Powder Technology 273 (2015) 118–124

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Rheology studies of NTO–TNT based melt-cast dispersions and influence of particle–dispersant interactions

R. Sarangapani [a,*], V. Ramavat [a], S. Reddy [a], P. Subramanian [b], A.K. Sikder [a]

[a] High Energy Materials Research Laboratory, Pune 411 021, India
[b] Armament Research and Development Establishment, Pune 411 021, India

ARTICLE INFO

Article history:
Received 22 April 2014
Received in revised form 1 December 2014
Accepted 5 December 2014
Available online 19 December 2014

Keywords:
Melt-cast formulations
Non-Newtonian
Viscosity
Yield stress
Thixotropic index

ABSTRACT

3-Nitro-1,2,4-triazol-5-one (NTO) is a promising candidate of insensitive munitions and it is currently explored to achieve shock insensitive melt-cast formulations. Rheology of melt-cast formulations helps in implementing viscous behaviour to application. In the present study, NTO based melt-cast formulations are prepared using TNT as a dispersant and the flow behaviour of non-spherical and spherical NTO formulations are studied along with the bench-mark Composition B. All measurements are made at 81, 83, 86 and 90 °C and at shear rates varying from 8.5 to 59.5 s^{-1}. Flow behaviour of these formulations at process temperatures exhibit non-Newtonian behaviour with yield stress. Time and temperature dependency of these formulations are also studied and about two fold increase in thixotropic index is observed in RDX/TNT in comparison to spherical NTO/TNT (60:40). In order to get more insight on the flow properties, molecular–orbital calculations were performed at B3LYP 6-311G (d, p) level. The calculated interaction energies revealed that stronger attractive forces exist in NTO–NTO than RDX–RDX pairs and similarly in NTO–TNT than RDX–TNT. Correlation with particle morphology confirms domination of morphology over intra/intermolecular interactive forces in determining the yield value. This comparative study establishes the role of above interactive forces and morphology on pourability of melt-cast formulations and further reveals that the flow behaviour of NTO based formulations is superior to RDX/TNT formulations.

1. Introduction

The rheological behaviour of concentrated explosive dispersions is technologically important in explosive industry. Specifically, melt-cast, plastic bonded explosives (PBXs) and rocket propellant formulations pose great challenge during their mixing and casting [1]. The ease of processability limits the solid explosive content in these formulations. Viscosity, in particular non-Newtonian viscous behaviour, is an important material property that contributes to a fluid's performance, and often is the main source of problems in handling, processing and application. Though the slurry behaviour of rocket propellants is explored to some extent, very scanty information is available on the flow behaviour of melt-cast formulations. Rheology of melt-cast formulations is a typical example of implementing viscous behaviour to application. Pourability is the main criteria in processing of these formulations that offers the advantage of a thorough homogenization of the suspension and is directly related to its yield value [2]. Hence this study attempts to understand the rheological behaviour of melt-cast suspensions.

Melt-cast formulations are structured fluids wherein solid explosive particles dispersed in molten explosive. 2,4,6-trinitrotoluene (TNT) is the widely used dispersant in most of the melt-cast formulations and its flow behaviour is well studied by Parry et al. [3–5]. Rheological behaviour of melt-cast formulations is, in general dominated by the interactions of the constituents. Many factors affect the stability of structured fluids, among them viscosity of the liquid phase in dispersions plays an important role. Dispersions have wide variations in performance depending on particle size, shape, concentration and any attraction with the continuous phase in which they are suspended. When there is a repulsive electrostatic or steric force between particles they tend not to settle rapidly, instead forming a network structure which will stabilize the suspension if undisturbed. Shearing or even Brownian motion can destroy the delicate structure and break down the fluids viscosity.

Composition 'B' consisting of 60% w/w RDX in molten TNT is commonly employed melt-cast formulation. However, in recent days there is a search for alternative to highly sensitive RDX in order to realize insensitive munitions (IMs). 3-Nitro-1,2,4-triazol-5-one (NTO) is a promising candidate to meet the IM criteria and hence NTO based formulations are being attempted to achieve shock insensitive formulations. 2,4-Dinitroanisole (DNAN) and N-guanylurea-dinitramide (GUDN) are also explored as TNT replacement in melt-cast formulations and many insensitive compositions such as PAX, OSX, IMX etc., are also developed based on NTO and DNAN [6–9]. Cliff and Smith [10] developed the baseline 50:50 NTO/TNT formulation (ARX-4002) by traditional melt-cast technique using single medium non-spherical-NTO having particle size

* Corresponding author. Tel.: +91 20 25912218; fax: +91 20 25869031.
E-mail address: sradha78@yahoo.com (R. Sarangapani).

http://dx.doi.org/10.1016/j.powtec.2014.12.013
0032-5910/

distribution (PSD) of 200–400 μm. This composition is less prone to sedimentation and shows a reduced sensitiveness to hazardous stimuli. However, the composition has resulted in increased viscosity and lower solid loading than RDX/TNT. In formulations, shape of the particles also plays a key role in realizing better packing and processability. It is reported that spherical particles of explosives improve the mix-fluidity of formulations and have a great impact on-scale to alter the performance and insensitivity towards a sudden shock [11]. Our previous studies discuss the optimized process for spheroidization of NTO and morphological characterization of NTO and RDX powders [12,13]. Flow behaviour of NTO powders and their bi/tri modal mixtures were also established and identified the bimodal mixture (70:30) of spherical-NTO of PSD 150 and 25 μm as the best choice for formulations based on their maximum tapped bulk density and Carr's index [14].

This study aims to compare the rheological behaviour of spherical and non-spherical NTO based formulations as the particle morphology tremendously affect the flow behaviour. The study is also extended to compare the flow behaviour of NTO based formulations with the RDX/TNT based formulation, widely known as Composition B. This comparative study can account the nature of interactions between dispersant (TNT) and explosive particles (RDX/NTO) as well as the morphology of explosives (non-spherical and spherical NTO) on the pourability. In order to have insight on the interactions among the dispersant-explosive particles, molecular orbital calculations have also been performed to establish the extent of interactions.

2. Experimental

2.1. Materials and methods

All the reagents and chemicals used in the present study were of AR grade and used as such. Spherical-NTO of specific particle size distribution was prepared from non-spherical-NTO as described in our earlier work [12] while RDX/TNT (60:40) composition was in-house available. NTO/TNT of varying percentage was prepared initially by dispersing predetermined amount of explosive in molten TNT. A jacketed stainless steel vessel equipped with stirrer was used for the above and the explosive powder was added in increments while the vessel was at about 95–98 °C. Homogenized slurry obtained from this process was used for the viscosity studies. In case of NTO, non-spherical NTO based composition (non-spherical NTO/TNT; 40/60) was also prepared for the comparison, however, composition beyond 40% NTO was not realized due to the non-pourability.

All viscosity measurements were conducted using Brookfield viscometer (RV-DVII+ Pro) equipped with small sample adapter (SC4-27) where shear rate and stress can be measured. The sample was placed in the chamber and heated through a hot fluid circulator. All measurements were made in 5 cycles of up–down ramps at the shear rates varying from 8.5 to 59.5 s^{-1} and average of ten readings has been plotted with the error bar. Experiments were carried out at four different temperatures viz. 81, 83, 86 and 90 °C.

In order to compare the results of different compositions power law flow model was adopted.

$$\tau = K \cdot \dot{\gamma}^{n}$$

where τ = shear stress, $\dot{\gamma}$ = shear rate, K = consistency index and n = flow index. Based on flow index value, material's flow behaviour can be divided into three categories. When n = 1 denotes Newtonian fluid, n < 1 means pseudo plastic materials or shear-thinning fluids and the case n > 1 represents dilatant or shear-thickening fluids [15]. In terms of the apparent viscosity, the above equation may be written as

$$\eta = K\gamma^{n-1}$$

where η is the viscosity.

In order to get more insight on type of flow, a plot of viscometer reading versus speed (RPM) was made. As described elsewhere [16], if the line is fairly straight then the composition will have the nature of Bingham flow, if it is curved, then it will be pseudo plastic or dilatant flow. In this case, an estimate of viscometer reading at zero RPM (X_1) was made by giving polynomial fit and this value of X_1 was subtracted from all other reading comprise the graph. The plot of the new values on log–log scale lead to fairly straight line, the angle of this line formed with Y-axis (RPM) was measured to calculate power law index of these fluid as given below

$$\overline{N} = \tan\theta$$

where θ = angle for plot line with Y-axis. If θ is <45° then it is pseudo plastic. The value of angle was calculated for various compositions at temperature 86 °C.

The flow curves of the melt-cast compositions can be expressed mathematically using number of equations, depending on the actual material. In the present study, choice of model was restricted to Casson fit since flow behaviour of melt-cast compositions was similar to chocolate flow curves. The mathematical expression according to Casson is

$$\sqrt{\tau} = \sqrt{\tau_c} + \sqrt{\eta_c\,\dot{\gamma}}$$

where τ_c = yield point, $\dot{\gamma}$ = shear rate, and η_c = Casson viscosity.

The viscosity and temperature relationship modelled using an Arrhenius equation.

$$\eta = Ae^{E_f/RT}$$

where η is the viscosity of the fluid, T is temperature in Kelvin, A is a constant, E_f is the activation energy for flow, and R is the universal gas constant. The above equation may be written as

$$\ln\eta = {E_f}/{RT} + \ln A.$$

A plot of ln η versus (1/T) gave a straight line with a slope of E_f/R.

Molecular orbital calculations were employed in order to calculate the interaction energies of different ingredients viz. dimers of TNT, RDX and NTO along with RDX–TNT and NTO–TNT. The geometries of the molecules under investigation were fully optimized without any symmetry restriction using density functional theory (DFT) [17,18] at the B3LYP functional with the 6-311G (d, p) basis set in the Gaussian 03 software package [19]. All of the optimized structures were characterized to true local energy minima on the potential-energy surface without imaginary frequencies. Interaction energy (IE) was calculated as follows

$$\begin{aligned}
IE_{(TNT)} &= \text{Total Energy}_{(TNT\ dimer)} - 2\ \text{Total Energy}_{(TNT)}\\
IE_{(explosive)} &= \text{Total Energy}_{(explosive\ dimer)} - 2\ \text{Total Energy}_{(explosive)}\\
IE_{(TNT\text{-}explosive)} &= \text{Total Energy}_{(TNT\text{-}explosive)}\\
&\quad - \left[\text{Total Energy}_{(TNT)} + \text{Total Energy}_{(explosive)}\right].
\end{aligned}$$

Molecular electrostatic potential were computed for the optimized geometries at same level of theory.

3. Results and discussion

Melt-cast dispersions posses typical rheological behaviour, hence it is of great importance to characterize their flow behaviour especially the thixotropy as the most common one and useful to establish the relationship between structure and flow.