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## RHEOLOGICAL STUDIES ON VIRGIN, PLASTICIZED AND SOLID FILLED HTPB BINDER SYSTEM

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### ABSTRACT

The rheological studies on pure HTPB polymeric fuel binder system have been carried out as a function of shear rate (rpm) at different time intervals using Brookfield viscometer. The results obtained clearly indicate that the system behaves almost as a Newtonian fluid. However, with the lapse of time, the viscosity is seen to increase significantly at all shear rates. This is attributed to progressive increase in degree of cross-linking. Exactly a similar behavior is exhibited by plasticized binder at all shear rates with the difference that viscosity build up is at slower rates in comparison to pure binder due to dilution factor (reduced concentration) of reactants leading to reduced rate of cross-linking. The propellants (solid filled binder) also reflects similar behavior but with considerable increase in viscosity due to availability of lesser fluid responsible for flow.

**Keywords :-** HTPB (hydroxyterminated poly(butadiene)), AP (ammonium perchlorate), TDI (toluene-2,4-diisocyanate, rheology, viscosity, binder, DOA (dioctyl adipate), propellant, micron ( $\mu$ ) etc.

### Introduction

A rocket propulsion system based on reaction principle is self contained as it carries propellant required for its operation. Almost all present day rockets / missiles make use of chemical propellants. The propellant is a balanced source of chemical energy which is converted into useful kinetic energy (KE). This leads to suggest that maximum KE must be realized which can only be achieved by increasing the chemical energy of propellant. This, in turn, can be possible by increasing the energetics of binder system / by loading higher percentage of AP, the oxidizer. Yet another approach to increase the propellant energy content is to incorporate light metal powder in propellant formulations. Efforts made to introduce high energy groups <sup>[1]</sup> in the polymeric binder backbone proved to be only of limited practical utility. Attempts made to achieve the next objective led to the development of hydrocarbon type binders such as PBAN (poly (butadiene-acrylonitrile)), PBAA (poly (butadiene-acrylic acid)), CTPB (carboxyterminated poly (butadiene)) and finally HTPB. The last binder system showed its worthiness and superiority over others in line in the sense that it was found capable of very high solids (86 wt% - 90 wt %) loading without sacrificing the ease in processability and that too with improved mechanical properties and enhanced internal ballistic characteristics. The energy content of the propellant system can however be further improved by incorporating light metal powders which evolve extremely high amount of thermal energy <sup>[2]</sup> without producing combustion products causing health and environmental hazards. In light of above facts, HTPB

was selected as the binder system for the study of rheology of pure and plasticized systems as well as that of the propellant slurries based on it with the viewpoint of data collection for postgraduate dissertation of second author in Propulsion Stream of Space Engg. and Rocketry department, BIT Mesra, Ranchi as well as extending help to VSSC Trivandrum (Kerala). The present communication deals with the rheological studies of pure and plasticized binder system as well as that of propellant slurries of varying compositions.

### Research Methodology

#### Formulation of HTPB Binder System

HTPB prepolymer (mol. wt. $\approx$ 4000)	Polymer Fuel Complex (PFC), VSSC Trivandrum
Toluene-2,4-diisocyanate (TDI)	Mitsubishi Japan
Trimethylol propane (TMP) (0.1 wt%)	PFC, VSSC Trivandrum
Alkanol amine- amide type (Ped-O-Bond)	Propellant Engg. Division (PED), VSSC Trivandrum

All the above constituents make a total of 11.0 wt%.

#### Formulation of Propellant

Amide coated ammonium perchlorate (AP)	68 wt% , APEP, Alwaye, Kerala
Aluminium powder (18 – 20 $\mu$ )	18 wt%, Metal Powder Co. Madurai, India.
Plasticizer (dioctyl adipate, DOA)	2.8 wt%, RPP, VSSC Trivandrum
Additives - Phenyl $\beta$ -	0.1 wt%, RPP, VSSC

naphthyl amine (Nonox-D) as antioxidant	Trivandrum
Monochloro trifluoro ethylene (VOLTALF oil) as processing aid	0.1 wt%, RPP, VSSC Trivandrum
Ferric oxide (catalyst)	0.5 wt% to 2.0 wt%, Creative Chemicals, Bombay

## Experimental

### Analysis of Particle Size (PS) And Particle Size Distribution (PSD) of AP

The oxidizer, ammonium perchlorate, of  $\approx 500 \mu$  obtained from manufacturer was dried at  $100^\circ\text{C}$  for 2 - 3 hours and was used as such as coarse fraction. The fine AP, however, was obtained by grinding the coarse fraction in a pin mill (French make). One hundred gram sample of each fraction was subjected to sieve analysis to determine their PSD.

### Rheological Studies of Binder System

Viscosity studies of binder system (HTPB + TDI) were accomplished with the help of Brookfield viscometer (model: HBT, USA) using disc type spindles of diameter (D) equal to 47.15 mm and thickness (T) of 1.59 mm for HB-II and D equal to 34.74 mm and T of 1.59 mm for HB - III spindles at different shear rates (rpm) and at different time intervals.

### Effect of Plasticizer Level on Binder Viscosity

HTPB binder system containing the plasticizer, DOA, up to a level of 10%, 20% and 30% by weight of HTPB have been used in the present study. In each case binder system was de-aerated for about 10 minutes prior to the addition of TDI. After thoroughly mixing the contents, viscosity measurements were carried out at  $31^\circ\text{C} \pm 2^\circ\text{C}$ . Variation of viscosity with time was studied reckoning the moment of TDI addition as zero hour.

### Effect of Oxidiser PSD on Viscosity of Propellant Slurry

Propellant mixes of desired formulations were prepared in a sigma blade mixer (Type: VC23, HP1, No. V5914, Malaxeurs, France) of 4 kg capacity. However, the mixing was actually carried out in a batch of 3.5 kg only using materials from the same lot to minimize batch to batch variations possibility of ingredients. All the process variables like mixing duration, sequence of addition of materials to the mixer, time interval of application of vacuum etc. were kept the same in all the cases.

Requisite amounts of HTPB, DOA and voltalef oil were mixed in a separate stainless steel container with a PVC

rod. A part of this mix was transferred to the sigma blade mixer maintained at  $55^\circ\text{C} \pm 2^\circ\text{C}$  by hot water circulation from temperature controlled bath. The nonox-D was also added to it. The contents of the mixer called "premix" were mixed for 15 minutes. The 'sub mix' obtained by mixing TMP and POB dissolved separately in remaining part of mix was then added to the mixer containing 'premix' and was mixed for another 15 minutes. Aluminum powder in requisite amount was then added followed by mixing for half an hour. The coarse AP in nearly two equal installments and fine AP in a single lot were then added followed by mixing for duration of 10 minutes after each addition. Finally, the contents were mixed for an hour under a vacuum of 3-5 tor. The curative, TDI was then added and mixed for 10 minutes under ambient conditions followed by mixing for another 10 minutes under vacuum.

Four samples of propellant slurries were prepared by varying the oxidizer PSD in terms of coarse to fine (C/F) ratios of 4:1, 2.33:1, 1.5:1 and 1:0 at a fixed solid loading of 86 wt%.

The viscosity of each mix was then determined as a function of time. All the propellant viscosity measurements were made at  $55^\circ\text{C} \pm 2^\circ\text{C}$  maintained by hot water circulation from a temperature controlled bath.

### Effect of Catalyst Level on Viscosity of Propellant Slurry

Keeping all the parameters mentioned above (86 wt%) solid at a given C / F ratio as constant, arbitrarily selected  $\text{Fe}_2\text{O}_3$  amounting to 0.25%, 0.5%, 1.0% and 2.0% by weight of the total weight of the propellant were used in the present case. In order to keep the total solids loading of 86 wt% as constant, the amounts of AP and Al were proportionately reduced. It may be mentioned here that  $\text{Fe}_2\text{O}_3$  was mixed with the 'premix' prior to addition of 'sub mix'.

## Results and Discussion

### Oxidiser PS AND PSD

Solid oxidizer and metal powder play a vital role in determining the processability [3-5], mechanical properties [6, 7] and combustion characteristics [8-13] of composite solid rocket propellants. Actually, the processability of propellant has been reported [4] to be strongly dependent on the ratio of volume fractions of filler and binder defined by the relation

$$S/L = VPS / [100 - VPS] \quad \dots\dots\dots (1)$$

where S and L stand for solid to liquid ratio in terms of their volume fractions and VPS refers to volume percent of filler. It has also been claimed that propellant formulations are easily processable when S / L ratio lies

between 2.0 and 3.5. This has been found to be true when attempted to pack up the coarse particles retained between 60 – 100 mesh and fine particles between 200 and 350 mesh (British Standard) sieves geometrically<sup>[14]</sup>.

Though the PSD can be determined in a number of ways described elsewhere<sup>[15]</sup> but for most of the practical purposes where  $PS \geq 40 \mu$  is involved, sieve analysis is frequently used as it is simpler, informative and much less time (hardly an hour or so) consuming. This simplest method, generally used everywhere, involves the study of the variation of cumulative wt.% versus PS. Assuming, the particles to be spherical, analysis of PS and PSD of coarse and fine AP particles by aforesaid method has been used here. It is found that the coarse and fine particles mean diameters are  $315\mu$  and  $49\mu$  respectively.

The average particle diameter<sup>[16]</sup> of bimodal AP blends corresponding to different C / F ratios on weight basis has been obtained by the relation

$$D_w = \Phi_c D_c + \Phi_f D_f$$

..... (2)

where D and  $\Phi$  refer to particle diameter and weight fraction respectively. The subscripts w, c and f stand for weight average, coarse and fine AP particles respectively. The results obtained are found to best fit the equation<sup>[16]</sup>

$$D_w = 2.956 F + 315.0$$

..... (3)

where F is the weight percent of fine particles in bimodal blend of AP. It is anticipated that the PSD analysis data would be of immense help in explaining at least qualitatively the rheological behaviour of propellant slurries.

### Rheology of HTPB Binder

The viscosity data of HTPB binder system containing TDI (4.9 wt% of HTPB) at different shear rates (rpm) has been shown in **Figure 1**. It is seen that (i) the apparent viscosity of HTPB-TDI system is almost independent of shear rate in the rpm range of 5-50 covered in the present study and (ii) the viscosity of the binder system goes on increasing at all shear rates with the lapse of time. The former observation clearly indicates that the system shows almost Newtonian behavior in the whole shear rate range. The second observation can be attributed to the cross-linking reaction between hydroxyl groups of HTPB and isocyanate groups of TDI, the curing agent, which starts as soon as they are mixed together. The viscosity of HTPB pre-polymer ( $\approx 4000$  cP at ambient temperature) is seen to be nearly equal to that of HTPB+TDI mix at zero hour lying between 3840 and 4032 cP. With the lapse of time the extent of cross-linking expectedly increases resulting in the proportionate increase in viscosity. Further, analysis of data at a given shear rate

reveals that viscosity varies with time exponentially according to relation<sup>[16]</sup>

$$\eta_{ap} = \eta_0 t^{-m}$$

which in the logarithmic form can be expressed as

$$\log \eta_{ap} = \log \eta_0 - m \log t \dots\dots$$

(4)

where  $\eta_{ap}$ ,  $\eta_0$ ,  $m$  and  $t$  are apparent viscosity at any time, at unit hour after TDI addition, exponent of time and time in hour respectively. Thus, a plot of  $\eta_{ap}$  against  $\log \eta_0$  should be a straight line. This has been found to be so as shown in **Figure 2** with the latter as intercept on the ordinate at unit hour and 'm' as the slope having values of 10224 cP and 0.583 cP per hour respectively. The value of the intercept indicates the apparent viscosity of binder system after one hour of addition of TDI while the slope indicates the rate of increase in viscosity of binder mix with time in hour.

### Effect of Plasticization on Binder Viscosity

It is reported<sup>[17-20]</sup> that the rheological behaviors of binder is significantly influenced by addition of plasticizer which in turn is expected to affect the nature of flow of propellant based on it. Therefore, it seemed essential to orient the study the rheology of plasticized HTPB binder system. The result with this viewpoint on the effect of varying degree of plasticization of binder system with respect to shear rate at different time intervals for 20 wt% of DOA has typically been presented in **Figure 3**. Exactly similar results are seen to be exhibited by 0, 10 and 30 percent of DOA by weight. A look at the figure also reflects that even with the increasing degree of plasticization, all the plasticized systems show Newtonian behavior at all shear rates and time intervals similar to virgin binder system. The viscosity build up rate, however, is found to be at its maximum in case of un-plasticized binder due to concentration factor. Expectedly, the data recorded in **Figure 4** as a plot of apparent viscosity versus time at all shear rates and with increasing level of plasticization reflects that it progressively decreases with increasing level of DOA. This is what one would expect in the light of continuously decreasing concentration of active reactants on plasticization. But surprisingly enough, very little difference in viscosity build-up data is seen in the plasticized binder containing 20 wt% and 30 wt% of DOA in comparison to that for 10 wt% which is not currently understood.

### Rheology of Propellant Slurries

The results recorded in **Figure 5 & 6** show the effect of oxidizer PSD on the viscosity of HTPB-AP-Al composite solid propellant slurry containing a total of 86 wt% of solids at different time intervals using TC- and TE- bar spindles at 2.5 rpm. It is seen that for a given PSD of AP, viscosity increases with time and at a

given moment it increases with increase in fine AP content (decreasing C/F ratio) in the bimodal AP. The former observation is understandable in the light of progressive increase in extent of completion of cross-linking reaction as discussed earlier in the case of binder system. Moreover, the use of amide coated AP particles may also be at least partly be responsible in increasing the apparent viscosity values besides their actual shape, size and macroscopic dimension due to bond formation capability between them and the binder matrix [21 & 22].

The latter finding, however, can be attributed to the factors like porosity variation and consequent changes in the volume fraction of oxidizer with increase in fine AP content. **Figure 5** also visualizes that propellant slurry containing only coarse AP registers lowest viscosity which goes on increasing with the incorporation of more and more of fine AP. This can again be explained in terms of porosity of bimodal AP and Al- powder. It is well known fact that the void size is much larger in the case of packing of coarse particles but lower in number as compared to that of fine ones where void size is comparatively much smaller but too large in number so that the total void volume becomes extra-ordinarily large. An explanation that can be put forward right here is that only a small part of fine AP particles and especially that of very fine Al- particles (18 -20  $\mu$ ) are being used to occupy the voids between coarse particles and the remaining fine particles of both the solids having higher porosities ultimately result in increase in the overall porosity to such an extent that is sufficient to imbibe major part of the liquid polymer to cause the rise in apparent viscosity. Another possibility that can be speculated is that the PS of fine solids is of such a size that does not completely fit into the voids formed between coarse particles. Consequently, the availability of liquid binder system responsible for flow would enormously decrease resulting in increase in frictional force and hence the apparent viscosity. This is supported by the viscosity- filler relationship described by the equation [21]

$$\{\eta / \eta_0\} = \{1 - \Phi / \Phi_m\}^{-2.5} \quad \dots (5)$$

Where  $\eta$ ,  $\eta_0$ ,  $\Phi$  and  $\Phi_m$  denote the viscosity of dispersion medium, propellant slurry, volumetric loading and the maximum possible loading respectively. The value of  $\Phi_m$  for a given system can be found by packing considerations. Subsequently, it can be inferred that increase in viscosity of propellant slurry is controlled by all the above factors as discussed elsewhere [8-10] but it is quite difficult to assess even qualitatively the extent of contribution of each in the light of existing data.

The study on the effect of solids loading at a fixed oxidizer PSD (C/F ratio = 2.33) on the viscosity of propellant slurry at different time intervals for a given shear rate (2.5 rpm) has also been studied. The apparent

viscosity is found to increase with solid loading. This is in accordance with that reported in literature [8-10, 19] showing strong dependence on solid to liquid ratio. This is due to the fact that the fluid part responsible for flow is considerably decreased thereby indicating the increase in frictional force leading to higher viscosity.

The experimental results on the variation of apparent viscosity of propellant slurry containing varying amounts of ferric oxide does not appear to give any simple correlation with its level. Nevertheless, it can certainly be inferred that the apparent viscosity of all the propellant slurries with varying level of  $\text{Fe}_2\text{O}_3$  (PS =  $6\mu$ ) except that having 0.5wt% show scattering of data points in a very narrow region which leads to conclude that apparent viscosity is relatively insensitive to its meager amount present in propellant formulation. If it is true, it would be an additional advantage of keeping intact the ease in processability of propellant slurries in line with that reported [3] in literature.

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