Pseudoplasticity of Propellant Slurry with Varied Aluminium Content for Castability Development

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Abstract. The modification of the percentage of aluminium is necessary to obtain certain specific impulse. But, it affects the pseudoplasticity of propellant in elapsed time that is important in casting. Therefore, this research attempts to investigate the pseudoplasticity of propellant slurry with varied aluminium contents and as time elapsed, the range of percentage of aluminium and time that allows propellant slurry to be well processed. The methods include measuring the viscosity of propellant slurries that contain 6, 8, 10, 12, 14, 16 and 18% of aluminium at varied shear rates until 40 minutes after mixing by using Brookfield viscometer. The graphs of viscosity versus shear rate were made to determine pseudoplasticity index. After that, the graph volume fraction versus pseudoplasticity index were made to be investigated. It is concluded that the more aluminium contents, the slurries with 6 to 12% aluminium contents exhibit more pseudoplastic behaviour, but the slurries with 12 to 16% aluminium exhibit less pseudoplastic. While, slurry of 18% aluminium exhibit high pseudoplasticity. In the correlation with the time, the slurry compositions of 6, 8, 14, 16% aluminium become more pseudoplastic as time elapsed. While, for compositions of 10, 12 and 18% aluminium, the trend becomes contrary. Based on the pseudoplasticity index, propellant slurries that contain 10 and 14% of aluminium are suitable for pressure casting. While for slurries with 6, 8 and 16% of aluminium are also suitable for vacuum casting. All of those suitability are possessed until 40 minutes after mixing. While, the composition of slurries that contain 12 and 18% of aluminium need to be modified to enhanced its castability.

1. Introduction

Composite solid propellant slurry comprises 10 – 15% of liquid contents and 85 – 90% of solid contents. The liquid contents that form binder for propellant, involve polyol such as Hydroxy Terminated Polybutadiene (HTPB) and curing agent such as Toluene diisocyanate (TDI). Beside those, plasticizer such as Dioctyl adipate (DOA) is usually enhanced. While, solid contents of propellant involve aluminium (Al) powder as metal fuel, and ammonium perchlorate (AP) as inorganic oxidator. Modification of solid contents that comprises the percentage, shape, size and kind of solid contents, are developed to obtain certain burning rate and specific impulse (Isp). For aluminium, modification of its percentage is usually done. According to Tuzun (2005), the optimum specific impulse can be reached with 18% of aluminium powder in propellant composition [1]. Any modification potentially affects the rheological properties of propellant slurry [2], [3], [4].

Rheology is the study of the deformation and flow of matter. It clarifies how a matter flows in different shear, temperature and time. The flowability of the matter is measured as viscosity ($\eta$). In propellant slurry, solid contents are adsorbed on specific areas of binder. Therefore, the viscosity of interstitial liquid ($\eta_0$), volume fraction ($\phi$) and maximum volume fraction of solid contents ($\phi_m$) affect
the viscosity of propellant slurry, as shown in equation 1. While, volume fraction of solid contents can be determined by using equation 2 which \( w \) is weight fraction and \( \rho \) is density [5][6][7]. Concerning those equations, the modification of aluminium percentage with constant percentage of solid contents automatically deducts AP percentage, changes the value of volume fraction as well as maximum volume fraction, affects the viscosity of propellant slurry. The change in viscosity also happen as long as the elapsed time after the addition of curing agent. It is because of polymerization of liquid contents that forms propellant binder. As the viscosity of liquid contents increase, the effect of the percentage of aluminium in the viscosity of slurry propellant also change [8].

\[
\eta = \eta_0 \cdot \left[1 - (\phi/\phi_m)\right]^2 \tag{1}
\]

\[
\phi = \{(w_{Al} : \rho_{Al}) + (w_{AP} : \rho_{AP})\} : \{(w_{Al} : \rho_{Al}) + (w_{AP} : \rho_{AP}) + (1 - w_{Al} - w_{AP})\} \tag{2}
\]

The change in viscosity affects the change in flow behaviour. As a high concentration suspension, propellant slurry is discovered possesses Non-Newtonian behaviour. Its viscosity depends on shear rate conducted on it. Based on previous studies, propellant’s slurry is pseudoplastic or shear thinning. Its viscosity declining in increasing shear rate. This property follows equation 3 and 4. In equation 3, the correlation between shear stress (\( \tau \)) and shear rate (\( \gamma \)) is affected by pseudoplasticity index (\( n \)). This index also affects the correlation between viscosity and shear rate in equation 4, as well as index of consistency (\( K \)). Index of pseudoplasticity clarifies the degree of pseudoplastic behaviour. Propellant slurry that possesses index value of which closer to 1 indicates behaviour that approaching Newtonian. By arranging the graph of \( \eta \) vs \( \gamma \), the value of \( n - 1 \) can be found as \( m \). By using equation 5, the value of \( n \) can be calculated. According to Dombe et al (2008), slurry of composite propellants usually have \( n \) of 0.6 – 1. [9], [3], [10]

\[
\tau = \tau_0 + \eta \cdot (\gamma)^n \tag{3}
\]

\[
\eta = K \cdot (\gamma)^{n-1} \tag{4}
\]

\[
n = m + 1 \tag{5}
\]

Pseudoplasticity plays important roles in mixing and casting of propellant slurry. In mixing, the viscosity of slurry around an impeller changes with increase of speed. It potentially leads to the formation of a zone of intense motion around the impeller (cavern) with essentially stagnant regions elsewhere (dead zone) [11], [12]. Therefore, pseudoplasticity become the basic reason of determining some mixing parameters such as impeller geometry, numbers of impellers, mixing time, impeller speed, type and maximum power of mixer. The optimization of those parameters leads to a better mixing performance [13], [14], [15], [16], [17].

In casting process, pseudoplasticity plays important roles in the success of the flow of propellant slurry into the intricate parts of rocket motor. Good flow in casting process is desired to avoid the forming of voids and other defects. It is because those defects can increase the burning surface and lead to abrupt increase in motor pressure and malfunctioning of motor. In order to be suitable with pseudoplastic behaviour of the propellant slurry, various casting technologies such as vacuum casting and pressure casting have been developed. Vacuum casting is reported to be suit with slurry that has pseudoplasticity index of 0.8 – 1. While, pressure casting is suitable for slurry with pseudoplasticity index of 0.6 - 1 [10][18]. Therefore, developing knowledges of pseudoplasticity of propellant slurry with the changes in percentage of aluminium is crucial.
Based on pseudoplasticity index, Muthiah et al (1992) reported that propellant slurries with 5 – 10% of aluminium have the best processibility until 6 hours after mixing. This research involves aluminium of 10 – 12 microns. Based on Prangili et al (2006), different size of aluminium results different viscosity in propellant slurry, the range that is mentioned by Muthiah et al can be different with the different size of aluminium [8], [19].

This research attempts to investigate the pseudoplasticity of propellant slurry with varied aluminium contents and as time elapsed, the range of percentage of aluminium with 30 micron in size and time that allows propellant slurry to be well casted. Those ranges are benefit in determining propellant composition with certain percentage of aluminium in order to reach certain specific impulse.

2. Method

Materials that were used in this research include HTPB, TDI, DOA, AP and Al manufactured by Dalian Chlorate Ltd. The compositions by weight include HTPB, DOA, Al, TDI, and AP. The composition of AP was coarse AP (200 microns) : fine AP (50 microns) is 1:1.

Propellant slurries were made by mixing HTPB, DOA, Al, fine AP and coarse AP for 95 minutes at 60 rpm in horizontal blade mixer. After that, TDI was added into the mixer and mixed well until 20 minutes. The mixing processes were conducted in 46 – 50 °C. The viscosity of the slurries were measured by using Viscometer Brookfield RVT spindle 07 with variation of rotational speed of 0,5; 1; 1,5; 2 rpm. The shear rate was determined by using equation 8. Equation 8 was derived from equation 6. In equation 6, N is rotational speed (rpm), R is radius of container (2.25 cm), Rb is radius of spindle (0,16 cm) and x is radius at which shear rate was being calculated (cm). As viscosity of pseudoplastic slurry is very sensitive toward shear rate, so the calculation was adjusted at x = Rb and equation 7 was obtained. With the substituions of the values of Ra and Rb, equation 8 was obtained [20][21]. The viscosities were measured at 10, 20, 30 and 40 minutes after the mixing process was finished. The graph of shear rate versus viscosity was made for each composition to get the value of m and index of pseudoplasticity based on equation 5. Volume fraction was calculated by using equation 2 with \( \rho_{AP} \) is 1,95 g/cm³ and \( \rho_{Al} \) is 2,7 g/cm³. The graph of time versus pseudoplasticity index and the graph of the value of volume fraction versus pseudoplasticity index were also made

\[
\gamma = \{2(2\pi/60).N.R_a^2.R_b^2\} : \{x^2 (R_a^2 - R_b^2)\}
\]

\[
\gamma = \{4(4\pi/60).N.R_a^2\} : \{R_a^2 - R_b^2\}
\]

\[
\gamma = N. 0,21
\]

3. Results and Discussions

Table 1. Volume Fraction of Compositions

| No | % Mass Al | % Mass AP | Volume Fraction |
|----|-----------|-----------|-----------------|
| 1  | 60        | 79        | 0,740           |
| 2  | 8         | 77        | 0,739           |
| 3  | 10        | 75        | 0,738           |
| 4  | 12        | 73        | 0,736           |
| 5  | 14        | 71        | 0,735           |
| 6  | 16        | 69        | 0,734           |
| 7  | 18        | 67        | 0,732           |

The increasing of percentages of aluminium deduct AP portion in propellant slurry, so that affect volume fraction and maximum volume fraction of solid contents of propellant slurry as well as its
viscosity. Therefore, the volume fractions were calculated by using equation 2 and its results are shown in Table 1. In table 1, as the percentage of aluminium increase, the percentage of AP and volume fraction decrease. It is because the size of aluminium (30 microns) is smaller than fine AP (50 microns) and coarse AP (200 microns).

In propellant slurry, after mixing, as time elapsed, polimerization reaction between hydroxyl groups of HTPB and isocyanate groups of TDI occurs and leads to form binder for solid contents as well as increase the viscosity of propellant slurry [22]. To investigate the effect of increasing viscosity on pseudoplasticity index, viscosity of propellant slurry is measured at 10, 20, 30, 40 minutes after mixing at various shear rates below 1 s\(^{-1}\). The measurements were limited only until 40 minutes because the longest duration of casting process that is desired is 40 minutes. While, the use of shear rates that are below 1 s\(^{-1}\) is to represent gravity casting that is usually used [18]. The datas from those measurements are plotted on the graph of shear rate versus viscosity. Those graphs are shown on Figure 1.

![Graphs showing shear rate versus viscosity](image)

**Figure 1.** The graph of shear rate versus viscosity of propellant slurry at 10 minutes (a), 20 minutes (b), 30 minutes (c) and 40 minutes (d).

It is shown on figure 1 that the viscosity of all propellant slurry composition decrease as shear rate increase. It exhibits pseudoplastic behaviour. This behaviour is caused by molecular structure of the binder and packing density of the filler. Binder that is used is polyurethane that is the result from the reaction between HTPB and TDI [23]. While, based on the packing density of the filler, various parameters such as particle size, interactions between particles, and interactions between particles and
suspending fluid play important roles [24][25]. The percentage of solid contents that are used in this research is 85% of which reported exhibits pseudoplasticity [8]. With the increase in aluminium content, the effects of those mentioned above are vary and to more understanding those effects on pseudoplasticity of slurry, the graph of volume fraction vs pseudoplasticity index is made, as shown in figure 2.

Figure 2. Pseudoplasticity Index of Each Composition.

In figure 2, propellant slurries with volume fraction of 0.736 – 0.74 (6 - 12% Al) shows that with the increase of aluminium content, propellant slurry become more pseudoplastic. In figure 1, as the aluminium content increase, the viscosity of propellant slurry also increase. To explain this trend, the effect of particle size of aluminium become significant. The size of aluminium that is used is 30 microns which almost equals to 0.155 times the size of largest particle used (coarse AP (200 microns)). That size of aluminium is reported thread throughout the binder effectively [8]. With small content of aluminium (6 and 8%), ability of aluminium flow along with the binder, when the shear conducted on it, is represented by pseudoplasticity index that close to 1 which are 0.8 – 0.9 and low viscosity. As the amount of aluminium increase, until 12%, the interaction among aluminium particles increase, forming flocs. The flocs inhibit the flow of propellant slurry so that the viscosity also increase as shown in figure 1. As the shear rate increase, the flocs break down so that the viscosity become lower and the slurry become more pseudoplastic [26]. It is shown clearly in figure 2 that the pseudoplasticity index decrease until 0.3 – 0.5 (12% of aluminium).

For propellant slurry of which volume fraction of 0.734 – 0.736 (12 – 16%), the trend that is mentioned above become contrary of which with the increase of aluminium content, the viscosity decrease as shown in figure 1 and slurry become less pseudoplastic. It is shown in figure 2 that pseudoplasticity index increase from 0.3 – 0.5 (12% of aluminium) until 0.8 – 0.9 (16% of aluminium). This trend shows the trend in reaching optimum packing network. In ideal packing network, the particles with different size are packed, filling the voids such that voids are minimum so that the viscosity become lower and less pseudoplastic [27][25].

Propellant slurry with 18% of aluminium (volume fraction of 0,732) has higher viscosity and more pseudoplastic than propellant slurry with 16% of aluminium. It can be caused by the agglomeration of aluminium. Agglomeration increases the viscosity because the binder entrapped between agglomerated particles so the binder hard to flow. De-agglomeration happens when shear rate increase and it causes the lower viscosity [28].

An agglomerate is formed as a combination of many small flocs. The amount of small flocs as well as viscosity of the binder causes different flow behaviour in elapsed time. The more time elapsed, the more molecular weight of polimeric binder, the more viscous binder, the more viscous the slurry, the larger flocs that are formed, the more pseudoplastic the slurry [29],[22],[26]. This trend is shown significantly from the measurement of 10 minutes to 20 minutes. It can because of the reactivity of 2,4-TDI is higher than 2,6-TDI [23]. As shown in figure 2, this trend happens to the slurry with low aluminium content (6 and 8% aluminium) and the slurry with optimal packing network (14 and 16%
aluminium). While, for 10, 12 and 18% of aluminium, as time elapsed, the slurry become less pseudoplastic. It because, many aluminium flocs that can not be broken down by the shear rates that are used.

Based on the pseudoplasticity index and criterias that reported by Dombé et al (2008) [10], propellant slurries that contain 6, 8 and 16% of aluminium are suitable for vacuum and pressure casting because its pseudoplasticity indexes are in range of 0.8 – 1. The slurries that contain 10 and 14% of aluminium are suitable for pressure casting only because its pseudoplasticity indexes are in range of 0.6 – 0.8. While, the composition of slurries that contain 12 and 18% of aluminium need to be modified to be suitable for casting.

4. Conclusions
The pseudoplasticity of propellant slurry with varied aluminium contents and as time elapsed have been investigated. Size of aluminium, packing network, agglomeration and flocculation of aluminium as well as the rising viscosity of the binder become complicated reasons. For compositions of 6 to 12% aluminium contents, the more aluminium contents, the higher the viscosity and the more pseudoplastic the propellant slurry. For compositions of 12 to 16% aluminium contents, the more aluminium contents, the lower the viscosity and the less pseudoplastic the slurry. While, the slurry of 18% aluminium possess high viscosity and pseudoplasticity. In the correlation with the time, the slurry compositions of 6, 8, 14, 16% aluminium become more pseudoplastic as time elapsed. While, for compositions of 10, 12 and 18% aluminium, the trend becomes contrary. Based on the pseudoplasticity index, propellant slurries that contain 6, 8 and 16% of aluminium are suitable for vacuum and pressure casting. The slurries that contain 10 and 14% of aluminium are suitable for pressure casting. All of those suitability are possesed until 40 minutes after mixing. While, the composition of slurries that contain 12 and 18% of aluminium need to be modified to enhanced its castability.

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