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Rheological Behaviour of HTPB-based Composite Propellant: Effect of Temperature and Pot Life on Casting Rate

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ABSTRACT

To study the rheological properties and the flow behaviour of HTPB based composite propellant, a typical mix was carried out with 86 per cent solid loading and toluene diisocynate (TDI) as curator. Viscosity of the propellant slurry was measured at different shear rates over a range of temperature from 40 °C to 60 °C at various time intervals up to five hours from end of mix. The data are analysed using power law fluid equation to determine the viscosity index (K) and pseudoplasticity index (m). From these, optimum casting temperature and useful pot life was evaluated. Casting rates at different temperatures were determined by Haegen-Poisseuille equation modified for non-Newtonian fluid flow, using K and m.

Keywords: Composite solid propellants, rheological behaviour, casting rate, HTBP-based composites, solid propellants, propellant grain, propellant flow, pseudoplasticity

1. INTRODUCTION

Composite solid propellants mainly contain a polymeric fuel binder, a metallic fuel such as aluminium (*Al*) powder and an oxidiser usually ammonium perchlorate (AP). The polymeric binder, which constitutes 15-25 wt per cent of the propellant generally consists of a telechelic liquid prepolymer, curing agent, plastisiser, ballistic modifier, bonding agent, and an antioxidant[1]. Composite propellants based on hydroxyl terminated polybutadiene (HTPB) resin are the most widely used solid propellants for launch vehicle and missile applications[2].

The flow behaviour of HTPB-based propellants assumes to have great importance because this is the main cause of many grain defects in the large-scale motors. Though several workers have studied the rheological behaviour of composite propellants still it is not very clearly understood[3-7]. Several parameters such as the raw materials, formulation, mixing temperature, vacuum level, and casting rate play significant role in the flow behaviour of the propellants[7-10]. To make a logical decision regarding propellant mixing and casting, the effect of temperature and time on viscosity and pseudoplasticity are considered to be essential in addition to the parameters such as volume of propellant slurry, bowl and casting pipe dimensions.

The trade-off between temperature and pot life is critical, since increasing the casting temperature decreases the viscosity but increases the rate of curing. So in the absence of these data, the tendency is to specify casting temperature lower than necessary to prevent curing reaction which results in unnecessary long casting time.

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The solid propellant rheology follows that of a non-Newtonian fluid, which means that the rheogram of shear stress versus shear rate is not a straight line. The grain geometry, the viscosity regime of the propellant slurry, and the level of vacuum, all control the quality of the propellant grain[11]. However, the flow characteristic of the propellant slurry within the mould is equally important that in fact, leads to achieve quality of the grain. The rheological characterisation of the slurry therefore, is a major concern in the propellant processing technology. Although, it is generally accepted that propellants are non-Newtonian, most of the experimental work has been based on Newtonian flow, i.e., viscosities are reported independent of shear rate or at only a single shear rate. For some propellants, this is misleading, especially if the extent of non-Newtonian is not constant. Viscosity is the measure of resistance to flow and for most materials, this measurement value changes depending on how fast the material is moved. In most materials, it is observed that the viscosity decreases, if moved faster[12]. Therefore, it is important to take into account the various ways in which the material flows during processing. Although it is understood how propellant flow is affected by viscosity, the effect of pseudoplasticity on flow behaviour of propellant has been least studied. Among the non-Newtonian properties of the propellants investigated for years by rheologists, pseudoplasticity is considered one of the most important aspects with respect to propellant flow.

In the present study, to understand the flow behaviour of the propellant as a function of time and temperature, the propellant slurry has been characterised in terms of pseudopasticity and viscosity index. The casting rate at different temperatures are computed using Haegen-Poisseuille equation.

2. EXPERIMENTAL

2.1 Materials

Hydroxyl-terminated polybutadiene (hydroxyl value = 43 mg *KOH*/g, polydispersity = 1.96, viscosity at 30 °C = 6100 cP, viscosity at 60 °C = 1470 cP, cis/trans/vinyl (%) = 16/64/20, NOCIL, India), ammonium perchlorate (AP) coarse (purity = 99.7 %), surface moisture = 0.08 %, size distribution (%): +500 µ=1.8, 500-355 µ=31, 355-300 µ=32,300-45 µ=35, –45 µ=0.2, Tamilnadu Chlorate, India), ammonium perchlorate fines (size distribution (%): + 106 µ=7.5, 106 - 75 µ=13, –75 µ=79.5), dioctyl adipate (saponification value=302 mg *KOH*/g, KLJ Polymer, India), toluene diisocynate (purity =99.2 %, a mixture of 2,4 and 2,6-isomers in 80:20 ratio,Takeda, Japan), aluminium (mean dia=25 µ, by laser diffraction method, Mepco, India) trimethylol propane (hydroxyl value = 1222 mg *KOH*/g , Mitsubishi, Japan) and 1-4-butanediol (hydroxyl value = 1225 mg *KOH*/g, Bayer) were used in the present study.

2.2 Methods

2.2.1 Preparation of Propellant Slurry

The propellant slurry was prepared by taking 86 per cent of solid loading in which 68 per cent is bimodal ammonium perchlorate and 18 per cent is aluminium powder. Toluene diisocynate (TDI) was used as a curing agent. The mixing was carried out in two phases. In the first phase, a premix was prepared by mixing all the ingredients except the curator and a homogeneous test of the slurry was carried out to confirm the uniform dispersion of ammonium perchlorate (AP) and *Al* powder. In the second phase, the final mix was prepared by adding TDI. The NCO/*OH* ratio was fixed at 0.8. The mix size of the above formulation was 100 kg.

2.2.2 Measurement of Viscosity Build-up

The propellant slurry samples were taken in 500 ml container of 84 mm dia and 110 mm length, immediately on completion of mixing cycle after TDI addition. To maintain the specified temperature range, i.e., 40 °C, 45 °C, 50 °C, and 60 °C, the slurry samples were kept under constant temperature (Brookfield) bath separately.

The viscosity measurements of the propellant slurries were carried out using a Brookfield HADV-II+ viscometer with T-E spindle. A helipath stand was used to avoid any channeling effect due to the spindle rotation. Viscosity measurements were made at 1, 2.5, 4, and 6 rpms respectively. The viscosity values reported is the average of twenty readings gathered at an interval of one second using Wingather software.

3. RESULTS AND DISCUSSION

3.1 Pseudoplastic Behaviour: Shear Rate versus Viscosity

Viscosity of the propellant slurry maintained at 40 °C, 45 °C, 50 °C, and 60 °C, were measured at different time interval on varying shear rate and plotted as a function of time. Figure 1 represents the propellant slurry maintained at 40 ºC. From these plots, viscosities at desired time intervals were computed by fitting the data to an exponential function of the general form $\eta = ae^{bt}$, where *a* and *b* are empirical constants. Similar procedure was followed for slurry maintained at other temperatures.

The viscosity values obtained as above are plotted against shear rate. Figure 2 plots the shear rate (rpm) versus viscosities of the slurry maintained at 40 ºC and an aging up to 240 min. From this plot, it is seen that with increase in the shear rate, the viscosity of the slurry decreases. This behaviour indicates the pseudoplastic nature of the propellant slurry. Similar trends were also observed for slurry maintained at 40 °C, 45 °C, 50 °C, and 60 °C.

For non-Newtonian fluid, it follows that if the viscosity decreases with shear, the rate of decrease is the measure of pseudoplasticity. The pseudoplasticity nature of the slurry is expressed in terms of pseudoplasticity index, which is a true physical property of the material[13].

The flow of highly loaded slurry can be more closely approximated by power law fluid model. The pseudoplasticity index (*m*) and the viscosity index (*K*) are calculated from the curves (Fig. 2) by fitting the data to the Power law equation, $\eta = Kx^m$, where, η is apparent viscosity, *x* is shear rate, *m* is pseudoplasticity index (PI) and *K* is viscosity index (VI). Newtonian fluids are the special case of power law fluids when *m* = 0, i.e., viscosity is independent of shear rate. For dilatant fluids, *m* is positive, while for pseudoplastics, *m* varies between the limits of 0 and –1.

In the present study, for the purpose of characterising the propellant, the minus sign of *m* has been excluded and it is reported in percentage. The pseudoplasticity index and viscosity index calculated as above are collected in Table 1. It is observed that the pseudoplasticity index of propellant slurry at 40 ºC and 45 ºC decreases whereas, the PI of slurry maintained at 50 ºC and 60 ºC are found to increase

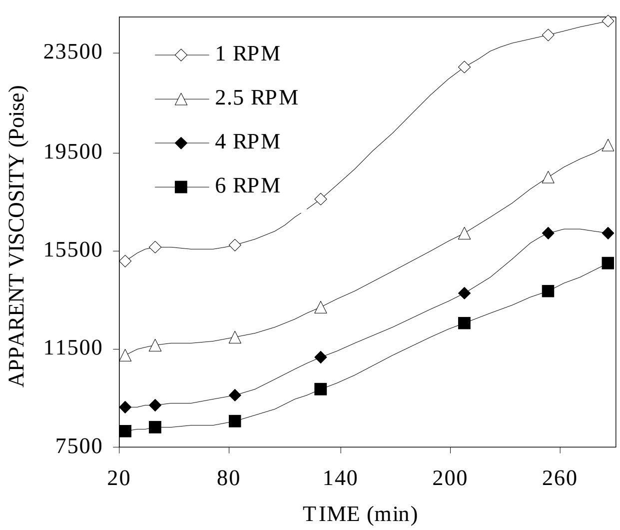

Figure 1. Viscosity as a function of time at various shear rates for sample maintained at 40 °C.

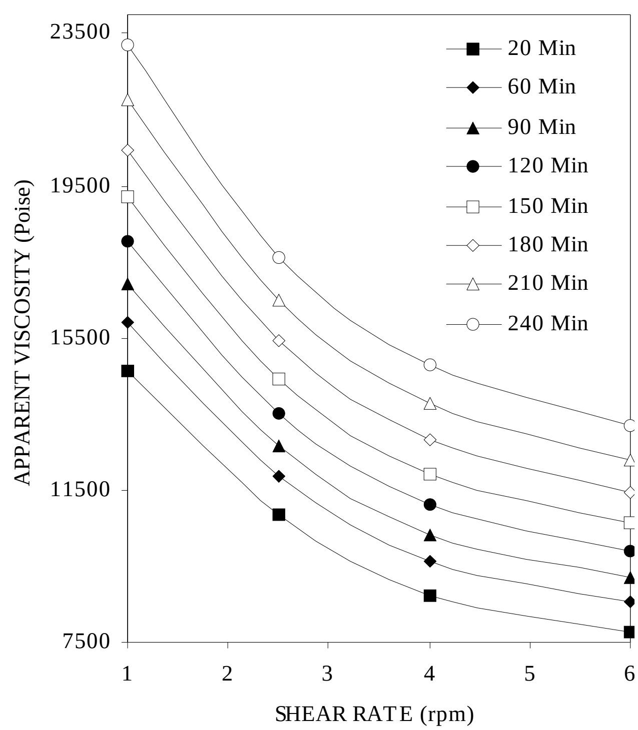

Figure 2. Viscosity (at various time intervals) versus shear rate (rpm) for slurry maintained at 40 ºC.

Table 1. Pseudoplasticity index (%) and viscosity index (Poise) of propellant paste maintained at different temperature on aging

Aging (Min)	Pseudoplasticity index (PI) / viscosity index (VI)			
	40 ºC	45 ºC	50 ºC	60 ºC
20	35.84/14703	33.18/11177	28.9/9102	23.05/5702
60	35.1/15983	32.5/12576	30.08/10757	26.81/7826
90	34.55/17015	31.98/13739	30.96/12193	29.64/9923
120	33.99/18114	31.46/15009	31.84/13820	32.46/12582
150	33.44/19284	30.94/16398	32.72/15664	35.29/15954
180	32.89/20529	30.43/17914	33.6/17754	38.11/20229
210	32.33/21855	29.91/19571	34.48/20123	40.94/25649
240	31.78/23267	29.39/21381	35.36/22809	43.76/32522

on aging. This observation indicates that the slurry maintained at lower temperature approaches Newtonian character on aging whereas the slurry at higher temperature behaves more non-Newtonian character.

However, the viscosity index of the propellant slurry is seen to increase on aging irrespective of the temperature. The increase in viscosity can be attributed to the curing reaction, and hence, the network build-up in the propellant slurry. Again, the lower viscosity index observed for samples maintained at higher temperature compared to sample at lower temperature is obvious. The increase of viscosity with ageing is attributed to the increase in cross-linking resulted due to the curing reaction and the rate of curing increases as the temperature of the slurry increases.

3.2 Effect of Temperature on Curing Reaction ($d\eta/dt$) and Pseudoplasticity Index

The change of viscosity as a function of propellant age is shown in Fig. 3. The viscosity build-up profile of the slurry maintained at various temperatures indicate that though the initial viscosity is less for sample at a relatively higher temperature, it increases at a faster rate on aging.

From the above plot, the rate of viscosity build-up e.g. $d\eta/dt$ was calculated and plotted against apparent viscosities. This is shown in Fig. 4. Since the rate of viscosity build-up depends on the extent of the cure reaction taken place at time t, it could be regarded as a measure of the concentration of the species responsible for the cure reaction at the corresponding time[14-16]. The linearity of the plots shows that the reaction follows a first-order kinetics and the slope of the lines can be considered as the measure of rate constant (k). The ratio of the rate constants of a reaction at two temperatures that differs by 10 ºC is known as temperature coefficient of the reaction[17]. The temperature coefficient of this cure reaction is calculated and found to be equal to 2, which shows that the rate of cure is almost doubled by increasing the temperature by

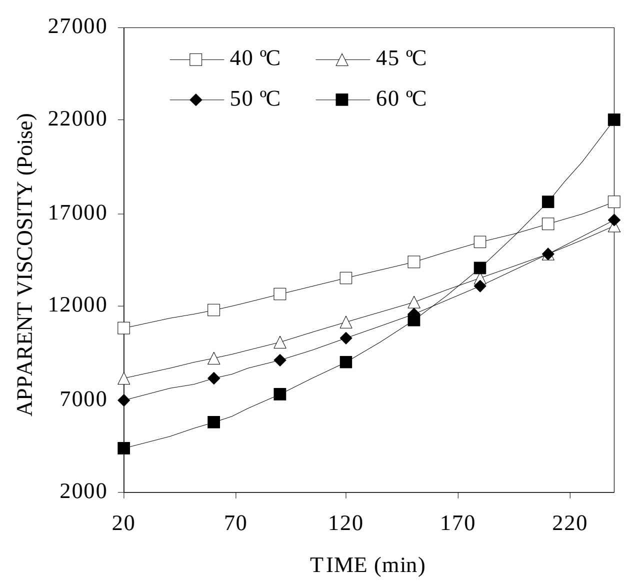

Figure 3. Viscosity build-up of propellant paste on aging at various temperatures.

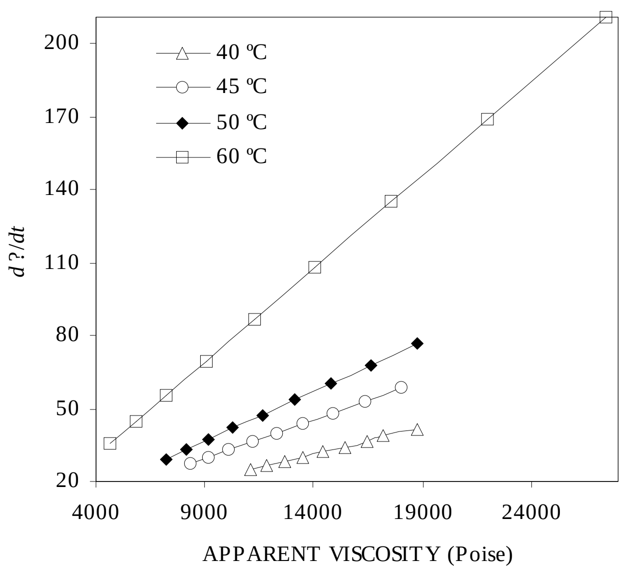

Figure 4. Rate of curing of propellant paste maintained at different temperatures.

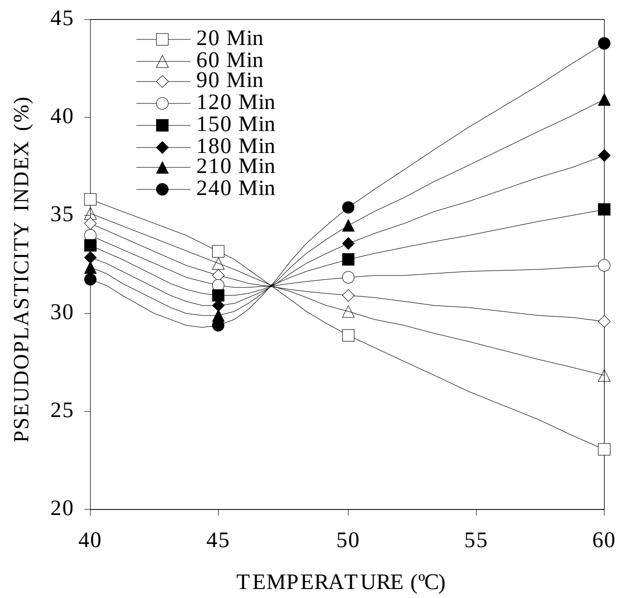

Figure 5. Pseudoplasticity index as a function of temperature at various time intervals.

10 ºC. This observation indicates that there is a predominant effect of temperature on the curing reaction and thereby suggests that the processing of the propellant slurry needs to be carried out at an optimum temperature so that better control over the critical parameters, viz., viscosity build-up, pseudoplasticity index, viscosity index can be achieved. Also, P. Chandrasekharan1[11], in his report has stressed that for good processibity as well as for achieving a quality propellant grain, the slurry should have minimum viscosity, minimum viscosity index and pseudoplasticity index. The slurry must be cast into the mould before the cure reaction has progressed to a point where good casting is not possible.

Figure 5 plots the variation of pseudoplasticity index with temperature. It can be seen from the figure that for samples aged up to 120 min and above, there is a decrease in pseudoplasticity index with increase in temperature up to 47 ºC and increases thereafter with further increase in temperature. However, for samples aged up to 90 min show always a decreasing trend of pseudoplasticity index with increase in temperature. Also, it is observed that all these curves cross at one point which correspond to pseudoplasticity index of 31 per cent and temperature 47 ºC. Therefore, it can be assumed that the slurry maintained at 47 ± 1 ºC gives consistent pseudoplasticity index and casting at this temperature would result a better quality of the propellant grain.

3.3 Determination of Casting Rate

The casting is a very important operation as in this, the propellant flows into all intricate parts of the motor case. Poor flow and filling often leaves voids and other defects causing increase in the burning surface[11]. This will ultimately result in increased chamber pressure and malfunction of the motor.

In a vacuum casting technique, the de-aerated slurry from the mixture bowl is pulled through the feed line into a vacuum chamber by application of vacuum. The slurry flows as a very thin layer and as it travels down gets de-aerated.

The casting rate can be determined using the Haegen-Poisseuille equation modified for non-Newtonian fluid flow[3,18]. The equation is represented as below:

$$D\Delta P/4L = K[\{(3n' + 1)/4n'\}(8V/D)]^{n'} \quad (1)$$

where

ΔP = Pressure drop

V = Flow rate or casting rate

L = Length of the casting pipe

D = Dia of the casting pipe

n' = 1 – (PI/100)

$D\Delta P/4L$= Shear stress at pipe wall

$[(3n+1)/4n](8V/D)$ = Shear rate at pipe wall

On solving Eqn (1) for casting rate, it gives

$$V = [D(D\Delta P/4LK)^{1/n'}]/[2(3n' +1)/n'] \quad (2)$$

In the present study, the casting rate at different temperatures are determined, considering the cast set up with a vacuum of 6 mm *Hg* through a 3.6 m length and 0.15 m dia pipe. The pseudoplasticity index and viscosity index are taken from Table 1 and flow rate of the slurries at various temperatures are calculated for the entire range of aging. The casting rate is reported in kg/min. The calculated values are shown in Table 2. It is observed that with aging of the propellant, there is a decrease in the casting rate. This is obvious as with aging of the slurry, the viscosity increases resulting decrease in flowability, i.e., lowering in casting rate. The same trend is observed for slurry at all the temperatures of the present study. On comparison between slurries at 40 °C to 60 °C, it is observed that the slurry maintained at 60 °C shows relatively higher casting rate up to 120 min, but at the same time, a fast decrease in the casting rate is also noticed. The casting rate in case of 60 °C drops down to 3.82 kg/min after a time interval of 240 min, which is very less as compared to that of 40 °C (9.51 kg/min). From these above observations, it is clear that slurry maintained at higher temperature gets cured fast and resulted in fast decrease in the casting rate and also makes the pot life lesser. These results will certainly guide one to select the correct temperature of casting considering the quantity of the propellant and cast set up.

Table 2. Casting rate of propellant paste at various temperatures and time intervals

Time (min)	Casting rate (kg/min)			
	40 °C	45 °C	50 °C	60 °C
20	17.69	27.60	37.82	70.11
60	15.71	23.28	29.72	46.65
90	14.39	20.53	24.67	33.41
120	13.21	18.15	20.39	23.27
150	12.14	16.07	16.76	15.70
180	11.18	14.25	13.71	10.23
210	10.30	12.66	11.15	6.40
240	9.51	11.27	9.02	3.82

4. CONCLUSIONS

The important conclusions drawn from the present study are:

- The pseudoplasticity index of the propellant slurry maintained between 40-45 °C decreases with increase in pot life, whereas, the slurry maintained between 50-60 °C shows a reverse trend. However, viscosity index increases with increase in pot life irrespective of temperature.
- The effect of temperature on curing reaction is very prominent. The rate of cure is found to be doubled by 10 °C rise in temperature.
- From the plot of pseudoplasticity index versus temperature for different aging of the slurry, it is found that slurry maintained at 47±1°C gives consistent pseudoplasticity index and therefore would result in better quality of the propellant grain.
- The slurry maintained at higher temperature cured fast resulting in fast decrease in the casting rate and also lowers the pot life.
- Depending on the quantity of the propellant mix and a particular cast set-up, one can optimise the casting rate by taking into consideration the effect of temperature and aging on rheological behaviour of propellant slurry.

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