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ROLE OF FILLER PARTICLE SIZE IN THE FORMULATION OF COMPOSITE SOLID PROPELLANT

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Abstract

Formulation of poly(vinyl chloride), PVC - ammonium perchlorate, AP, composite solid propellant has been accomplished in the light of different compositional variables such as plasticizer composition, particle size of AP and anticaking agent / burn rate accelerators. It has been found that the mixed plasticizer DOP3S1 [containing 75v% DOP, (dioctyl phthalate), and 25v% DOS, (dioctyl sebacate)] is the most suitable plasticizer for PVC resin at least for the present study. The rheological study of PVC – DOP3S1 plastisol shows that the system unequivocally behaves as a pseudoplastic thixotrope at least up to a storage time of 49 hours. The degree of thixotropy, however, shows a decreasing trend beyond this period. The rheological studies on virgin and aluminized propellants have been seen to follow the similar trend. The magnitude of apparent viscosity in the former case is seen to be many fold higher than those of plastisols whereas that of metallized propellants although also higher than plastisols but is found to be less than those of virgin compositions.

The porosity data for unimodal AP as a function of mean particle diameter has been found to vary linearly whereas coarse – fine AP blends show minimum porosity in the range of 30wt% – 33 wt% fine AP content which is substantiated by density and ambient burn rate data.

Introduction

Composite solid propellants are widely used in rocket motors for a variety of applications. PVC – AP propellant system also falls in this category. The plastisol under study is a suspension of fine PVC powder in a suitable plasticizer to which AP and other fillers like stabilizers, processing aids, burning rate modifiers, fine metal powder, etc. are added.

The plasticizers on the basis of their compatibility with PVC have been classified as primary, secondary and extenders^[1, 2]. The Primary or true plasticizers are compatible with PVC in all proportions up to 150 part per 100 part of PVC. Some of them are DBP (dibutyl phthalate), DOP (dioctyl phthalate), DIOP (diisooctyl phthalate), etc. The secondary plasticizers are, however, less compatible. The selection of a suitable plasticizer for polymer depends on properties such as solubility parameter, viscosity – temperature relationship, density, volatility, etc. The square root of cohesive energy, defined as the energy consumed in vapourising one molar volume of a component, known popularly as solubility parameter, can be estimated by the method due to Small^[2, 3].

The selection^[4, 5] of a plasticizer for PVC resin is generally considered in the light of following points: (i) solubility parameter of plasticizer should be equal to that of resin or at least very close to it, (ii) plasticizer should have low viscosity, volatility and freezing point

and high density, boiling point, flash and fire points, and (iii) hydrogen / carbon ratio and positive heat of formation should be as high as possible.

The concentration by volume of particle size distribution, PSD, of filler (AP, metal powder, etc.) are known to considerably affect the formulation and ease of processing of composite solid propellant especially when a high solid loading^[6] is desired which, in turn, is a major controlling factor of burning rate^[7- 11] and mechanical properties of propellants^[12, 13].

Considerable amount of work has been done in the past to understand the effect of filler particle size, PSD, and solid loading level on the rheological behavior of light suspensions and concentrated slurries like that of Einstein and Vand^[14]. Unfortunately, this is of no use to a propellant chemist whose interest is loading higher amounts of solid with a view to increase energy content and density of the system to cut down the hardware weight due to obvious reasons. Sarner^[15] has empirically given the relationship

$$Sv / Lv = (VPS) / (100 - VPS) \quad (1)$$

for propellants where Sv, Lv and VPS refer to volume of solid, liquid and volume per cent of solid respectively. Holzman⁶, however, has reported that the filler particles of sizes 50:5 μm used in 70 : 30 proportion give a pourable propellant mix. Unfortunately, no simple but logical correlation has so far been put forward except those by Kumar and

Gupta^[16, 17]. They have reported that the porosity (P), defined by the relation:

$$P = 1 - (V_p/V_b) \quad (2)$$

where V_p and V_b are the particle and bulk volumes of solid filler respectively obtained during packing studies of bimodal AP, bears direct and inverse relationship with apparent viscosity and density of propellant respectively.

Dallavalle and Gray^[18, 19] have elaborated the problem of packing of powders and the effect of varying particle size, PS, on properties such as bulk density controlling the rheology of suspensions etc.

In general, particles are irregular in shape which may be assumed as spherical in nature having the same volume / surface for the sake of convenience and statistical analysis. The nominal or equivalent diameter, d_n , for a particle of density, ρ , and number, N , per 100 g of material can be given as

$$d_n = (6/\pi \cdot \rho \cdot N)^{1/3} \quad (3)$$

Sometimes, effective diameter, d_e , defined as diameter of a sphere taking same time to fall between two fixed points in a medium is considered. These diameters appear to be more of an academic interest rather than practical utility.

In order to have a correlation of properties of the propellants with the filler particle size, the use of mean, median, and statistical diameter have been advocated from time to time. Unfortunately, none of these have been found to be satisfactory from the propellant viewpoint. It is apprehended that in almost all the laboratories / rocket propellant plants, PSD of filler in terms of coarse / fine ratio is selected having no theoretical / experimental background except that at times it clicks. This involves the wastage of time, labor, and money as the PSD is chosen on the basis of trials only. The formation of lumps or caking of AP during storage especially under humid conditions with fine particles poses another problem.

In the present communication keeping aside the arbitrariness, efforts have been made to throw some light on the selection of filler AP, Al etc. particle size, PSD, search for an anticaking agent especially transition metal compounds in powder or liquid form having potential to function as catalyst to enhance the burning rate of propellants .

Experimental

Propellant Composition

Following two propellant formulations were selected for the present study:

Ingredients	Composition (wt%)	
	A	B
PVC	12.5	15.0
Plasticizer (DOP3S1)	12.5	15.0
Solids (AP+Al+Fe ₂ O ₃)*	75.0	70.0
Tribasic lead sulphate (TBLS)	5 parts per 100 parts of PVC	
Lead stearate (LS)	1 part per 100 parts of PVC	

*The solid filler corresponding to minimum porosity have been used in both propellant formulations.

Selection of Plasticizer

This was accomplished on the basis of properties like solubility parameter, density and viscosity of DOP and DOS in varying proportions. Nevertheless, the final selection was made in the light of properties of cured PVC plastisols. Consequently, the mixed plasticizer having 75% and 25% by volume of DOP and DOS respectively was chosen and designated as DOP3S1.

Particle Size of AP

AP, obtained from VSSC Trivandrum was dried in an electric oven at ~1000 C for 2 - 3 hours and allowed to cool down to ambient temperature slowly in the oven itself for a sufficient time by switching it off. This was then pulverized using explosion proof Micro SH Bantom Pulverizer (NJ, USA). The AP, thus, obtained was segregated by sieves (British standard mesh) to get the so called unimodal powders of sizes 375, 200, 122, 85, 66, 52 and 23 μm respectively. The first was taken as coarse AP. The fine AP, however, was obtained by repulverizing the remaining sizes and was subjected to PSD analysis.

Anticaking Agent

Efforts have been made to search out a suitable powdery material which preferably is a constituent of the propellant formulation itself and thus preventing extra neutral solids loading. Several materials such as colloidal silica (dia.~ 1 – 100nm), LS (dia. < 46 μm) and Fe₂O₃ (dia < 46 μm) were tried. All of them were found to be satisfactory but ultimately ferric oxide was selected as it inherits an added advantage of excellently accelerating the burn rates.

Filler Particle Size Selection

This was based on the study of packing of particles and consequent porosity development. The porosity of unimodal, blended bimodals AP with aluminum powder has been determined using the tapping machine (Prasad Scientific Co., Bombay) at a

tapping frequency of 30 cycles/min and a tapping distance of approximately 1 inch. For each case, three samples of known weights (~35 – 40 g) were taken in 100 mL graduated glass cylinders and tapped till constant volume was obtained. The average volume, thus, obtained gave the bulk volume. The porosity in each case was then calculated using equation (2).

Preparation of PVC – Plastisol

The hot plasticizer, DOP3S1, was poured into the bowl of the water cooled sigma blade vertical mixer (Atlantic Research Corporation, model 60LP, USA) and was allowed to cool down to ambient temperature. PVC, TBLS and LS in requisite amounts were then added and mixed for 15 minutes under vacuum. The mix was then poured in a 500 mL glass beaker which, in turn, was placed in a cylindrical vacuum chamber and evacuated up to -600 mm Hg pressure for 15 minutes with simultaneous vibration (1800 c / min) to drive off the air bubbles trapped, if any. The resulting mix was then subjected to rheological studies.

Rheological Studies

A. Temperature Dependence of Plasticizer Viscosity

This was accomplished with the help of Brookfield viscometer (model LVTD, USA) using constant temperature bath and External Flow through Cooler (model EN-850, Brookfield, USA) at 10^o, 18^o, 25^o, 37^o and 48^o C respectively with the sample size of 16 mL.

B. Effect of Ageing On Plastisol Viscosity

This was studied at a fixed temperature of 37^oC with the same sample but at different storage times.

C. Preparation of Propellant Mix

The plastisol was prepared in the manner discussed above. The coarse AP (PS ~ 350 μm) in required amount was then added to the plastisol in nearly two equal installments followed by mixing for 15 minutes after each addition. Finally, the given amount of fine AP was added and mixed for another half an hour.

D. Rheology of Propellants

The propellant sample in the form of slurry was poured in a 500 mL corning glass beaker and was vibrated under vacuum for 15 min as detailed above. The rheological data of propellant samples at 37^oC were then recorded by the aforesaid viscometer using spindles – LV#4 and #TF as a function of shear rate (rpm).

E. Casting and Curing of Propellant

The propellant mix was cast in flat mild steel mould under vacuum up to a pressure of -660 mm Hg for 15 minutes with simultaneous vibration as discussed earlier. The curing was carried out in an electric oven initially at 100^oC for three hours followed by further heating at 130^oC for three hours and finally for another three hours at 150^oC. The oven was then switched off to allow slowly cooling down of propellant to ambient conditions to avoid thermal stresses.

F. Preparation of Propellant Strands

The flat propellant sheet was cut to the size of 5 mm² cross-section and 10 cm length. Two marks were put exactly 70 mm apart leaving sufficient space at both the extremes after coating the strands from all sides with inhibitor except that at both the ends.

G. Density Measurement

This was carried out by liquid displacement method. The weights of strands were accurately determined. They were then soaked in n-hexane for sufficient time to ensure that no empty space (void) is left in side the strands in order to determine their exact volumes. The strands were then removed and surface dried by filter paper.

H. Burn Rate Measurement

Strands were inhibited twice with inhibitor consisting of suspension of PVC (5 wt%) and TiO₂ (1 wt%) in tetra-hydro furan. They were dried for 2 hours in the open air after each coat. The strands were ignited electrically from the top and the time taken to burn between the marks was recorded with the help of a stop watch having an accuracy of 0.1 second.

Results and Discussion

On the basis of requirement and acceptability of parameters such as cohesive energy density, viscosity, density, volatility, H/C ratio, flash and fire points, etc., the mixed plasticizer DOP3S1 was chosen as the most suitable plasticizer for the present work. Fe₂O₃ was found to be the most effective anticaking agent with an added advantage of its potentiality to boost up the burn rate. Consequently, it was selected to deprive the AP from lump formation.

The data on the variation of porosity of unimodal AP has been found to decrease linearly at least up to a PS of 200 μm while it is seen to be more or less constant beyond this. This may probably be attributed to the shape of particles. This was confirmed by microscopic examination. The particles of diameter > 200 μm have apparently been seen to be cubic whereas the particles of diameter < 200 μm to be spherical. The data on the porosity of unimodal AP of different diameters containing 1 g of Fe₂O₃ per 100 g of

oxidizer are also seen to exhibit similar behavior but with the difference that the rate of decrease of porosity in this case is more pronounced than that observed for AP particles which may be attributed to filling up of the inter-particle space by finer Fe₂O₃ particles.

Following Dallavalle^[17], the median diameter, defined as the diameter for which 50% of the particles are less than the stated size, for coarse and fine AP was obtained from the plot of wt% of particles less than the stated size against particle sizes in **Figure 1**. Graphically, the median diameter values of 350 μm for coarse and 50 μm for fine have been found and used subsequently in further analyses.

The results on the effect of blending of fine AP in the so called unimodal AP particles (dia = 200, 350 and 375 μm) plotted typically in **Figure 2** reflect that with the increase in the fine AP content (containing 1wt% Fe₂O₃) in the bimodal oxidiser, the porosity decreases in all the blends, reaches a minimum value and then again increases. The minimum porosity was found to lie in the range of 30 wt% - 33 wt% of fine AP content which is in excellent agreement with the reported result^[6]. Further, an analysis of data show that minimum porosity, P_m, decreases in all the cases fitting the linear relation

$$P_m = \alpha D + P_m'' \quad (4)$$

where, D is the particle diameter, is the slope of line and P_m'' is the intercept.

The results, on the incorporation of increasing amount of fine Al – powder (diameter ~ 5 – 20 μm) on the variation of porosity of bimodal AP corresponding to minimum value and four neighboring blends (two on each side of minima) containing slightly less and more fine Al have been plotted in **Figure 3**. It is clearly seen that in all the five cases, porosity decreases, reaches to a minimum and again increases. A close look at the data further reveals that the lowest porosity is prominently exhibited by bimodal AP having minimum fine AP content. It is also noticed that the replacement of fine AP by Al – powder effectively brings down the porosity to the level of 25 wt% - 30 wt% leading to a more energetic and denser propellant without penalizing the ease of processing.

The results on the dependence of Newtonian viscosity of plastizers on temperature is found to best fit the Arrhenius equation

$$\ln \eta = \ln A - E_{vis} / RT \quad (5)$$

where η, A, E_{vis}, R and T refer to coefficient of viscosity, pre-exponential or frequency factor, energy of activation for viscous flow, gas constant and absolute temperature respectively. The value of A and E_{vis} has been estimated to be 2.417 x 10⁻¹³ cP and 9.4 kcal mol⁻¹.

The data on the viscosity of PVC plastisol clearly show that

- (i) the system is pseudoplastic (shear thinning) in nature,
- (ii) it also exhibits thixotropic character which increases up to 49 hours of storage at 37 °C beyond which (66 – 128 hours) it decreases, and
- (iii) the apparent viscosity, η_{ap}, increases with storage time.

This is understandable as at storage temperature slow physico-chemical interactions would be taking place. This gets support by the increase in degree of thixotropicity at least up to 49 hours. Beyond this period, loop area of η_{ap} – rpm plot is found to decrease which can be attributed to the increased degree of solubilization of PVC particles in the dispersion medium. Assuming it to follow the first order rate equation^[20], the rate of viscosity build - up can be given

$$d\eta_{ap} / dt = k(1 - u) \quad (6)$$

where k is rate constant and u is the concentration of dispersion medium absorbed by PVC particles at any time t. Eqn. (6) for a small change can be written as

$$\eta_{ap} = k(1 - u) \times t$$

Considering $u \ll 1$, the above equation can be rewritten as

$$\Delta\eta_{ap} = K \times \Delta t \quad (7)$$

where K is a new constant and can be taken as pseudo-rate constant. One can, thus, expect that the plot of Δη_{ap} - values versus Δt should be a straight line passing through origin. This is found to be so in the present case **Figure 4** but preceded by a small induction period in each case probably due to the time required for solvation of PVC particles.

The results, on the rheological studies of PVC – filler (AP + Al) propellant containing 70 wt% of solid corresponding to minimum porosity, show that similar to plastisol the virgin propellant also behaves as a pseudo-plastic thixotrope but registering many fold increase in η_{ap} - values perhaps due to incorporation of non-interacting AP particles coupled with the lesser availability of fluid due to its partial embayment in empty spaces between the particles. The aluminized propellants are also seen to behave in the similar fashion but with considerable decrease in η_{ap} compared to those of virgin propellant mixtures although the total solid loading is the same. This finding is of enormous practical importance from both propellant processing and performance viewpoints. This appears to be quite obvious as the dispersion medium which otherwise

filled in voids becomes available for flow because of occupancy of voids by fine Al – powder. The propellant containing 75 wt% solid is found to follow the similar trend.

The results on porosity, η_{ap} of propellant slurries containing minimum porosity blends [(coarse + fine) AP + Al], density and ambient burn rate clearly suggest that it is the compaction of loaded solids that plays the most vital role in controlling the internal ballistics of rockets beside the facilitated processing. It is seen that increase in porosity of solid filler enhances η_{ap} at all shear rates covered in the present study on account of lesser availability of dispersion medium due to the fact that its considerable amount is used up in filling the empty spaces between the solid particles. This becomes amply clear from the higher density data recorded for propellant formulations with denser solid packing. The burn rate data collected under ambient conditions are also seen to have direct relationship with porosity. In a way it also substantiates that denser (less porous) the propellant slower the burning rate. Actually it has been found to be so in present study. The density data of aluminized propellants are found to be significantly higher than those of virgin compositions. This is as per expectation since low density AP is replaced by highly dense Al-powder. The burn rate recorded at atmospheric pressure and temperature, however, is found to be less for metalized propellants than those of virgin compositions. This is again in accordance with the expectation as oxidizer (AP) concentration is significantly decreased due to aluminization. This may at least partly be due to incomplete combustion of aluminum particles hence lesser heat transfer from the flame zone to the burning surface.

Conclusions

The filler PS and PSD seem to be of immense importance. The blended solid powders blessed with minimum porosity show their worthiness in the ease in propellant processing, giving higher density causing in drastic reduction in hardware weight with higher energetics are expected to be a boon for the personnel working in this field.

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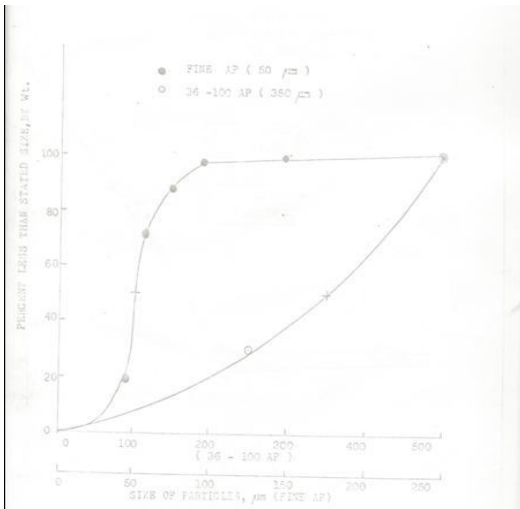


Figure 1

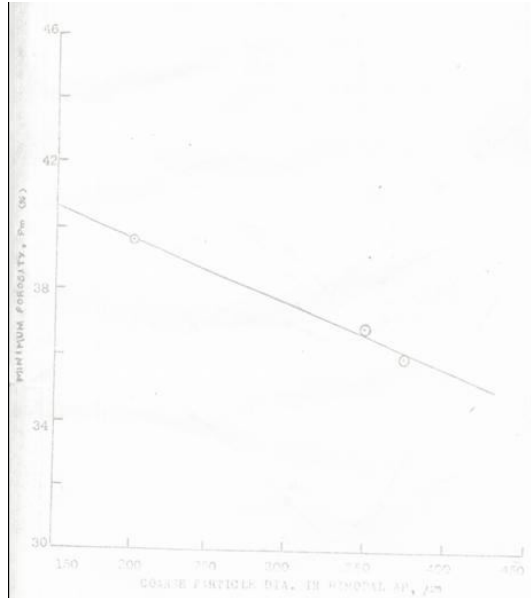


Figure 2

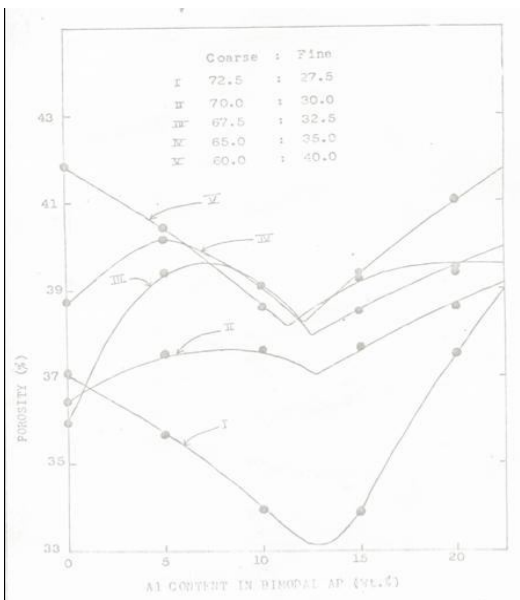


Figure 3

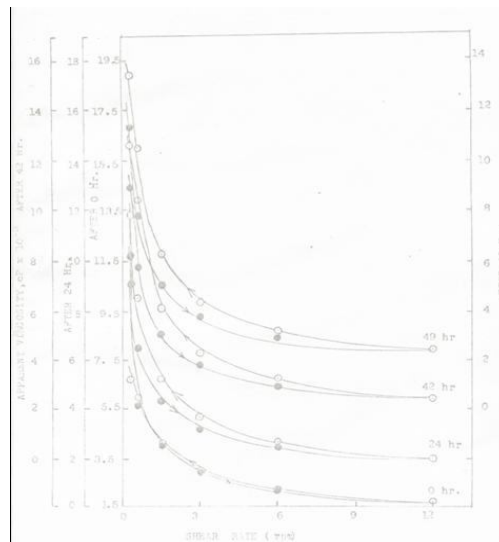


Figure 4