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Thermal decomposition and kinetics of plastic bonded explosives based on mixture of HMX and TATB with polymer matrices

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ABSTRACT

This work describes thermal decomposition behaviour of plastic bonded explosives (PBXs) based on mixture of l,3,5,7-tetranitro- 1,3,5,7-tetrazocane (HMX) and 2,4,6- triamino-1,3,5-trinitrobenzene (TATB) with Viton A as polymer binder. Thermal decomposition of PBXs was undertaken by applying simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC) to investigate influence of the HMX amount on thermal behavior and its kinetics. Thermogravimetric analysis (TGA) indicated that the thermal decomposition of PBXs based on mixture of HMX and TATB was occurred in a three-steps. The first step was mainly due to decomposition of HMX. The second step was ascribed due to decomposition of TATB, while the third step was occurred due to decomposition of the polymer matrices. The thermal decomposition % was increased with increasing HMX amount. The kinetics related to thermal decomposition were investigated under non-isothermal for a single heating rate measurement. The variation in the activation energy of PBXs based on mixture of HMX and TATB was observed with varying the HMX amount. The kinetics from the results of TGA data at various heating rates under non-isothermal conditions were also calculated by Flynn–Wall–Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods. The activation energies calculated by employing FWO method were very close to those obtained by KAS method. The mean activation energy calculated by FWO and KAS methods was also a good agreement with the activation energy obtained from single heating rate measurement in the first step decomposition.

1. Introduction

Plastic bonded explosives (PBXs) based on l,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) or 2,4,6-triamino-1,3,5- trinitrobenzene (TATB) with various polymer matrices have been formulated in the literature [1–16]. Polymer matrices; Viton A; a vinylidene fluoride - hexafluoropropylene copolymer, Kel-F 800; a vinylidene fluoride - chlorotrifluoroethylene copolymer, polytetrafluoroethylene, Estane 5703; a poly(ester urethane) block copolymer etc. are mainly used for PBXs formulation due to their higher loading density, homogeneity, better dimensional integrity and higher thermal stability than TNT based melt cast compositions. The role of polymeric matrices is to minimise their sensitivity, improved mechanical and high thermal properties [17].

TATB based PBXs formulations such as LX-17 and PBX 9502 [18–21] have been developed for nuclear bomb, missiles and space applications. TATB has a high thermal stability, insensitive in terms of impact and friction but poor performance. The performance of formulations has been enhanced either to use new explosive molecule having better performance than TATB or admixture of high energetic materials which has a high performance and comparatively less sensitive to ensure the safety parameters [22–24]. Therefore, PBXs based on HMX and TATB have been formulated with polymer matrices; Estane, Viton A and Kel-F 800 to some extent compromise with insensitivity [25,26]. These formulations have been characterized in terms of density, detonation velocity, ignition temperature and other explosive properties which

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are covered under few reports and in paper also [27–37]. The thermal decomposition behaviour and kinetics are very important because it ensures safety parameters during handling, processing, production and storage [38–40]. PBXs based on HMX or TATB have been extensively investigated for the thermal decomposition behaviour and its kinetics [41–44] by means of non-isothermal thermogravimetry (TGA) and differential scanning calorimetry (DSC). The kinetic parameters of HMX based PBXs with Viton A [45], C4 [46], Formex [47] and Semtex [48,49] have been investigated and published. Brunham and Weese [50] have investigated the kinetics of PBXs with three endothermic binders; Estane 5703, Viton A and Kel-F 800 by performing TG measurements at different heating rates, exhibited that Viton A and Kel-F 800 were more thermally stable than HMX and TATB. Craig et al. [51] have been studied thermal behaviour of PBXs based on HMX or TATB with same endothermic binders, exhibited longer times to thermal explosion than those of pure HMX or TATB in the one-dimensional time to explosion and in other thermal experiments [52,53].

Moreover, the decomposition kinetic models with different polymeric matrices have been published as both kinetic parameters and reaction models are the key factor for the prediction of the thermal hazard properties. It has been reported that the effect of the polymer matrices on the decomposition mechanism has been significantly observed and resulting in very different reaction models. Tarver and Tran have also been measured the decomposition models to predict of explosion and the locations within the explosive charges [54]. However, the thermal decomposition behaviour and kinetics of PBXs based on mixture of TATB and HMX with Viton A are less addressed in an open literature. In our previous study [55], the mechanical and explosive properties of PBXs based on mixture of HMX and TATB have been investigated and published.

In the present work, the thermal decomposition behaviour of PBXs based on mixture of HMX and TATB with Viton A as polymeric matrices is studied by employing Simultaneous Thermal Analysis (STA) and DSC. The kinetic parameters namely the activation energy and pre-exponential factor are determined under non-isothermal conditions for a single heating rate measurement. The three dynamic TGA measurements at different heating rates are also used to investigate activation energy as a function of reaction conversion through non-isothermal condition by employing Flynn–Wall–Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods.

2. Experimental

2.1. Materials

HMX which is prepared in-house by nitration of hexamine by Bechmann reaction was used for PBXs formulation. Other ingredient TATB obtained from High Energy Material Research Laboratory Pune, India was used as received. Viton A; copolymer of vinylidene fluoride and hexafluoropropylene manufactured by 3M DuPont Corporation was served as a polymer binder as received. Methyl ethyl ketone procured from SD Chem. Ltd. Pvt. India was used as received.

2.2. Preparation of PBXs

PBXs formulations were prepared from a mixture of TATB and HMX with Viton A by slurry coating process as described in our previous work [55]. In this process, a mixture of HMX and TATB was dispersed with 3000 ml of a water with continuous stirring at 60 °C. Then, polymer solution prepared in a methyl ethyl ketone was added to the above mixture. The temperature was raised to 90 °C to evaporate the solvent from the solution. Then, the polymer was precipitated on the surface of energetic materials. Finally, filtered and dried to get PBXs. In this way, PBXs from a mixture of HMX and TATB at varying mass ratios (10:80, 20:70, 30:60, 40:50, 50:40, 60:30, 70:20 and 80:10 respectively) with 10 weight percent of Viton A were formulated and designated as HT1080, HT2070, HT3060, HT4050, HT5040, HT6030, HT7020 and HT8010 respectively. For comparison, HMX/Viton A and TATB/Viton A formulations (90:10 by weight percent of HMX or TATB with Viton A) were also formulated.

2.3. Characterization of PBXs

Non-isothermal thermo-gravimetric (TG) analyses of PBXs were carried out by Simultaneous Thermal Analyzer (STA), manufactured and supplied by METTLER TOLEDO, Model Mettler Toledo 851[e]. The samples were subjected to heating from 25 °C to 600 °C at heating rate 10 °C/min under nitrogen atmosphere. HT4050 sample was also subjected to heating from 25 °C to 600 °C at different heating rates 10, 20 and 30 °C/min under nitrogen atmosphere.

DSC analyses were carried out in sealed standard 40 μL aluminum crucible using a Differential Scanning Calorimeter (DSC), manufactured and supplied by METTLER TOLEDO, Model DSC 823[e]. 4.0 ± 0.5 mg weight of the sample was used for each experiment. The samples were scanned from 25 °C to 600 °C for each experiment at heating rate 10 °C/min under nitrogen atmosphere. TG and DSC analyses of pure HMX, TATB and Viton A were also monitored under similar conditions.

3. Results and discussion

3.1. TG/DTG studies

Fig. 1 shows TG thermograms of HMX, TATB, Viton A and PBXs namely HT1080, HT2070, HT3060, HT4050, HT5040, HT6030, HT7020, HT8010, HMX/Viton A and TATB/Viton A. TG thermogram of HMX shows that 99.9% weight loss occurs in a single step as a sharp thermal decomposition strips at 280 °C [18,56]. TG thermogram of TATB shows 87.7% weight loss in a single step over a wide range of the temperature (300 °C –450 °C). The main weight loss occurs within a range of 350 °C –385 °C due to the thermal decomposition of TATB [52]. TG thermogram of Viton A shows that weight loss occurs in a single step at a high temperature within a range of 458 °C –504 °C due to the thermal decomposition of polymer matrices.

TG thermograms of PBXs; HT1080, HT2070, HT3060, HT4050, HT5040, HT6030, HT7020 and HT8010 show that the weight loss occurs in a three steps, but the thermal stability causes a decay of a first one. The weight loss occurs in the first step at 278 °C–287 °C due to thermal decomposition of HMX; while weight loss occurs in a second step in a range of 307 °C–374 °C due to the thermal decomposition TATB. The weight loss occurs in a third step in a range of 456 °C–498 °C due to thermal decomposition of polymer matrices. HMX/Viton A and TATB/Viton A samples also show two steps weight loss; the weight loss in the first step is due to decomposition of the HMX or TATB, whereas weight loss in the second step is due to decomposition of polymer matrices. Thermal decomposition % obtained at different stages during decomposition process from TG thermograms is summarized in Table 1.

As far as thermal stability is concerned, it is reported that small weight loss of a materials at a certain temperature, more is thermally stable. The results indicate that 9–72% weight loss of PBXs based on mixture of HMX and TATB is occurred in the first step due to thermal decomposition of HMX. It is also observed that the decomposition % in the first step is increased with increasing HMX