

A method of determining processing behaviour of plastic bounded propellants and explosives

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ABSTRACT

Plastic bounded explosives and composite rocket propellants usually contain a crystalline energetic material embedded in an elastic polymer matrix. It is important to obtain a high solid loading of the crystalline material since it is closely related to the final performance of the product. In order to obtain such a high loading, multimodal particle size fractions are needed. These must be combined in different ways to achieve the lowest possible viscosity. A method based on measuring viscosity at one or several shear rates has been developed to optimize two different particle sizes in a liquid polymer matrix. This method is presented in this paper and some of the difficulties with this method and how these are circumvented are also discussed.

INTRODUCTION

Plastic bonded explosives and composite rocket propellants usually contain a crystalline energetic material embedded in an elastic polymer matrix^{1,2}. The purpose of the polymer matrix, also known as the binder, is to form a solid, elastic body of the crystalline energetic ingredients with sufficient mechanical properties. The binder is also used as a fuel since it contains mainly hydrogen and carbon.

When plastic bonded explosives and composite propellants are manufactured, the solid ingredients are mixed into the liquid

prepolymer. The mixture is then cast in a mold and cured at an elevated temperature. In this way, a solid and elastic explosive or propellant with the desired shape is formed. The viscosity of the uncured formulation, η , must be low enough to allow casting and the pot life must be long to achieve good mixing. If the volume fraction of the solid, ϕ_2 , is increased, the viscosity increases as seen in Figure 1, based on the modified Roscoe equation³, where η_l is the viscosity of the uncured liquid binder and ϕ_m is the theoretical maximum volume fraction of randomly close-packed monomodal spheres and is equal to 0.63³. ϕ_m is sometimes also called the critical solids loading and is often close to the tap density for the powder⁴.

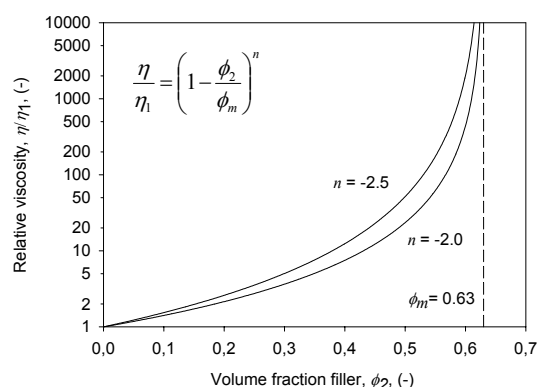


Figure 1 Relative viscosity vs vol. fraction of randomly packed monomodal spheres.

When ϕ_2 approaches ϕ_m , the viscosity increases dramatically and a solid loading of

0.63 cannot be obtained with monomodal spheres.

To be able to obtain a high performance, it is of major importance to achieve a very high solid loading in the final formulation. Theoretical calculations show that for e.g. a composite propellant similar to the one used in the space shuttle, 70 volume % of energetic material (ammonium perchlorate) is needed to obtain maximum performance. Such a high solid loading cannot be achieved with a monomodal particle size, as is shown in Figure 1. Bimodal or trimodal particle sizes are thus often used to optimize the solid particle packing and improve the overall solid loading.

Theoretically the size ratio for bimodal particle mixtures should be at least 7:1, with 73% large and 27% small spheres, to obtain optimum solids loading. This increases ϕ_m to 0.86⁴. Real powders however seldom have a perfect spherical shape and its particle size is often characterized by a size distribution. The greater the deviation from a perfect sphere, the lower ϕ_m ⁴.

The size ratio between large and small particles is in reality determined of what materials or batches that are available. Due to this and the irregularity of real powders, the optimum weight ratio between the large and the small particles must be determined experimentally.

For powders containing monomodal irregular particles, ϕ_m can be experimentally determined by measuring the tap density. This method is however not ideal for bimodal powder mixtures due to particle size segregation.

This paper presents a method of optimizing the distribution of crystalline energetic materials in a binder to obtain a high solid loading. The paper also discusses some of the difficulties with this method and how these are circumvented. The method is used

for both propellants and explosives and therefore only explosives will be mentioned from here on. Results from the optimization of two types of energetic particles in a polymer matrix are given in this paper.

EXPERIMENTAL

The viscosity of the mixture of binder and solid energetic material was measured with a StressTech Melt Reometer from Reologica AB, Sweden. The measurements were done at 40°C with a plate-plate (\varnothing 20 mm) measurement system. The measurements were done at a constant shear rate of 0.2 s⁻¹ or at varying shear rates between 0.2 and 2.5 s⁻¹.

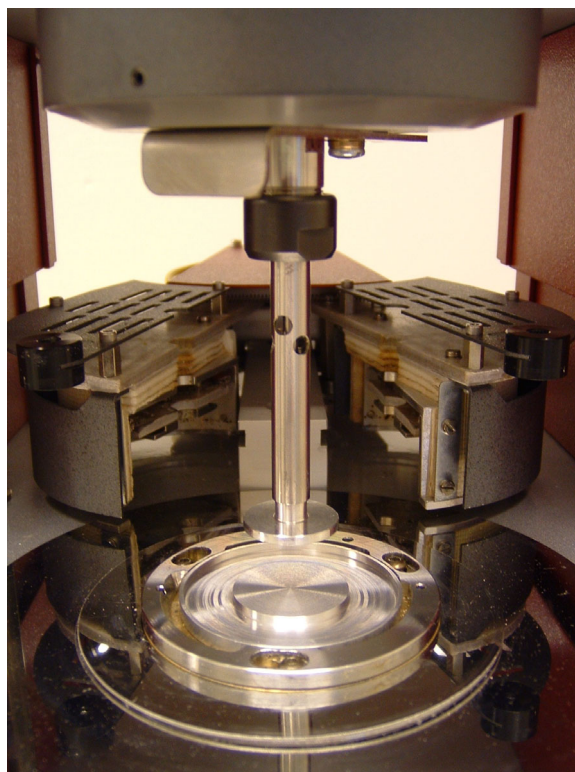


Figure 2 The measurement system of the StressTech Melt HR Rheometer.

RESULTS AND DISCUSSION

One important aspect during formulation of explosives, and especially optimization of particle size distribution, is the particle shape of the solid energetic material. The particle shape of the crystalline energetic

material used in the two examples presented in this study is shown in Figures 3 and 4.

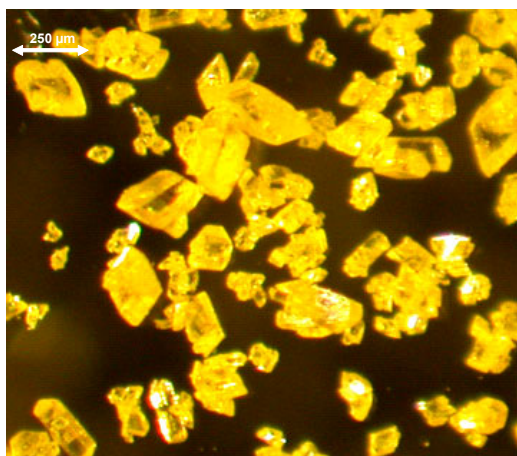


Figure 3 Crystalline 1,1-diamino-2,2-dinitroethylene (FOX-7). Not sieved.

The particles of FOX-7 are cubic in shape (Figure 3). Smaller particles of FOX-7 have a more irregular shape. The particles have, however, a lower aspect ratio compared to the crystalline particles of CL-20 which are rhombic-shaped (Figure 4). A particle with a high aspect ratio is difficult to use in cast-cured formulations since the flow behaviour of the mixture of binder and particles is poor (which results in high viscosity already at low solid loading). Another problem associated with energetic particles with a high aspect ratio or needle-like shape is the sensitivity to friction and impact. A needle-shaped particle is in general more sensitive than a rounded particle of the same material.

Since the viscosity of polymers is dependent of the shear rate, the rheology measurements should be performed at shear rates relevant to the processing. When casting propellants the shear rate is in the range of 0.1 to 1 s^{-1} .

There are several ways of optimising an explosive formulation with respect to viscosity and particle sizes using a rheometer. At Printz Maurits Laboratory in the Netherlands the castability (i.e. the shear viscosity) is determined by measuring the viscosity of the mixture at varying shear

rates⁶. In the controlled rate mode the viscosity is determined as a function of shear rate in the range of $0.2 - 2.5 \text{ s}^{-1}$. The viscosity at the shear rate of 1 s^{-1} is then used for determining the limit of castability (Figure 5).



Figure 4 Crystalline hexanitrohexaazaisowurtzitane (CL-20). The large fraction.

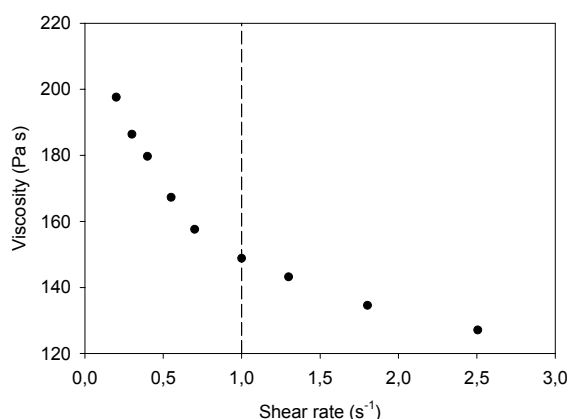


Figure 5 Viscosity at a 67/33 weight ratio between large and small FOX-7 particles. Total amount FOX-7 = 60 wt%.

We have used this method when optimizing FOX-7 based explosives, containing two particle sizes. A mixture of 60 weight% of FOX-7 and 40 weight% of a liquid polymer ($\eta_1 = 47 \text{ Pa s}$ at 25°C) was prepared. The ratio between large ($238 \mu\text{m}$) and small ($32 \mu\text{m}$) particles were then varied and the viscosity was measured (at shear rates varying from $0.2 - 2.5 \text{ s}^{-1}$). A ratio between large and small particles that resulted in the lowest viscosity was established (Figure 6).

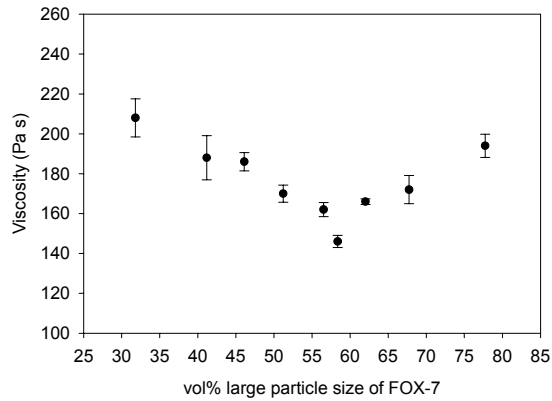


Figure 6 Viscosity at different ratios between large and small particles. Total amount FOX-7 = 60 wt%. Shear rate = 1 s^{-1} .

Within the range of 0.2 and 2.5 s^{-1} , it was shown that the FOX-7 particles were not that sensitive to shear rate and good, reproducible measurements were obtained. When using the same method for the higher aspect ratio CL-20 particles, the results were poor and not reproducible. It seem like the stretched CL-20 particles disturb the flow more than the more symmetrical FOX-7 particles and we therefore decided to measure the viscosity at a constant shear rate of 0.2 s^{-1} (at higher shear rates the flow properties became poor.) Figure 7 shows the viscosity as a function of time and it is shown that as the shearing proceed, the particles get more oriented and the viscosity decreases.

The ratio between small and large particles was then found, based on the end value as seen in Figure 7.

The overall solid loading was then studied by adding FOX-7 or CL-20 at the optimised ratio between small and large particles until a viscosity of 450 Pa s was reached. This limit value is based on experience from large-scale casting at FOI.

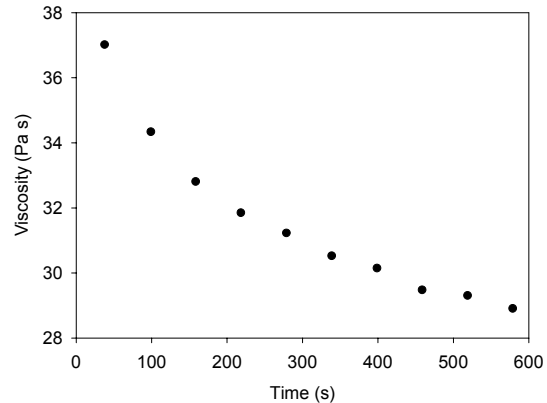


Figure 7 Viscosity at a 52.5/47.5 weight ratio between large and small particles. Total amount CL-20 = 50 wt%. Shear rate = 0.2 s^{-1} .

CONCLUSIONS

A method based on measuring viscosity at one or several shear rates has been developed to optimize two different particle sizes in a liquid polymer matrix. There are two ways of using this method: measure viscosity at a constant shear rate or at varying shear rates. Particles with a low aspect ratio (close to 1) can be optimised at either constant or varying shear rates, whereas particles with a high aspect ratio can only be optimised at a low constant shear rate. It is likely that the particles with a high aspect ratio disturb the flow during rotational shear and no reproducible measurements were obtained.

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