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THERMAL DECOMPOSITION AND SHELF-LIFE OF PETN AND PBX BASED ON PETN USING THERMAL METHODS

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Abstract. Binders exert a strong influence on the safety and explosion properties of polymer-bonded explosives (PBX) based on pentaerythritol tetranitrate (PETN). In this paper, the thermal behavior and decomposition kinetics of two PBX samples formulated from PETN were evaluated along with a PETN sample using various thermal techniques and analytical methods. The experimental results demonstrate that the nitrocellulose (NC) binder accelerated the thermal decomposition process and hence reduced the thermal stability and shelf-life of the PBX compared to PETN, whereas the polystyrene (PS) binder seems to play no negative influence on the thermal stability of PETN in the PBX composition.

Keywords: kinetics, PBX, PETN, shelf-life, thermal decomposition.

Classification numbers: 2.8.3; 2.9.3; 2.10.3.

1. INTRODUCTION

Pentaerythritol tetranitrate ($C_5H_8N_4O_{12}$, PETN), which is a nitrate ester explosive, is widely used for military and civilian purposes because of its high energy density properties [1-3]. However, PETN is highly sensitive to mechanical pulses such as impact and friction, and resistant to compression. To overcome these problems, one of the methods is mixing PETN with some selected polymeric binders, commonly referred to as polymer-bonded explosive (PBX) [1, 3, 4]. The polymeric binder coating, that binds the explosive granules, can absorb impact impulse, reducing the sensitivity of explosives to mechanical shocks. In addition, it can also improve the mechanical and chemical properties of explosive [5, 6].

The thermal behavior and decomposition kinetics of high energetic materials are very important because it ensures safety parameters during the production, transportation, and storage of high explosives. Compared to single high explosives (e.g. PETN), the thermal decomposition behavior and kinetics of PBXs are more complicated due to the addition of binders and other additives [3, 5, 6]. Nevertheless, similar to single explosives, these vital parameters of PBXs can be evaluated using the Arrhenius kinetic constants of their thermal decomposition reactions [7-

10]. Thus, an accurate prediction about the shelf-life and thermal hazard potential of the PBXs can be achieved.

This study aims at investigating the thermal behavior and decomposition kinetics of several PBX formulations along with a single PETN to evaluate their shelf-life and thermal hazard potential. The PBXs and PETN samples were first prepared in a laboratory. Then, thermal analysis experiments with these explosive samples were conducted to establish their thermogravimetry (TG), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) curves. Based on TG/DTG and DSC curves, the thermal decomposition parameters of the explosives samples were determined using Kissinger and Ozawa methods [11-13]. Finally, the shelf-life of each sample was evaluated using vacuum stability test (VST).

2. MATERIALS AND METHODS

2.1. Materials

PETN (i.e. class 1 with melting temperature ≥ 139.0 ºC) was imported from India. Polystyrene (PS) was prepared in our laboratory, with an average molecular weight of 80,000 u. Nitrocellulose (NC) with a nitrogen content of 12.20 % (code as NC-NB) was commercially obtained from Z company. Dioctyl phthalate (DOP) from Merk was used as a plasticizer to prepare the binder from PS and NC-NB.

2.2. Preparation of PBXs

PBXs of two different formulations (i.e. coded as PBX-80 and PBXN-80) were prepared from a mixture of PETN (80 wt.%) with the binder (DOP/PS or DOP/NC). In this process, PS or NC-NB and DOP were quantified and then dissolved in a corresponding solvent. Preparation of the PBXs was carried out by mixing 80 wt.% of PETN with 20 wt.% of the binder (in which the ratio of plasticizer/polymer is 2/1). The formulations were mixed in a special beaker for 30 minutes at room temperature. The obtained mixture was subsequently dried at 90-95 °C for 5 hours. The compositions of these PBXs are provided in Table 1.

Table 1. Compositions of PBXs based on PETN.

PBXs	PETN/wt.%	DOP/wt.%	PS/wt.%	NC-NB/wt.%
PBX-80	80	13.3	6.7	---
PBXN-80	80	13.3	---	6.7

2.2. Experimental techniques

TG/DTG and DSC curves of the samples were established using A NETZSCH STA 409 PC/PG (provided by Netzsch-Gerätebau GmbH) and a Diamond DSC (Perkin Elmer). The TG and DSC analysis experiments were conducted at various heating rates (e.g. 4, 6, 8, and 10 K.min^{-1}). Nitrogen was circulated through the heating chamber at a flow rate of 20 ml.min^{-1}. The TG/DTG curves were plotted in the temperature range from 105 ºC to 240 ºC, and the DSC curves were plotted in the range from 50 ºC to 250 ºC.

VST tests of the explosive samples were conducted using a STABIL apparatus (provided by OZM Research, Czech Republic) following the STANAG 4556-2A standard [14]. Prior to the

VST tests, sample vials (with 2.0 g of explosive samples) were stored in a vacuum oven at 60 ºC for 3 hours. During the test, the sample vial was heated at constant temperatures (e.g. 80, 90, 100, and 110 ºC) for 48 hours under a vacuum pressure (≤ 0.672 kPa). The released gas volume was recorded using a pressure transducer connected to a computer [8]. The schematic diagram of the STABIL apparatus is provided in Figure 1.

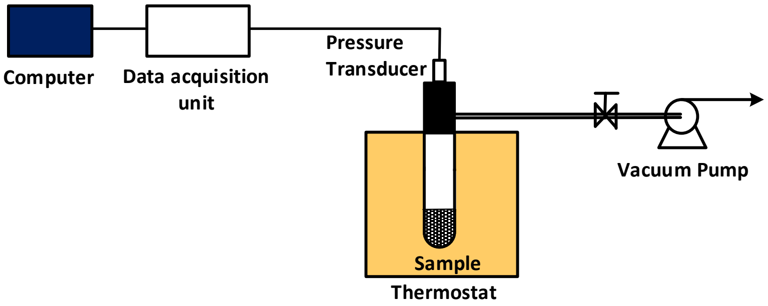


Figure 1. Schematic diagram of Vacuum Stability Testing (STABIL).

2.4. Kinetic parameters calculation using the Kissinger and Ozawa methods

All the kinetic studies could start with the basic equation that relates the rate of weight loss at a constant temperature to the fractional decomposition:

$$\frac{d\alpha}{dt} = k.f(\alpha) \tag{1}$$

where *dα/dt* is the rate of weight loss; *α* is the fractional decomposition at any time; *k* is the rate constant; *f(α)* is a function called reaction model:

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

where n is an order of reaction. According to Arrhenius equation, the temperature dependence of the rate constant k is given by:

$$k = A.\exp(\frac{-E_a}{RT}) \tag{3}$$

where E_a is the activation energy (kJ.mol^{-1}); *T* is the absolute temperature (K); *R* is the gas constant (8.314 J.K^{-1}.mol^{-1}) and *A* is the pre-exponential factor (min^{-1}). Combining Eq. (1) and Eq. (3) we obtain:

$$\frac{d\alpha}{dt} = A.\exp(\frac{-E_a}{RT})(1-\alpha)^n \tag{4}$$

a. Kissinger method

Because the maximum rate occurs when $d^2\alpha/dt^2 = 0$, differentiation of Eq. (4) gives:

$$\frac{E_a\beta}{RT_P^2} = A.n(1-\alpha)^{n-1}\exp(\frac{-E_a}{RT_P}) \tag{5}$$

where T_P is the temperature peak of the DTG curve or DSC curve at linear heating rate $\beta = dT/dt$. Kissinger method [5, 11, 12] assumed that the product $n(1-\alpha)^{(n-1)}$ is independent of *β*. So, the following expression is derived:

$$\frac{d\left[\ln\left(\frac{\beta}{T_P^2}\right)\right]}{d\left(\frac{1}{T_P}\right)} = -\frac{E_a}{R} \tag{6}$$

The value of activation energy is calculated from the slope $(-E_a/R)$ of the straight line when plotting $ln(\beta/T_P^2)$ against $(1/T_P)$.

b. Ozawa method

At linear heating rate $\beta = dT/dt$, equation (4) can be written as:

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp(\frac{-E_a}{RT})dT \tag{7}$$

Ozawa method [9, 11, 13, 15] assumed that A, $f(\alpha)$ and E_a are independent on T, whereas A and E_a are independent on conversion rate α. By separating and integrating Eq. (7), the resulting Ozawa equation is:

$$\log\ f(\alpha) = \log(\frac{AE_a}{R}) - \log\beta - 2.315 - 0.4567\frac{E_a}{RT_P} \tag{8}$$

The straight line obtained by plotting $log\beta$ against $(1/T_P)$, and E_a values could be determined from the slope $(-0.4567E_a/R)$.

2.5. Explosive shelf-life prediction using vacuum stability test (VST)

The shelf-life of an explosive is defined as a time duration (i.e. normally at the temperature of 25 ºC), within which the explosion properties and safety (e.g. stability, strength, and sensitivity) of the explosive remain in acceptable ranges. In this study, the VST method was used to determine the thermal vacuum stability and hence to estimate shelf-life of the explosive sample. The gas evolution rate (k) of the explosive samples was calculated using Eq. (9) [4, 16]:

$$k = \frac{1000\,.V}{22.4M} = \frac{44.6}{M}V \tag{9}$$

where k was the number of moles of gas released per one mole of explosive per day, V was the volume of gas (i.e. at standard pressure and temperature) generated by 1.0 of explosives per day ($cm^3.g^{-1}.day^{-1}$), and M is the molecular weight of the explosive (g). The k value is a function of temperature, and can be expressed using the Arrhenius equation:

$$\log k = A - \frac{B}{T} \tag{10}$$

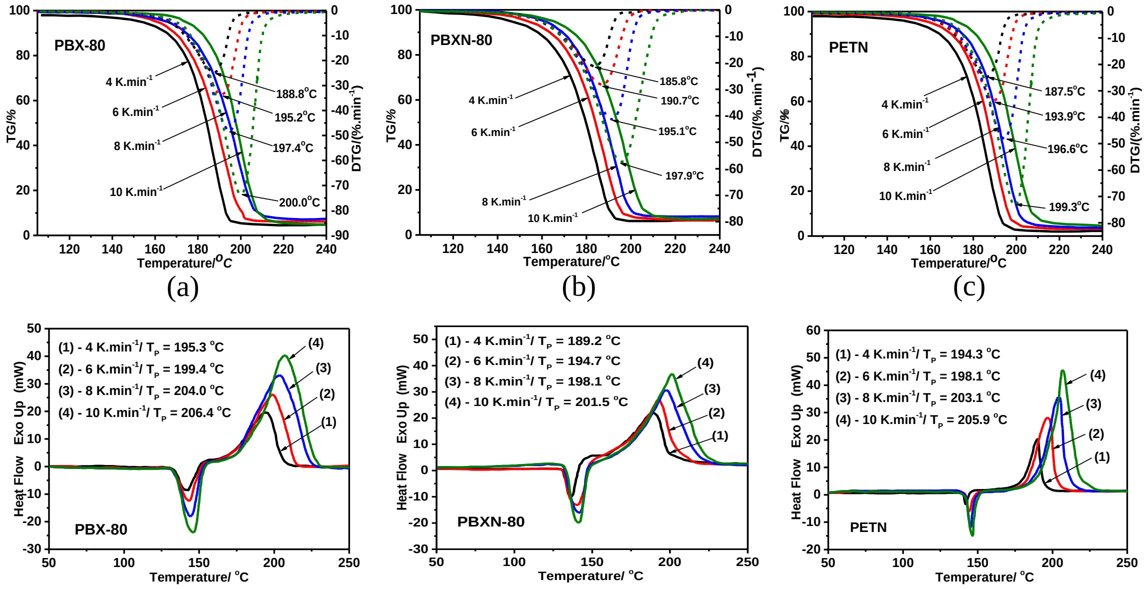
where A and B are constants that can be calculated from a straight line obtained by plotting $\log k$ against $(1/T)$. Given the values of A and B, the k values at 25 ºC (i.e. 298 K) of the explosive samples could be calculated. The shelf-life (in days) of the explosive samples ($t_{5\%}$) was then calculated using the Eq. (11) [3, 4,1 3]:

$$t_{5\%} = \frac{0.0513}{k_{298}} \tag{11}$$

3. RESULTS AND DISCUSSION

3.1. Kinetics of the thermal decomposition studies using non-isothermal analysis

TG/DTG and DSC curves of PETN and PBX samples at four heating rates 4, 6, 8, and 10 K.min^{-1} were recorded and listed in Figure 2.



(a) (b) (c)

(d) (e) (f)

Figure 2. TG/DTG curves of (a) PBX-80, (b) PBXN-80, (c) PETN and DSC curves of (d) PBX-80, (e) PBXN-80, and (f) PETN under various heating rates.

The obtained TG curves of PETN, PBX-80 and PBXN-80 (Figure 2, a-c) indicate a mass loss in one step, related to the thermal decomposition of PETN. It has been shown that only a single decomposition process has been observed for PETN and PBXs. It also shows that the decomposition temperature of PETN is higher than that of PBXN-80 but slightly lower than that of PBX-80.

The early decomposition of PBXN-80 may be due to the effect of exothermic decomposition of NC and the release of gaseous products from the early decomposition of PETN in the binder matrix. On the other hand, the decreasing content of PETN in the PBX-80 composition leads to a slight increase its decomposition temperature.

TG/DTG results were supplemented by DSC studies which were performed at the same heating rates (Figure 2, d-f). The DSC curves show an endothermic peak followed by an exothermic for all of the samples. The initial endothermic peaks at about 140-145 ºC are due to the melting of PETN, which confirm that all of the samples decompose in the liquid state. The PETN exothermic peak is well formed, showing signs of uncontrolled decomposition processes. However, for the PBXN-80 sample, the sharp exothermic peaks are corresponding to rapid heat evolution due to a fast combustion process.

The differences in the thermal stability of explosive samples were evaluated by the activation energy values (Table 2 and Table 3) calculated using Kissinger and Ozawa methods. This result confirmed that pure PETN has a higher activation energy than those of PBXN-80 (i.e. PETN has higher thermal stability than PBXN-80). Especially, these show the effect of the binder matrix on the thermal decomposition of pure PETN. The NC-based binder decreases the temperature decomposition of PETN hence reduces the activation energy of the thermal decomposition of PBXN-80. It is also noteworthy that amongst the investigated explosives samples, the activation energy of PBX-80 is higher than that of PETN (i.e. PBX-80 has higher thermal stability than PETN).

Table 2. The kinetic parameters from non-isothermal TG/DTG data of PETN and PBXs.

Material	Kissinger method				Ozawa method			
	Slope	E_a (kJ.mol^{-1})	*logA* (min^{-1})	R^2	*Slope*	E_a (kJ.mol^{-1})	*logA* (min^{-1})	R^2
PETN	*15.948*	132.59	14.50	0.9846	*7.3309*	133.45	14.60	0.9862
PBX-80	*17.011*	141.43	15.51	0.9714	*7.7933*	141.87	15.56	0.9742
PBXN-80	*15.220*	126.54	13.81	0.9978	*7.0061*	127.54	13.92	0.9980

Table 3. The kinetic parameters from non-isothermal DSC data of PETN and PBXs.

Material	Kissinger method				Ozawa method			
	Slope	E_a (kJ.mol^{-1})	*logA* (min^{-1})	R^2	*Slope*	E_a (kJ.mol^{-1})	*logA* (min^{-1})	R^2
PETN	*16.179*	134.51	14.71	0.9831	*7.4374*	135.39	14.81	0.9849
PBX-80	*16.992*	141.27	15.48	0.9908	*7.7909*	141.83	15.54	0.9917
PBXN-80	*15.584*	129.56	14.15	0.9978	*7.1746*	130.61	14.27	0.9987

From the results in Table 2-3, the matching of activation energies obtained by differential methods confirms the accuracy of obtained results. As seen, the activation energies of PETNand PBXs calculated by Kissinger and Ozawa methods based on TG/DTG and DSC data are very close to each other. In particular, the activation energy of the thermal decomposition of PETN reported here is also in good agreement with that reported by M. Kunzel et al. [7] (with the E_a(PETN) = 137.4 kJ.mol^{-1}), and by H. R. Pouretedal et al. [17] (with the E_a(PETN) = 136.9 kJ.mol^{-1}) [17]. This comparison showed an insignificant difference between the results.

3.2. Isothermal analysis and shelf-life of PBXs and PETN

Table 4. The VST data and some thermal decomposition parameters of PETN and PBXs.

Material	VST (cm^3.g^{-1}.day^{-1})				*A*	*B*	k_{298}.10^6	E_a (kJ.mol^{-1})
	80 °C	90 °C	100 °C	110 °C				
PETN	0.020	0.052	0.122	0.375	13.45	5656.2	2.95	102.97
PBX-80	0.018	0.049	0.112	0.342	13.41	5665.9	2.51	103.14
PBXN-80	0.029	0.060	0.142	0.545	13.52	5651.0	3.63	102.87

The volume of gas (i.e. at standard pressure and temperature) generated by 1.0 g of explosives per day (*V*) of PETN, PBX-80, and PBXN-80 at difference temperatures (Table 4) indicated that the *V* value determined from the VST test of PETN is higher than that of PBX-80 (i.e. PBX-80 has the higher thermal stability than PETN). In turn, PETN has a higher thermal stability than PBXN-80. Based on the VST data, the coefficients *A* and *B* in Eq. (10) were determined and then, the activation energy values of PETN, PBX-80 and PBXN-80 were calculated using the Ozawa method (Table 4).

The E_a values of PETN and PBXs calculated based on VST results were in the range from 102 kJ.mol^{-1} to 103 kJ.mol^{-1}. The difference of these E_a values compared to the E_a values (in the section 3.1) can be attributed to that, while the E_a derived from isothermal experiments (VST tests) is an average over the range of temperatures selected for the experiments, whereas the E_a derived from non-isothermal experiments (TG/DTG and DSC tests) is an average over a variable range of rising temperatures [18].

Shelf-life and thermal hazard potential of the PBXs and PETN can be estimated by vacuum stability tests (VST). The volume of gas released when the explosive sample is heated is an index for its thermal stability and hence its shelf-life and thermal hazard potential. To make a quantitative the effect of the binder on the thermal stability of PBXs, the shelf-life or time required for 5 % decomposition of PETN and PBXs were calculated following Eq. (3-5) and provided in Figure 3.

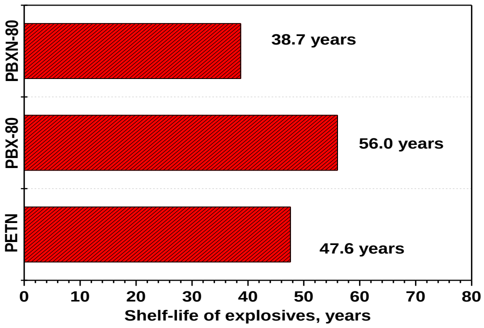


Figure 3. Estimated shelf-life of the PBXs and PETN samples.

The shelf-life at ambient temperature (25 ºC) of PETN, PBX-80 and PBXN-80, calculated according to VST results, is approximately 47.6, 56.0 and 38.7 years, respectively. The results can be compared with K. S. Jaw and J. S. Lee's report [4] – calculated shelf-life of Datasheet A-EL506A (85 % PETN, 15 % binder) is 22.3 years and calculated shelf-life of PBXN-301 (80 % PETN, 20 % Sylgard 182) is 40.2 years.

4. CONCLUSIONS

Thermal behavior and decomposition kinetics of the PBXs with various binder contents were evaluated in comparison with the pure PETN. The experimental results demonstrate that the introduced binder (plasticised NC) accelerated the thermal decomposition process of PBXs, resulting in reductions in their decomposition temperatures and activation energy (E_a) as compared to PETN. On the other hand, the use of the inert binder does not adversely affect the thermal stability of PETN in PBX composition. This result also explained that the thermal stability of PBX-80, PETN and PBXN-80 is decreased, in order of respective.

In addition, when using different binders in PBX composition, the shelf-life of PBX will have a big change, such as PBX based on PETN, the shelf-life of PBX-80 (containing PS-based binder) gave longer almost 20 years than that of PBXN-80 (containing NC-based binder).

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