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Rheology of HTPB Propellant: Effect of Mixing Speed and Mixing Time

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ABSTRACT

The effect of mixer blade speed and mixing cycle time on the rheological behaviour of an optimized HTPB-based propellant formulations has been studied keeping the temperature constant. Variations in yield stress and viscosity at unit shear rate have been determined as a function of time for different mixing speeds. The effect of mixing on the extent of pseudoplasticity has been represented in the form of a bar chart. A correlation in terms of shear and yield stresses has been developed for viscosity index, i.e., the viscosity at unit shear rate as a function of mixer blade speed.

NOMENCLATURE

σ	shear stress
σ_o	yield stress
$\dot{\gamma}$	rate of shear
$\eta_{\dot{\gamma}=1}$	viscosity at unit shear rate
n	pseudoplasticity index
R	speed of the leading blade in rpm
t	time elapsed after the addition of curative and completion of mixing cycle in hours

1. INTRODUCTION

Composite propellants based on hydroxyl terminated polybutadiene are gaining importance because of their improved energetics and superior mechanical properties in launch vehicles and advanced missiles.

Information about the processing characteristics of HTPB-based composite propellants is essential for realising defect-free propellant grains. Propellant rheology has been studied in detail by Osgood[1], Klager *et al*[2], Killian[3], and Manjari[4]. The effect of compositional parameters like ammonium perchlorate (AP) particle size distribution, total solid loading comprising AP and aluminium has been reported elsewhere[5]. The effect of temperature on rheology has been studied by Muthiah *et al*[6]. Ramohalli[7] has reported the influence of mixing time on the burning rate and tensile modulus of AP-HTPB composite propellants. Prabhakaran *et al*[8] studied the effect of process variables during composite propellant manufacture and found that the mixing time has hardly any effect on unloading viscosity, burning rate, mechanical properties and thermal conductivity. They also found that increase in the mixing speed reduced the unloading viscosity and mechanical properties without affecting the burning rate. Once the propellant composition is optimized and processing temperature is chosen based on better processability and longer pot life, it is desirable to assess

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the effect of parameters like mixer blade speed and mixing cycle time on different rheological parameters, viz., yield stress, pseudoplasticity index, viscosity at unit shear rate, etc. The results of a study on these aspects are presented in this paper.

2. EXPERIMENTAL

Propellant Formulation:

Ammonium perchlorate oxidizer	68.0 %
Aluminium	18.0 %
HTPB, DOA, TMP and TDI	14.0 %
	100.0 %

Material Characteristics:

Oxidiser : Ammonium perchlorate
Coarse size : 300 – 320 microns
Fine size : 40 – 45 microns
Coarse : Fine = 80 : 20
Source : APEP, VSSC

Metallic additive : Atomized aluminium powder
Size : 10 – 12 microns
Source : MEPCO, Madurai

Plasticizer : Diethylhexyl adipate (DOA)
Source : Indo-Nippon, Bombay

Additive : Trimethylol propane (TMP)
Dried to 0.1 per cent moisture content before use
Source : KEK, Japan

Curative : Toluene di-isocyanate
2,4- and 2,6-isomer mixture (ratio 80:20)
Used as received.
Source : Mitsubhishi, Japan

Coarse AP was used after drying and sieving through 1 mm sieve to eliminate any foreign particles. Fine AP was obtained by grinding coarse AP in a pin mill grinder under nitrogen blanket.

Propellant mixing was done in a 500 ml Guittard sigma mixer. The speed of the mixer leading blade was varied from 10 rpm to 60 rpm by a variable speed drive mechanism at a fixed gear ratio. Mixing temperature was maintained at 50±1 °C in all experiments. Mixing cycle was varied from 60 to 240 min in different combinations.

Contraves' rheometer (Model Rheomat-30) was used for rheological measurements. The propellant slurry was extruded into the cup for each measurement for ensuring reproducibility of results. The shear rate was varied from 0.0 to 0.997/s over a period of 1 min. Rheograms were obtained by plotting shear stress against the rate of shear, at 1h intervals up to 6 h, after addition of the curative. Each rheogram was analysed for yield stress (σ_o, viscosity at unit shear rate ($\eta_{\dot{\gamma}}$), and pseudoplasticity index (n).

In the first set of experiments, mixer leading blade speed was varied from 10 to 60 rpm at five different settings. Correspondingly, the speed of the other blade got varied from 7 to 44 rpm at a fixed speed ratio. The mixing temperature was maintained at 50±1 °C and the mixing cycle time was kept at 120 min.

In the second set, the mixing cycle time was varied from 60 to 240 min (Table1). Mixing temperature was maintained at 50±1 °C, keeping the blade speeds at 25 and 18 rpm.

Table Mixing cycle

Premix time* (min)	Vacuum mixing after AP addition (min)	Time after TDI addition (min)	Total mixing time (min)	Av. time for mixing of AP (min)
6	14	40	60	57.5
30	50	40	120	102.5
30	110	40	180	142.5
60	80	40	180	155.0
90	50	40	180	167.5
90	110	40	240	202.5

* In six equal intervals: (1) addition of HTPB, DOA, TMP (TMP is melted at 60 °C in HTPB-DOA mix), (2) aluminium addition, (3) half the quantity of coarse AP added, (4) rest of the coarse AP added, (5) half the quantity of fine AP added, and (6) rest of the fine AP added.

In all the experiments, the time of mixing after TDI addition was kept constant at 40 min, which has been found to be optimum for TDI dispersion.

3. RESULTS AND DISCUSSION

As reported earlier, HTPB propellant slurry exhibited a time-dependent flow behaviour, in addition to shear rate and temperature dependence. The rheological behaviour of the propellant slurry can be represented by the equation:

$$\sigma - \sigma_o = \eta_{\dot{\gamma}=1}^{\circ} [\dot{\gamma}]^n \qquad (1)$$

Viscosity at unit shear rate is usually referred to as the consistency index.

Eqn (1) shows that the flow of HTPB propellant slurry is non-Newtonian[9], since $\sigma_0 \neq 0$ and n is also not necessarily equal to 1. The purpose of the present investigation was to study how σ_0 and n depend on mixing time and mixing speed in order to have a deeper insight into non-Newtonian behaviour of the slurry from the viewpoint of processing considerations.

3.1 Influence of Mixing Time

The influence of increased mixing time after AP addition (keeping the time of mixing after curative addition the same) on viscosity at unit shear rate is depicted in Fig. 1 with cure time as a parameter.

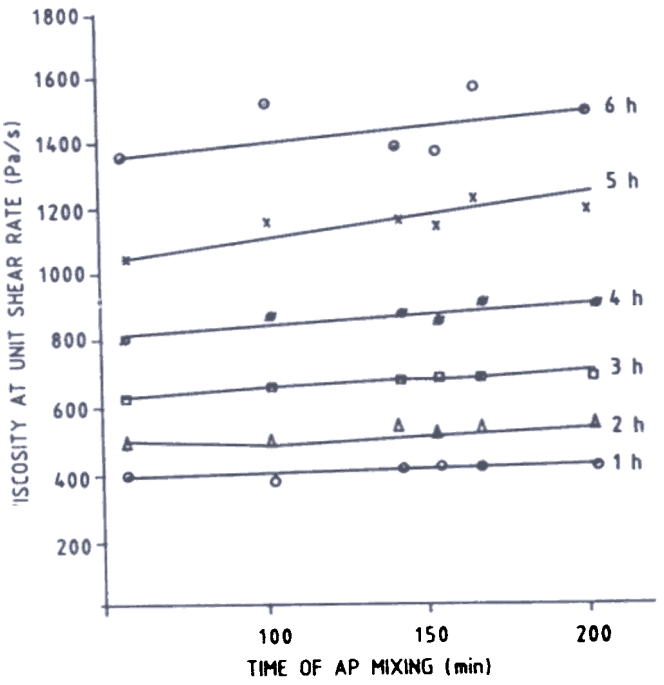

Figure 1. Effect of mixing time on viscosity at unit shear rate.

Increase in mixing time has a tendency to decrease the viscosity due to better binder-filler wetting. Also, it has a tendency to increase the viscosity through reduction in AP particle size brought about by the increased shearing action. It is known that a propellant formulation having finer particles of AP exhibit higher unloading viscosity and viscosity build-up. These contradictory effects have resulted in more or less constant viscosity during the initial phase of curing.

Yield stress variations as a function of mixing time at different time intervals after curative addition are depicted in Fig. 2. It is seen that there is a slight decrease up to about 170 min of mixing and then increase in the

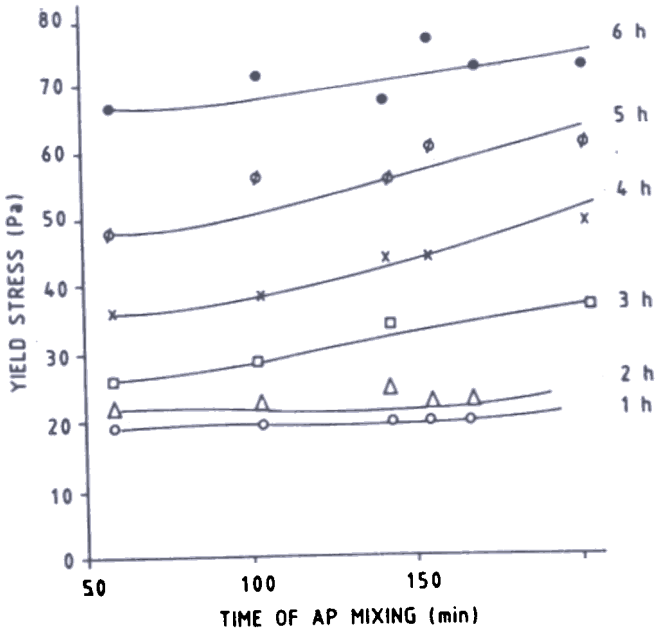

Figure 2. Effect of time on yield stress

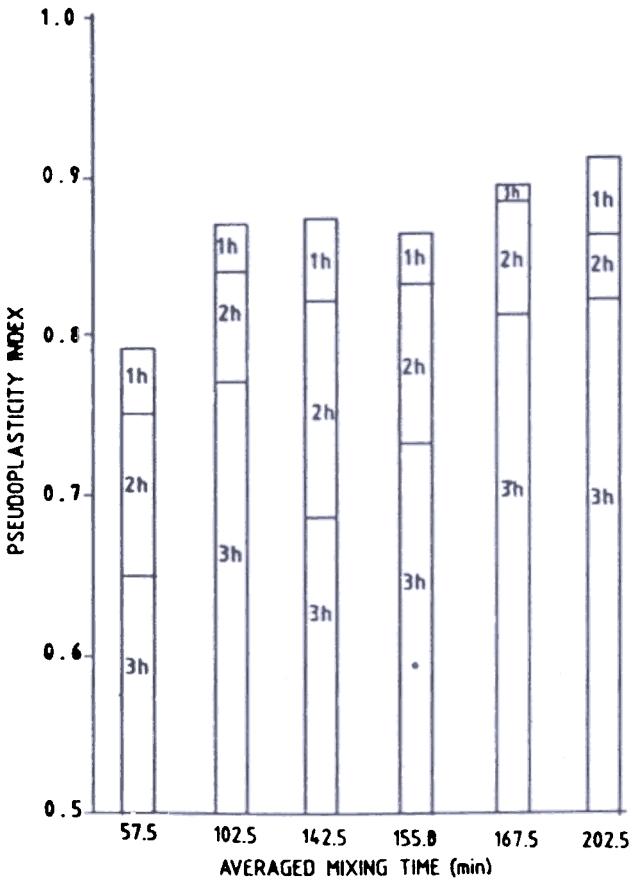

Figure 3. Effect of averaged mixing time on pseudoplasticity index.

first 2 h. After 2 h, it increases with increase in mixing time.

The influence of mixing time on n value is depicted in the form of a bar chart in Fig. 3. A gradual increase in the value of n with time is obvious. The slurry becomes less and less pseudoplastic as the mixing time increases. This is due on the one hand to the AP grinding effect, making the particles smaller and smoother, and on the other to the improved wetting of the solid particles by the liquid.

Higher values of yield stress and consistency index at mixing times beyond 180 min are attributable to the grinding or shattering of the coarse AP by blade impact. Ramohalli[7] has attributed the increase to the continual decrease in mean AP particle size with increase in mixing time, probably due to the shattering of AP upon blade impact. He has also correlated the increase with increase in burn rate and tensile modulus. Quantitative assessment of this effect is still at infancy though Ramohalli predicted a burn rate increase of 3-4 per cent for 100 min. Thus, the results indicate mixing time to be an important parameter which has to be finalised on the basis of other experimental conditions like blade speed, pot life required and casting rate.

3.2 Influence of Mixing Speed

The effect of variation in mixing speed is depicted in Figs. 4-6. It is seen from Fig. 4 that the viscosity index remains more or less constant irrespective of the mixing speed during the initial phase of curing. But as time elapses, viscosity index increases with mixing speed. Yield stress values plotted in Fig. 5 show an increasing trend at all speeds and time intervals after curative addition. This could be due to two effects: (i) at higher mixing speeds, the extent of AP grinding increases, producing more and more finer AP particles resulting increase in the viscosity; and (ii) at higher mixing speeds, chances of bulk transfer of slurry instead of shearing action are more, leading to increase in viscosity. The effect of mixing speed on pseudoplasticity index, n, is depicted in Fig. 6. It is seen that as the mixing speed increases, the slurry tends to become less and less pseudoplastic, i.e., n value becomes nearer to unity. Initially, up to 2 h, n value is low due to reduced contact time between solid and liquid ingredients. At a time interval of 2-4 h after curative addition, the pseudoplasticity indicates maximum values at all speeds. Beyond 4 h, the curing reaction takes over and the n value again comes down.

An analysis of the cure reaction rates as a function of mixing speed (Fig. 7) shows that the reaction rates remain more or less constant irrespective of the mixing speed.

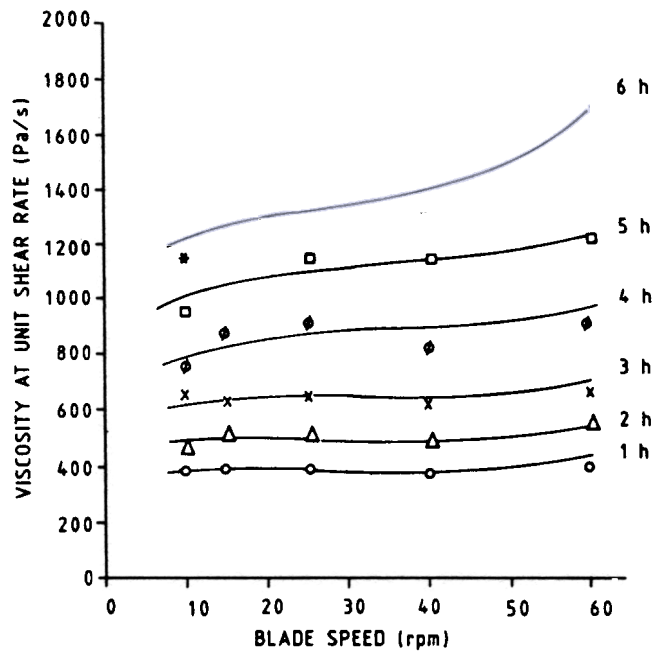

Figure 4. Effect of blade speed on viscosity at unit shear rate.

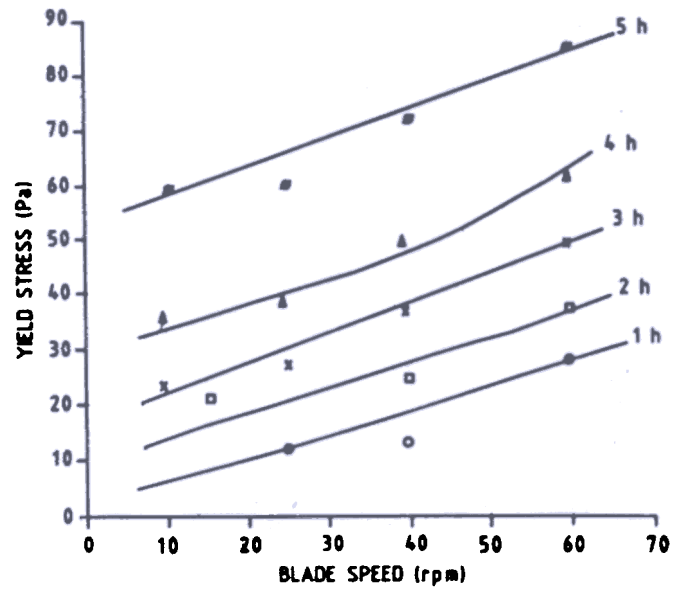

Figure 5. Effect of blade speed on yield stress.

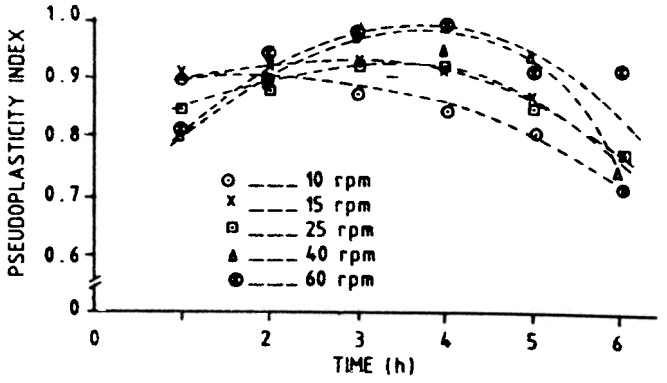

Figure 6 Effect of blade speed on pseudoplasticity index

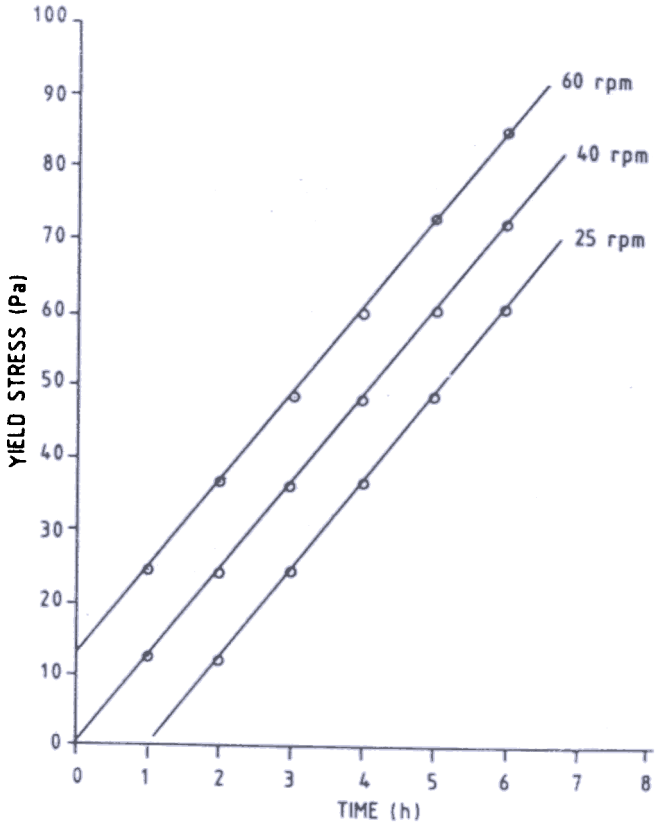

Figure 7 Effect of blade speed on yield stress.

The yield stress is found to increase linearly with the speed of mixing as per the following relationships:

$$\text{Up to 25 rpm: } \sigma_0 = 11.92\,t - 11.92 \quad (2)$$

$$\text{Above 25 rpm: } \sigma_0 = 11.92\,t + 0.67\,(R\text{-}25) - 11.92 \quad (3)$$

The results of the present study indicate that mixing time and speed of mixing directly reflect the viscosity and viscosity build up. It is, therefore, necessary to optimise these parameters based on the final propellant requirements, viz., burning rate, mechanical properties and economics (longer mixing time calls for more mixers and longer durations of the schedule). It follows that based on these cosiderations and rheological input, the mixing time for the HTPB propellant formulations could be fixed as 180 min at mixing speed 25:18 rpm.

4. CONCLUSION

HTPB propellant slurry shows a time-dependent flow pattern. The rheological parameters depend on the mixing parameters like mixer blade speed and mixing cycle time to some extent. A speed of 25 rpm seems to be the optimum, beyond which, too much shear could shatter the AP particles. Continued mixing further leads to breakage of AP particles, thereby affecting the coarse to fine AP ratio.

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