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THERMAL BEHAVIORS OF PETN BASE POLYMER BONDED EXPLOSIVES

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The thermal behaviors of three pentaerythritol tetranitrate (PETN) base polymer bonded explosives (PBX), Detasheet A (EL506A, red) and Datasheet C (EL506C, yellow-green) that supply by DuPont Co., PBXN-301 were investigated using thermal techniques in this work. The thermal properties of PETN base polymer bonded explosives, such as vacuum thermal stability (VTS), time to ignition, auto-ignition and shelf life of PBX that calculation from Arrhenius equation by the length of time for 5% decomposition were also examined. By comparing the thermal properties, VTS and shelf life of PETN base polymer bonded explosives, the application and storage of Datasheet C (EL506C, yellow-green) should be considered carefully, owing to the ingredients of Datasheet C (EL506 C, yellow-green) containing nitrocellulose. Binders that using in this study seems play no significant effect on the decomposition for polymer bonded explosives, because the decomposition temperature of binders is always higher than that of PETN.

Keywords: *PETN base, polymer bonded explosives, thermal behaviors*

Introduction

Pentaerythritol tetranitrate, $C_5H_8N_4O_{12}$ (PETN) is one of the high power and shattering as known high explosives with a relative effectiveness factor (R.E. factor) of 1.66, possess a specific gravity of solids of 1.76 and a confined detonation velocity of over 7.620 m s^{-1}. PETN is used as a priming composition in detonators, a base charge in blasting caps, and a core load for detonating fuse. PETN is also used often in detonating cord of which it is the explosive core, it develops a detonation velocity of 6400 m s^{-1}. Detonating cord is insensitive to friction and ordinary shock, but may be exploded by rifle fire. In demolition charge, PETN base plastic explosives were also applied, commonly called Flex-X or sheet explosive, it consists of 4 half-pound sheets of flexible explosive packed in a plastic envelope, each sheet is approximately 76.2 mm wide, 304.8 mm long and 6.35 mm thick. PETN was more sensitive to shock or friction than TNT or tetryl, and it is never used alone as a booster. Datasheet is an explosive similar to plastic explosives, originally manufactured by DuPont containing PETN with nitrocellulose and a binder. It was manufactured in thin flexible sheets with a rubbery texture, and is generally colored either reddish/orange (commercial) or green (military). In use, it is typically cut to shape for precision engineering charges. Compared to other explosives Datasheet is stable in processing. It is detonated with a blasting cap or primer cord but not by small-arms fire, heat, water, pressure, or concussion. But datasheet is relatively expensive compared to other explosives. PBXN-301 is an insensitive explosive of U.S. Navy and also a PETN base polymer bonded explosive, the content of PETN in PBXN-301 is 80%, by mixing and extruding then casting/or pressing, they were produced various PBX products in a batch process ranging from five to one thousand pounds to reduce waste and provide for developmental and low rate production for new products. Through the precision roll milling, extrusion and hydro-cutting it can accommodate most design configurations from blocks and sheet to strips and tubes and maintain high dimensional tolerances for military applications [1, 2].

Plastic bonded explosives, commonly referred to as PBX generally consist of a PETN, RDX or HMX base explosive, plasticizers and binders resulting in a less sensitive, water-proof explosive. In most of the plastic bonded explosive formulations, bonding/wetting agents are used to achieve high tensile strength of explosives [3–5]. The plastic coating, that binds the explosive granules, typically 5 to 20% of each formulation by mass, is what gives each PBX its distinctive characteristics, pressing a PBX molding powder convert it into a solid mass, with the polymer binder providing both mechanical rigidity and reduced sensitivity to accidental detonation. The choice of binder affects hardness, safety, and stability. Too brittle a PBX

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can sustain damage in normal handling and succumb to extreme temperature swings or thermal shocks, while too soft a PBX may be susceptible to creep and may lack dimensional stability or strength. Plastic bonded explosives are used in various forms such as sheet, detonating cord, paste and pressing powders.

Thermal analysis is a useful technique for the characterization of explosives [6–11]. And the thermal decomposition studies of the explosives have been reported [12–22]. The thermal analysis techniques have the advantages, especially in small amount of samples, quickly and frequently yield sufficient information for the accurate determination of kinetic parameters for the reaction. In this work, the thermal properties of three PETN base polymer bonded explosives were investigated by dynamic DSC/TG techniques firstly, then vacuum thermal stability (VTS), shelf life, time to ignition, auto-ignition temperature data and its relative kinetic parameters were also investigated.

Experimental

PBXN-301 was self-prepared by mixing PETN with Slygard 182 according MIL-E-82740(OS) [23], Datasheet A (EL506A, red), Datasheet C (EL506C, yellow-green) were supplied by DuPont Co. USA. The formulations of three PBX were listed in Table 1. Perkin-Elmer 7 series thermal analysis system (TG/DSC) were used in this work, under nitrogen atmosphere and with a 50 mL min^{-1} flow rate and 10 to 50°C min^{-1} heating rate. The auto-ignition temperature, kinetic parameters were also investigated by reference MIL-STD-T514.1, MIL-STD-650-T515.1 and following dynamic TG/DSC techniques. The vacuum thermal stability of PBX was also measured by reference MIL-STD-650-503.1 from 70 to 120°C.

Results and discussion

DSC/TG curves of PETN base polymer bonded explosives can be seen in Figs 1–5, the relative thermal characteristics of thermal analysis data were listed in Table 2. In Fig. 1, the DSC curve of PETN with a 20°C min^{-1} heating rate shows a sharp endothermic peak between 100 to 150°C, then following a broad exothermic peak between 200 to 250°C [24]. In Figs 2 and 3, DSC curves of two PETN base polymer bonded explosives, the exothermic peak that around 40–50°C is the tip hook with the thermal analysis equipment, then following an endothermic peak around 150°C and an exothermic between 200 to 250°C. Binders that compounding in polymer bonded explosives seems no significant effect on the decomposition reaction of PETN, except the endothermic peaks/the exothermic peaks on the DSC curve of Datasheet A, which are all slightly shift to lower temperature by comparing the melting temperature and the decomposition temperature at same heating rate in Table 2. Although the thermal behavior on decomposition and DSC curves seem showing no significant difference between PETN and PETN base polymer bonded explosives, but the melt-

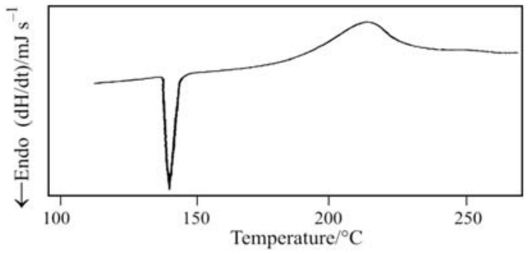

Fig. 1 DSC curve of PETN, under static air atmosphere with a 20°C min^{-1} heating rate

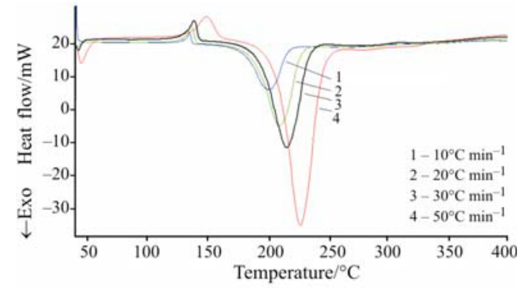

Fig. 2 DSC traces of Datasheet A (EL506, red), under N_2 atmosphere with 10~50°C min^{-1} heating rate

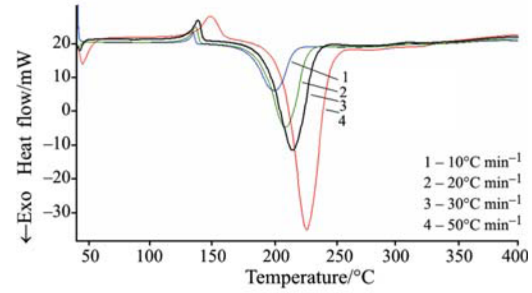

Fig. 3 DSC traces of PBXN-301, under N_2 atmosphere with 10~50°C min^{-1} heating rate

Table 1 Ingredients of three PETN base polymer bonded explosives

PBX	PETN/%	Binder	Sylgard 182	Nitrocellulose	Acetyl tributyl citrate
Datasheet A (EL506A, red)	85	15			
Datasheet A (EL506C, yellow-green)	63			8	29
PBXN-301	80		20		

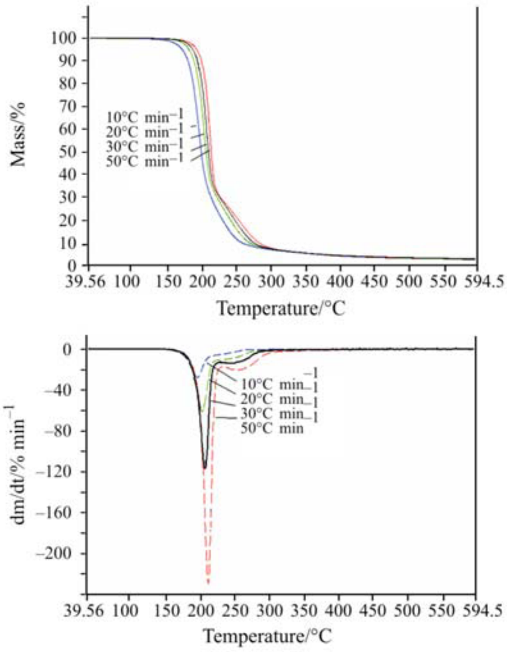

Fig. 4 TG/DTG traces of Datasheet A (EL506, red), under N_2 atmosphere with 10~50°C min^{-1} heating rate

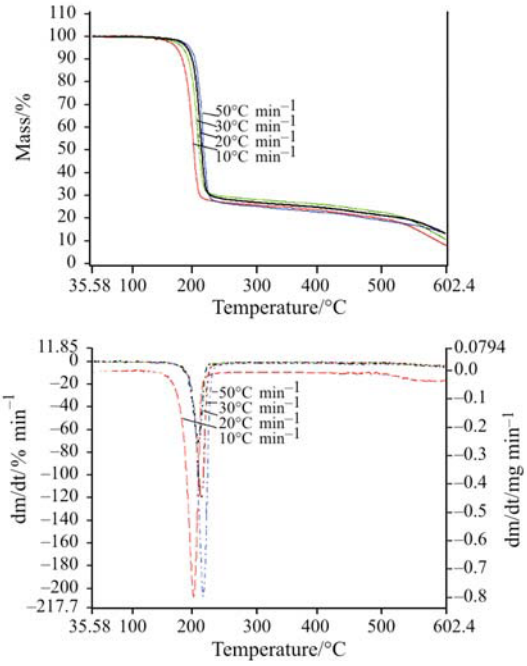

Fig. 5 TG/DTG traces of PBXN-301, under N_2 atmosphere with 10~50°C min^{-1} heating rate

ing temperature of PBXN-301 shown 30°C higher than that of PETN does, and Datasheet A gave only 0.8°C lower than PETN. In TG traces, two decomposition stages of Datasheet A was found in TG curves, this is different from the TG curves of PBXN-301. On the maximum decomposition temperature of PETN base polymer bonded explosive, the TG/DTG curves of Datasheet A were also slightly shifting to lower temperature, this result was similar to that result of DSC.

The kinetic parameters of decomposition for two PETN polymer bonded explosives were determined via DSC by using Kissinger method [25]. And the relevant equation of kinetic analysis is:

$$\ln(\phi / T_p^2) = \ln(AR / T) - E / RT_p \qquad (1)$$

where ϕ is heating rate and T_p is peak temperature of a DSC scan at that rate. In this experiment, T_p's at various rates were collected, and values of $\ln(\phi / T_p^2)$ were plotted *vs*. values of $1/T_p$. A slope of straight line through the data points was obtained by linear regression. The activation energy, E, was determined from the slope, the results are tabulated in Table 3. PBXN-301 gave higher activation energy on melting (endothermic peak) but both PETN and other two PETN base polymer bonded explosives are all gave a lower value on activation of decomposition reaction than that of PBXN-301, this indicate that PBXN-301 was hard to melting, it will applied consideration to higher temperature environmental, and this result is agreed with on melting approach in DSC analysis.

The main charge of munitions will be degraded under service or storage with time, the vacuum thermal stability procedure that hold in NAWC [26] for estimating shelf life of the main charge of munitions has been conducted. The shelf life was the length of time, at ambient temperature (25°C), required for materials to deteriorate noticeably, to the extent that the desired properties (strength, stability, etc.) may no longer hold. Vacuum thermal stability data are expressed herein as gas evolution from explosives, expressed as cc g^{-1} day^{-1} at a given temperature. To determine the shelf life, the gas evaluation data is expressed in terms of rate=(mol gas)/mol explosive/day for a minimum of two temperatures; to determine the rate, where VTS gives cc g^{-1} day^{-1}, if M is the molecular mass of the explosive, and if it is assumed that one milli-mol of gas occupies 22.4 cc, and milli-mol of 1 g of explosive is $1000/M$, then rate is expressed by Eq. (1).

$$\text{rate (day)}=1000(\text{VTS})/22.4M=44.6(\text{VTS})/M \qquad (1)$$

the relationship between rate γ and temperature, T (K) is expressed by Arrhenius equation:

$$\log\gamma=A-B/T \qquad (2)$$

where A and B are constant, and the rate at 25°C (298 K), γ_{25}, is then obtained from Eq. (2):

$$\log\gamma_{25}=A-B/298 \qquad (3)$$

According to the experience of material degradation, especially for explosives, the shelf life is defined by the length of time for 5% decomposition, this period of time, t (5%) is expressed by

$$t(5\%)=0.0513/\gamma_{25} \qquad (4)$$

Table 2 Enthalpy and peak temperatures of endothermic/exothermic for PETN and PETN base polymer bonded explosives

Heating rate/°C $\min^{-1}$	$\Delta H_m/\Delta H_d$/kJ kg^{-1}, T_m/T_d/°C		
	PBXN-301	Datasheet A (EL506A)	PETN
10	105.13/–944.13 142.67/202.17	77.57/–1268.37 135.17/202.17	
20	113.22/–948.93 147.33/214.33	82.92/–1166.69 137/210.67	
30	109.96/–927.67 148.5/219.01	88.60/–1082.37 139/216	
50	115.49/–846.43 151.67/227.5	84.75/–1014.57 149.17/216.01	
10.71			202 [5]
21.88			83.7/–681.6 141/213 [16]

$\Delta H_m/\Delta H_d$ – heat of fusion/heat of decomposition; T_m/T_d – melting temperature/decomposition temperature.

Table 3 Kinetic parameters on melting and decomposition for PETN and PETN base polymer bonded explosives

Explosives	E_m/J mol^{-1}/R^2	E_d/J mol^{-1}/R^2	log A/s^{-1}
PBXN-301	257.26/0.9838	119.07/0.9898	14.4
Datasheet A (EL506A)	132.58/0.9752	119.66/0.9724	14.2
PETN		112.3	10.4

R^2 – correction coefficient of linear regression analysis.

In Eq. (4), the constant, 0.0513 that has been used by NAWC was obtained after personal communication with Pakulak, in fact the length of time for 5% decomposition at ambient temperature (25°C), require for a material to deteriorate noticeably, to the extent that the desired properties (strength, stability, etc may no longer hold), and the constant in Eq. (4) may be variable with different materials. The shelf life or time required for 5% decomposition of explosives and relative data for estimation of shelf life were listed in Table 4, the shelf life of PBXN-301 excess 40 years, because of the binder of PBXN-301 was silicone rubber Sylgard 182, the shelf life of silicone rubber was 371000 years. In this work, we try to evaluate the constant from Eq. (2) but invalidity, so we introduced Eq. (4) and using the constant, 0.0513 to estimate the shelf life of polymer bonded explosives. In fact, the explosive in munitions are always hermetically, but the testing condition of VTS was opening, this may be an error effect on estimation the shelf life.

The measurement of time-to-ignition is often assumed for the purpose of the modeling and estimating safety. The deflagration or detonation is described by first-order Arrhenius equation. Many energetic materials appear to obey such a law except for a region at long ignition delay [27].

$$\ln t_r = E_a/RT + \text{const.} \tag{5}$$

where t_r is the reaction time constant, which is inversely proportional to rate constant, k and E_a is the activation energy in Eq. (5), we assume adiabatic condition was controlled, that is the energetic materials or at least some small critical region of it rapidly comes to the temperature ignition. The moment there is a delay in the ignition, the sample is generating heat which eventually leads to thermal runaway and igni-

Table 4 Average gases production (cm^3 g^{-1}) at different temperature (48 h) and shelf life of PETN base polymer bonded explosives

Explosives	Average gases production/cm^3 g^{-1}, shelf life or time required for 5% 48 h, under 5~15 mm Hg decomposition of explosives								
	80°C	90°C	100°C	110°C	120°C	A	B	$\gamma_{25}\cdot 10^6$	shelf life, t(5%)/ day
Datasheet A (EL506A)	0.018	0.029	0.04	0.067	0.402	4.34	2546	6.29	815=2.23 years
Datasheet C (EL506C)	0.0063	0.025	0.175	1.495	0.942				
PBXN-301	0.023	0.023	0.0485	0.101	0.6376	9.73	4529	3.45	14685=40.2 years

Table 5 Time-to-ignition temperature of PETN base polymer bonded explosives

Explosives	Testing temperature (°C)/reaction time (s)				
Datasheet A (EL506A)	235/15.4	246/10.7	254/7.4	261/5.9	269/4.9
Datashhet C (EL506C)	235/12.7	241/10.2	247/8.3	257/7.0	268/5.0
PBXN-301	235/8.2	242/7.4	247/6.6	254/5.9	264/4.9

Table 6 Auto-ignition temperature, explosion temperature and activation energy of auto-ignition temperature for PETN base polymer bonded explosives

Explosives	Auto-ignition temperature/°C	Activation energy of auto-ignition/kJ mol^{-1}	Explosion temperature/°C 5°C min^{-1} from 100 to 400°C
Datasheet A (EL506A)	267.1	79.9/R^2=0.996	183
Datashhet C (EL506C)	268.3	61.9/R^2=0.994	181
PBXN-301	263.2	40.7/R^2=0.998	179

R^2 – correction coefficient of linear regression analysis

tion. Table 5 listed the testing temperature and reaction time of PETN base polymer bonded explosives. And the activation energy of ignition within 5 s, auto-ignition temperature, explosion temperatures for three PETN base polymer bonded explosives were shown in Table 6. The auto-ignition temperature, explosion temperature, and activation energy of auto-ignition temperature for PBXN-301 were slightly lower than that of Datasheet, especially in activation energy of auto-ignition, this indicated that PBXN-301 is easy to ignition when a steady trigger energy was input.

Conclusions

Three different binders that used in PBX seems to play no significant effect on the decomposition reaction of polymer bonded explosives, owing to the main decomposition reaction are always control by PETN, and the decomposition reaction of binder almost takes place at higher temperature by following the decomposition of PETN, except the low decomposition temperature binder was used, such as nitrocellulose. But the mass loss properties against temperature of binder and its additives will drastically affect the vacuum thermal stability and shelf life of polymer bonded explosives. Using different binder in polymer bonded explosive, the VTS and shelf life of polymer bonded explosive will induce a big change, such as PETN base PBX, the shelf life of PBX containing silicone rubber binder gave almost 20 times than that of PBX containing nitrocellulose.

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