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Size and Shape of Ammonium Perchlorate and their Influence on Properties of Composite Propellant

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ABSTRACT

Most of the composite propellant compositions contain solid loading up to 86 per cent. The main solid ingredients of composite propellant are ammonium perchlorate (AP) and aluminium powder. Therefore, it is a must to characterise these to improve processibility and quality of composite propellant. Effect of particle size on propellants slurry viscosity and ballistic parameters are well documented, however, the effect of oxidizer particle shape is not reported. In the present study, different methods for size and shape characterisation are discussed and effect of size and shape of AP on composite propellant properties are studied. The data indicate that as size of AP decreases, propellant slurry viscosity increases and burn rate increases. The particles having higher shape factor provides less endof mix (EOM) viscosity of propellant slurry and burn rate. Further, effect of size of ground AP on shape is also investigated. From the data thus obtained, it is inferred that as size of ground AP decreases, shape factor decreases, and particles become more irregular in shape.

Keywords: Ammonium perchlorate, average particle size, particle shape, composite propellant, shape factor

1. INTRODUCTION

Composite propellants (CPs) are the most important class of solid rocket propellants. Basically, a composite propellant contains an oxidiser mainly ammonium perchlorate (AP) (60-80 %), a binder such as hydroxy terminated polybutadiene (HTPB) (10-15 %) and metallic fuel like aluminum powder (15-20 %)[1]. The rheological and visco-elastic properties of propellants are mostly governed by the nature of solid ingredients, their size and shape, and also on binder part used[2]. However, burn rate of propellant is considered to be the single most important property governing the ballistic performance of solid motor, which in turn depends mostly upon particle characteristics of oxidiser, burn rate catalyst, and metal fuel[3-6]. Among the three factors, more contributory factors are considered to arise from oxidiser AP and that is mainly from ground oxidiser. Further, the finer particles in ground oxidiser greatly influence the burn rate of the propellant than coarser one in ground oxidiser[7-8].

Further, ballistic properties are also affected by particle shape. If particles of oblong shape are mixed in a propellant to a maximum packing level, it is quite likely that the particles develop some sort of preferred direction of alignment in packets of propellant block. This would give rise to different burning rates along different directions of flame propagation[9].The volume packing of filler particles directly determines mechanical and rheological properties of the propellant. The ideal packing network assumes the fine AP particles occupying the void spaces in the coarse AP packing network; in turn the AP particles thread their way in between the voids created by fine AP packing. This results in better packing network leading to lowering viscosity and improved mechanical properties. In continuation of this work, many researchers have also studied[10-12] the effect of particle size in composite propellant formulations and their findings also indicate better solid loading, lower viscosity, and better packing as well as change in ballistic properties.

The lowering in the viscosity is mainly governed by size and shape of particles. As the particles become more spherical, packing efficiency increases, which is responsible for lowering the viscosity. Thus, by selecting suitable size, shape, and proportion of solid ingredients, it is possible to increase solid loading of the propellant compositions. The increase in solid loading gives better performance of rocket motor. Keeping in mind the advantages of size, shape, and proportion of solid ingredients, a systematic study was carried out to characterise AP particles of two different sources.

2. EXPERIMENTAL

2.1 Materials

Ammonium perchlorate (AP), procured from Ammonium Perchlorate Experimental Plant (APEP), Alwaye and Pandian Chemicals Ltd (PCL), Cuddalore was used in bimodal distribution having particle size 300 μm and 60 μm. Hydroxyl-terminated polybutadiene (HTPB) having number average molecular weight (Mn) 2300-2900 was procured from Anabond Pvt Ltd, Chennai. Aluminium powder having average particle size 15 $\pm$ 3 μm was procured from MEPCO, Madurai, and

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used as such. Other ingredients, such as dioctyl adipate (DOA), toluene diisocyanate (TDI), β-phenyl naphthylamine (Nonox-D), tri-methylol propane (TMP) and 1,4- butanediol (n-BD) used as plasticiser, curative, antioxidant, cross-linker and chain extender, respectively, were also procured from trade and used as such.

2.2 Characterisation

2.2.1 Importance of Particle Size and Shape on Characteristion

The particles of coarse AP procured from trade do not have consistent size and shape. Therefore, before using it in a composite propellant composition, it is essential to determine their size and shape.

2.2.2 Role of Particle Size Measurement

The particle size measurement is of two types, i.e., primary measurement and secondary measurement. Primary measurements are direct, as carried out by microscopy while secondary measurement are derived from the effects of some well studied physical phenomenon like settling, diffraction, or permeatry[13]. As a result, against the plethora of measurement techniques, there exists a different figure of particle sizes such as martin, feret, surface, stokes, sieve diameters, etc. Other factors to be borne in mind before measurement include the end-use of powder, sensitivity of the analyser for the particle size envisaged. The industrial powders with large polydispersity cannot be adequately described by average particle size alone but distribution of various constituent fractions. Three standard distributions, namely Normal, Log-Normal and Rosin-Rammler-Bennett were used to simulate the size distribution of powders, and thus provide an accumulated view of particle size measurements[14].

Conventionally, the particle size of AP is determined using sieve analysis. However, by sieving, it is not possible to characterise powders below 40 µm. Moreover, conventional methods are also handicapped by being manual in nature, and hence prone to human error. So, the focus of particle characterisation was shifted from the usual time-consuming and less-accurate conventional methods to the laser-based techniques.

2.2.3 Role of Particle Shape Measurement

The need nowadays is not only for the measurement of size and size distribution, but also for the measurement of shape and shape distributions. Particle shape is a fundamental powder property affecting powder packing, and thus bulk density, porosity, permeability, cohesion, flow ability, caking behaviour, attrition, interaction with fluids, etc.

The shape of particle can be measured using dynamic shape analyzer. There exist shape parameters[15-17] like roundness, chunkiness, irregularity, compactness, statistical shape indices, fourier coefficients, fractal dimensions, aspect ratio, etc. However, the most important shape parameter is shape factor obtained by digital dynamic shape analyzer, which is based on image analysis technique. The shape factor is defined as follows:

$$\text{Shape factor} = 4\pi A/P^2$$

where, A is the projected area of the particle, P is the perimeter of the projected particle area (for perfect spherical particle Shape factor =1).

Based on size and shape measurement techniques, the solid powder ingredients were analysed and used in composite propellant formulations. The particle sizes of solid ingredients were determined by laser-based particle size analyzer CILAS, France, model- 1064, in non-aqueous medium. Shape factor of AP was determined by Dynamic Shape Analyzer, DSA-10 of Ankersmid make.

2.2.4 Characterisation of Propellant

The viscosity of propellant slurry was measured using Brookfield viscometer, model HBT dial type. The mechanical properties like tensile strength, per cent elongation and E- modulus of cured propellant samples were evaluated using dumbbells on tensile testing machine, Hounsfield conforming to ASTM D638 at a cross head speed of 50 mm/min at ambient temperature. Solid strand burn rate (SSBR) was measured using acoustic emission technique in nitrogen atmosphere.

2.3 Procedure

All the experimental mixes of composite propellants were carried out at 15 kg batch level in vertical mixer. In mixing of ingredients, first liquid ingredients(except curative) were charged and mixed well for half-an-hour followed by vacuum mixing for another half-an-hour to drive out entrapped air. After this, aluminium powder and AP were added one by one. After addition of complete solid portion, mixing was done under vacuum for half-an-hour. In the mean time, temperature of mix was brought to 37±3 °C and TDI was added and further mixing is done for half-an-hour. Then, slurry was cast into 100 mm ID mould and cured at 50 °C for five days. The cured propellant was used for determination of various propellant properties.

3. RESULTS & DISCUSSION

3.1 Effect of Particle Size of AP on Slurry Viscosity and Burn Rate

Different experiments were carried out using APEP and PCL AP in bimodal form by varying coarse-to-fine ratio, or changing average particle size of AP. The prepared compositions containing 86 per cent solids were analysed for end of mix (EOM) viscosity. The value of propellant slurry viscosity on changing the average particle size of AP is shown in Fig. 1. The variation of viscosity with change in average particle size can be expressed in the form of following equations.

$$\text{EOM (APEP)} = 0.5503P^2 - 222.26P + 28913$$

$$\text{EOM (PCL)} = 0.5942P^2 - 234.01P + 28184.$$

where, particle size (P) is in µ.

It is clear from the figure that as the average particle size of the AP decreases, the EOM viscosity increases.

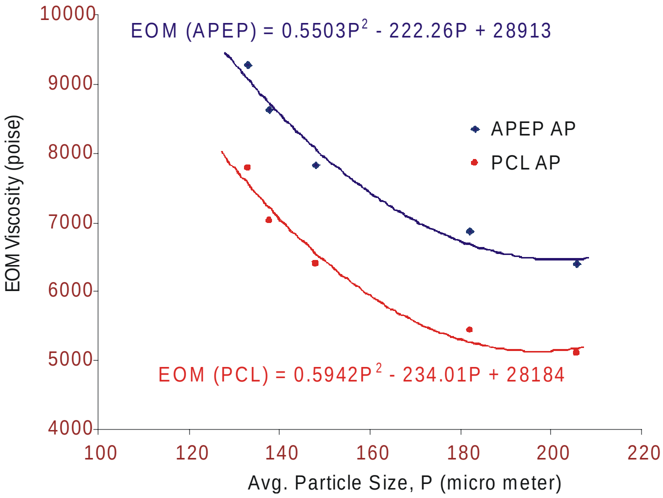

Figure 1. Effect of particle size of AP on viscosity of propellant slurry.

This is due to the fact that as size decreases, surface area of the AP particles increases. Thus, less binder (liquid) is available for wetting of the powder. Hence, slurry viscosity increases. Moreover, the decrease in viscosity is more prominent in case of PCL AP as explained under effect of shape on propellant properties

In the same way, effect of particle size of AP of both sources on burn rate was studied and results are shown in Fig. 2. The variation of burn rate with change in average particle size can be expressed in the form of following equations

$$\text{BR (PCL)} = 878.19\ P^{-0.8646}$$

$$\text{BR (APEP)} = 452.31\ P^{-0.722}$$

where, P is the particle size in μ, and BR is the burn rate in mm/s.

The figure reveals that as the average particle size of AP decreases, burn rate increases. It is due to increase in the surface area of the AP particles. Since burning is a surface phenomenon, as surface area increases, burn rate also increases. The decrease in burn rate is more prominent in case of PCL AP as elaborated under effect of shape on propellant properties.

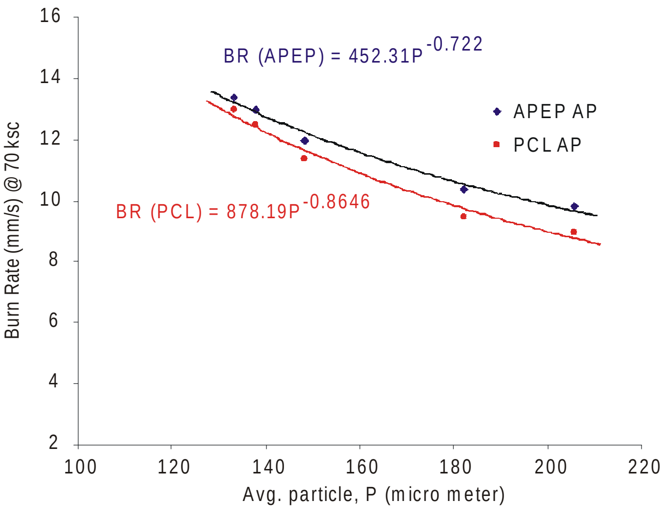

Figure 2. Effect of particle size of AP on Burn rate of propellant compositions.

3.2 Effect of Particle Shape of AP on Propellant Properties

APEP and PCL AP particles were analysed for particle shape using (DSA)-10 of Ankersmid make. Around 5000 particles of both PCL and APEP were measured using free-fall cell of the system. The resultant shape factor graphs for PCL and APEP are shown in Figs 3 and 4, respectively.

It is clear from these figures that the mean shape factor for PCL AP is 0.8767, whereas the shape factor for APEP AP is 0.7843. Thus, it is clear from the data that particles of PCL AP are more spherical than particles of APEP AP. The images of PCL and APEP AP were also taken using DSA and are presented in Figs 5and 6, respectively.

It is clear from the figures that AP particles of PCL make are more round (spherical) than APEP particles which is responsible for lowering in viscosity as well as burn rate.

To study further, particle size distribution of PCL and APEP APe were also determined using British Standard Sieves (B.S.S.). The resultant distributions are given in Table 1.

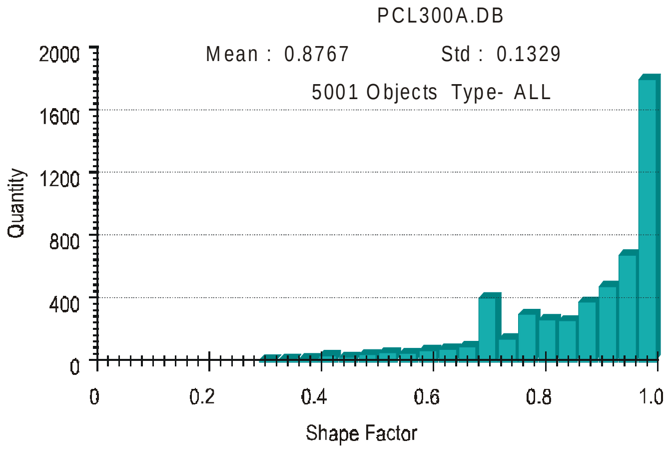

Figure 3. Shape factor distribution of PCL AP.

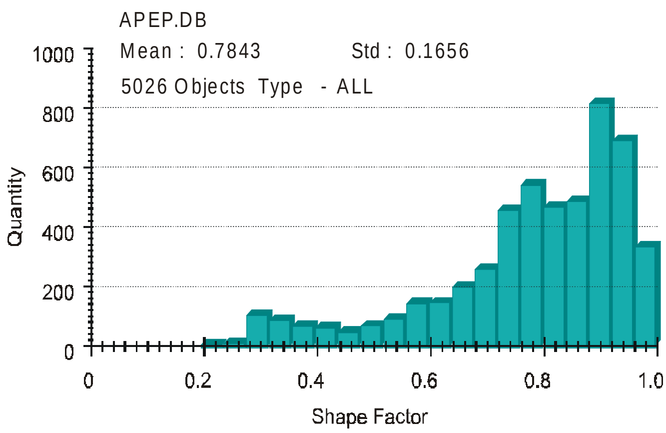

Figure 4. Shape factor distribution of APEP AP.

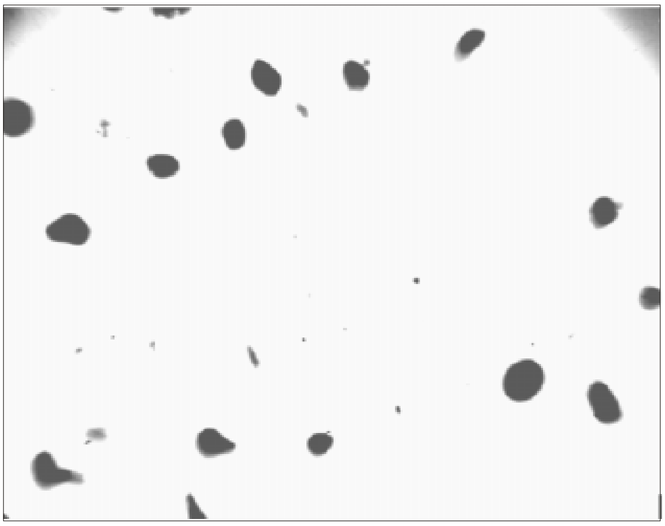

Figure 5. Photograph of PCL AP on dynamic shape analyser.

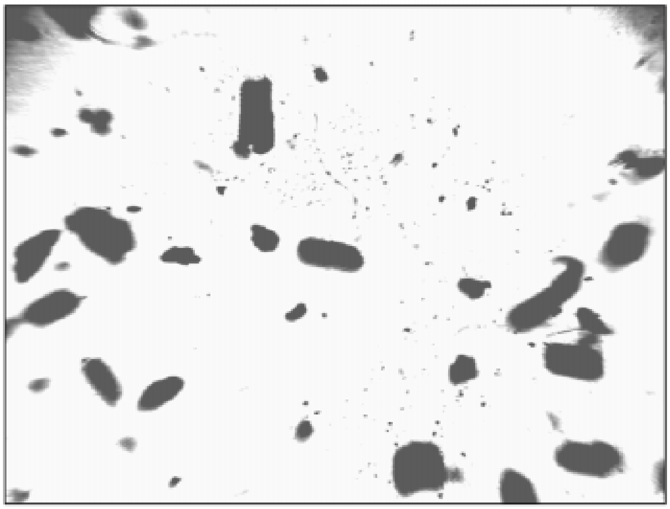

Figure 6. Photograph of APEP AP on dynamic shape analyzer.

It is clear from the table that the average particle size and size distributions of PCL and APEP AP are more or less the same.

Based on size and shape analyses data, to have the actual effect of these values on propellant properties, APEP and PCL make AP were used in propellant compositions as per the method described earlier. The resultant propellant properties are shown in Table 2.

The data reveal that due to more spherical nature of particles of PCL AP, EOM viscosity of propellant slurry was less compared to APEP AP. However, propellant compositions having PCL AP gave less burn rate compared to propellant compositions containing APEP AP. This is due to the fact that burn rate is affected by surface area of AP particles. As the shape factor of particles increases, the particles become more spherical. Thus, surface area of particles decreases. The decrease in surface area is responsible for decrease in burn rate of propellant which is shown by PCL AP as it has less surface area. The difference in mechanical properties is not significant for the studied compositions having same percentage of HTPB binder.

3.3 Effect of Grinding on Particle Shape of AP

In continuation to this work, AP of APEP having average particle size 300 µm was ground using a fully assembled REICO ACM-10 grinding mill. The mill parameters were set to get particles having average size of 35 µm, 50 µm, 60 µm, 70 µm, and 80 µm as measured by CILAS particle size analyser. All ground AP powders were analysed for shape using DSA-10. The variation in shape factor with particle size is shown in Fig. 7.

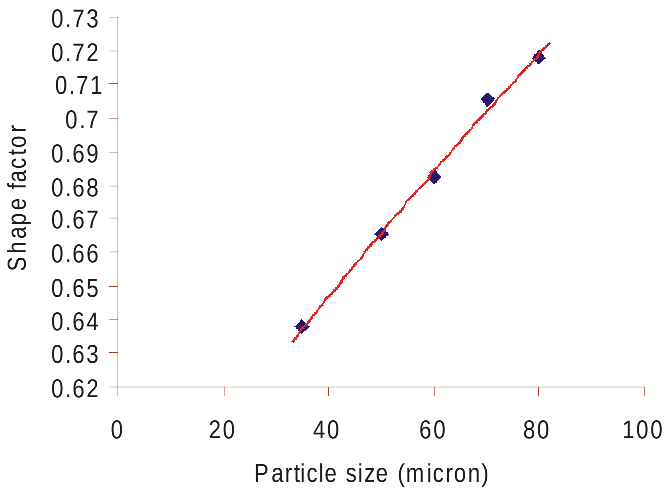

Figure 7. Effect of particle size of ground AP (APEP) on shape factor.

Table 1. Particle size distribution of AP (PCL & APEP)

B.S.S	PCL Ammonium perchlorate per cent	APEP Ammonium perchlorate per cent
+30	1.45	1.0
+44	22.60	24.95
+52	24.80	15.40
+60	37.4	34.45
+85	9.35	16.90
+100	2.35	5.55
-100	2.05	2.20
Average Particle size	313.72 µm	309.72 µm

Table 2. Effect of particle shape of AP on propellant properties

Source of AP	Per cent HTPB	End of Mix Slurry viscosity, poise	E-modulus, ksc	Tensile strength, ksc	Per cent elongation	SSBR mm/s @ 33 ksc
APEP	10.08	8640 at 40 °C	59.9	8.38	38.36	5.00
PCL	10.08	7360 at 40 °C	59.6	7.43	32.31	4.32
APEP	10.09	8320 40 °C	45.47	7.5	41.91	5.01
PCL	10.09	6880 at 40 °C	45.24	6.88	37.96	4.45

The figure reveals that as particle size decreases, shape factor decreases. It indicates that ground particles become more irregular as these become finer. The same findings were also observed using PCL AP during grinding.

4. CONCLUSIONS

Different methods were employed to characterise the size and shape of solid ingredients. AP particles having higher shape factor gives less EOM viscosity of propellant slurry and subsequently less burn rate. Also, the shape factor of AP decreases on subsequent grinding. Thus, characterisation techniques are important in maintaining and improving the quality of finished product in terms of compaction, density, mechanical properties & burn rate and also help in smooth processing of propellant compositions.

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