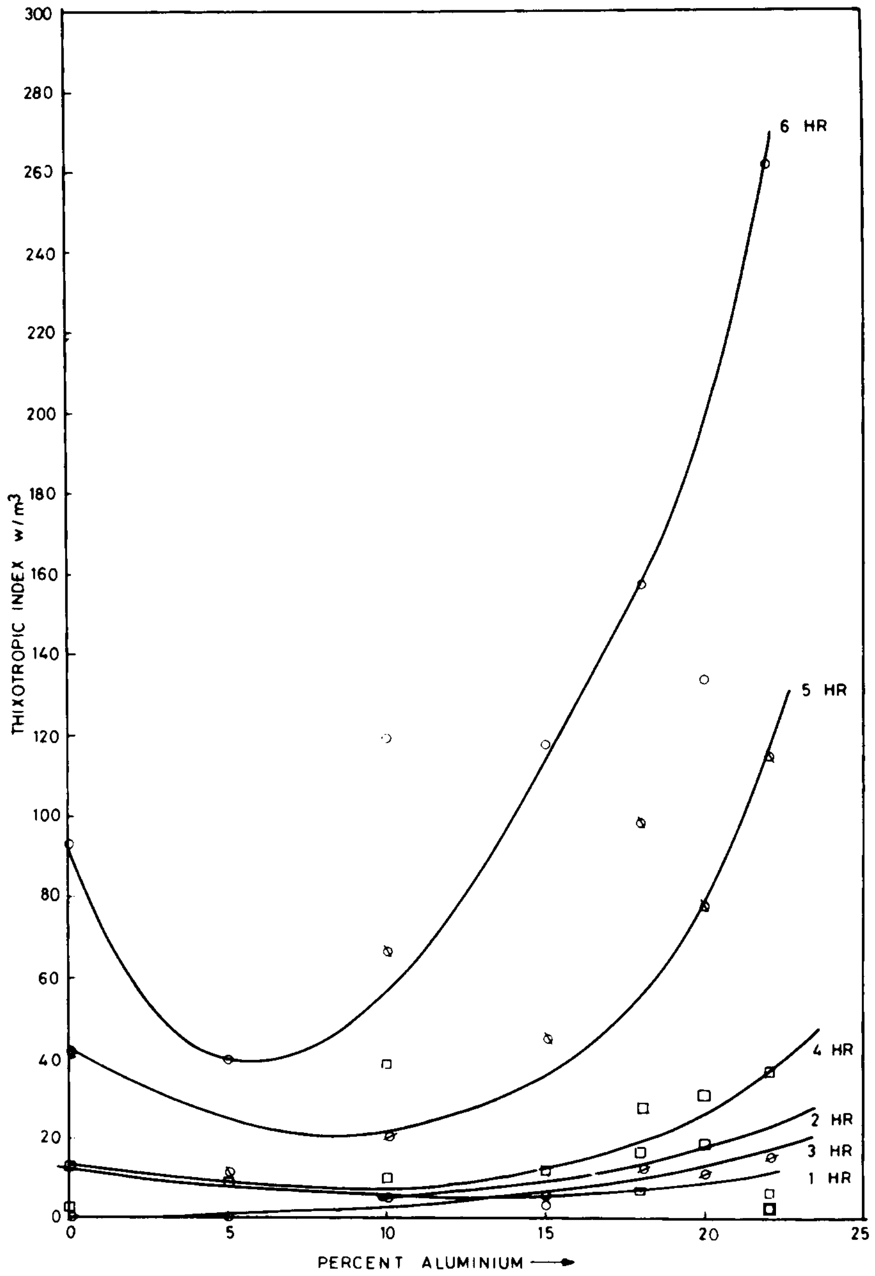

Figure 10 Effect of aluminum variation.

pellant is extremely important. Sweeney and Geckler[11] reported, based on their experiments using glass beads, that packing the particles to increase the bulk density results in a decrease in the vicosity of the suspension. When the diameter of smaller particles is less than 0.155 times that of the larger ones, the packing is so effective that the smaller particles continuously thread throughout the matrix, occupying the free space between the bigger particles and resulting in more availability of fluid and imparting also a bearing effect. This causes a reduction in the viscosity. Yang et al.[10] predicted the viscosities of HTPB-based propellants and compared them with the experimentally observed values for bimodal oxidizer HTPB propellants. The minimum theoretical and observed viscosity appears when coarse-to-fine particles are in closed packing and the ratio is around 70 : 30.

In Figures 5–7, the change of yield stress, consistency index, pseudoplasticity index, and thixotropy index with percent solid loading are given. The yield stress increases with an increase of solid loading.

The increase is steep after 4 h, indicating the difficulty in the processability of these slurries. Though the stoichiometric requirement for the HTPB propellant calls for 90% solid loading, the processability and castability considerations restrict it to 86–88% to produce defect-free grains. The operational propellants sacrifice energetics for better processibility and operate at 86% solid loading.

Figures 8–10 represent the different rheological parameters with respect to aluminum content at hourly intervals for 6 h. The propellant processing does not show a significant change for the variation in aluminum content, as the AP particles for all the four parameters, i.e., yield stress, consistency index, pseudoplasticity index, and thixotropic index, show the best processability in the range of 5–10% aluminum loading. However, the optimum quantity of aluminum is based on the burning rate and specific impulse consideration rather than on processability considerations.

CONCLUSIONS

There is an optimum ratio of coarse to fine at which the propellant slurry remains castable for a longer time. As the fine content is increased from 0 to 50%, the yield stress and consistency index increase exponentially. Up to a 3 : 1 ratio of coarse to fine, there are small variations in yield stress and consistency index. The pseudoplasticity index is found to be maximum at this ratio, indicating that the shear thinning effect is minimum. At 50°C, the slurry exhibits a reasonable pot life.

Though the yield stress increases with increasing solid loading, based on processibility and castability considerations, the operational motors use 86–87% solid-loaded propellants. The variation of aluminum content on these rheological parameters show very little change in view of the spherical nature of aluminum particles. However, the aluminum loading is fixed depending on the energetics considerations in operational propellants.

The experimental help rendered by Mrs. M. Rajan and Mr. L. P. Pandureng and the rheological data reduction by Mrs. T. John are acknowledged with thanks. Thanks are also due to Prof. S. K. De of IIT, Kharagpur, for helpful suggestions and encouragement.

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Received April 3, 1989
Accepted July 16, 1991