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Thermal properties and shelf life of HMX–HTPB based plastic-bonded explosives

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Abstract

Plastic-bonded explosives (PBXs) with different amounts of polymer and based on explosives with different particle size distributions have been compared for their thermal properties and shelf life. Chung Shan Institute of Science and Technology has extensive experience with the processing of hydroxyl terminated polybutadiene (HTPB)-based PBXs. The investigation showed that the shelf life of HMX-based formulations is longer than 60 years at ambient temperature. The thermal properties of three HMX-based formulations such as specific heat, linear thermal expansion coefficient, auto-ignition temperature and kinetic parameters concerning the explosion, explosion temperature, etc. are very close with the exception of glass transition temperature.

Keywords: Plastic-bonded explosive; HMX; HTPB

1. Introduction

Maximum performance has long been the driving force behind research in the field of explosive compounds for the military warhead. TNT, which was used before the First World War, was replaced by RDX–TNT mixtures in the period between the two wars. When HMX was industrialized in the 1950s, it further increased the performance level with the use of octols and explosives with thermoplastic binder with high HMX content. As a result of several major accidents involving military ordnance systems, new ordnance systems that respond only mildly when subjected to hazardous stimuli are being developed [1]. A major approach to moderating the response of ordnance to these stimuli has been the development of relatively insensitive polymer bonded explosive (PBX) fillings containing the powerful but sensitive nitramine explosive, RDX or HMX, encapsulated and desensitized by immobilization in a rubbery polymer matrix. The most widely used PBX compositions are prepared by dispersing the explosive ingredients in a liquid monomer/pre-polymer and then casting the mixture into the ordnance and curing to form the polymer matrix.

In our earlier paper [2] we reported the decomposition studied of PETN, RDX, HMX and HNS by thermo-analytical techniques, i.e. DSC, TG/DTG. In this paper we present the thermal properties of three kinds of PBXs studied by some thermal techniques that differ from regular non-isothermal DSC, and TG techniques except decomposition kinetic parameters.

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Table 1
Composition of PBXs

PBX no.	HMX% (5–20 μm)	HMX%		Al% (Al-H5)	HTPB%	IDP%	DOA%
		125–185 μm	160–250 μm				
PBX-A	28	58			9.88	2.74	
PBX-B	28		58		9.88	2.74	
PBX-C	10		55	20	11.84		1.5

2. Experimental

We have developed a cast-cured formulation shown in Table 1. The high explosive (HE) is HMX and hydroxyl terminated polybutadiene (HTPB) is the binder. The explosive and the HTPB is mixed batchwise in a 5 gal tank with an agitator. Samples for testing were taken from a batch production of 21 kg. The auto-ignition temperature, explosion temperature after 5 s heating and shelf life that was estimated by vacuum thermal stability (VTS) data were carried out by a different thermal method.

3. Results and discussion

The explosives in the missile warhead are chemically stable. However, the main charge of warhead can degrade under service or storage with time. To alleviate any suspicions of chemical degradation contribution to the shelf life of the main charge explosives, the VTS method that was established by NAWC [3] was supposed to be conducted. The shelf life is the length of time at ambient temperature (25 °C) required for a material to deteriorate noticeably to the extent that the desired properties such as stability, strength, etc. may no longer hold. The VTS data are expressed herein as gas evolution from an explosive, expressed as $\mathrm{cm^3/g/day}$ at a given temperature. To determine the shelf life, the gas evolution data is expressed in terms of rate = (mole gas)/(mole explosive)/day for a minimum of two temperatures, the relationship between rate γ and temperature T (K) is expressed by the Arrhenius equation:

$$\log(\gamma) = A - \frac{B}{T} \tag{1}$$

The rate at 25 °C (298 K) γ_{25} is then determined from Eq. (2):

$$\log(\gamma_{25}) = A - \frac{B}{298} \tag{2}$$

where A and B are constants. 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 Eq. (3):

$$t_{(5\%)} = \frac{0.0513}{\gamma_{25}} \tag{3}$$

To determine the rate, where VTS gives $\mathrm{cm^3/g/day}$, if M is the molecular weight of the explosive, and if it is assumed that 1 mmole of gas occupies 22.4 C.C., and mmole of 1 g of explosive is $1000/M$, then the rate is expressed by Eq. (4):

$$\mathrm{Rate/day} = \frac{1000(\mathrm{VTS})}{22.4M} = \frac{44.6(\mathrm{VTS})}{M} \tag{4}$$

The shelf life or time required for 5% decomposition of explosives and relative data for estimation of shelf life were listed in Table 2.

Table 2
The shelf life and relative data of PBXs

Material	VTS ($\mathrm{cm^3/g/day}$)			A	B	$\gamma_{25\,^\circ\mathrm{C}} \times 10^6$	Computed shelf life $t_{(5\%)}$, day
	80 °C	100 °C	120 °C				
PBX-B	0.00075	0.0024	0.00725	5.72	3414.4	1.8217	28160 (=77 years)
PBX-C	0.00235	0.00404	0.03535	7.89	4034.7	2.067	24818 (=67 years)

Table 3
Summary of thermal properties of PBXs

Materials	Glass transition temperature (°C)	Specific heat (J/g °C) (−54–74 °C)	Linear thermal expansion coefficient ($\times 10^5$ °C^{-1})
PBX-B	−88	0.93–1.3	9.49 (25–75 °C)
PBX-C	−81	0.93–1.25	9.67 (25–75 °C)

Table 4
Calculation of activation energy, frequency factor, explosion temperature and auto-ignition temperature for PBXs[a]

Materials	Activation energy (kJ mol^{-1})	Frequency factor (Z) $\times 10^3$	Explosion temperature (°C)	Auto-ignition temperature (°C)
PBX-A	154.9 (0.993)	4.5	384.7 ± 0.9	238–240
PBX-B	50.7 (0.995)	2.3	388.2 ± 1.0	241–243
PBX-C	57.6 (0.933)	5.9	389.3 ± 0.9	238

[a] ($-\gamma_b$): Correlation coefficient for linear regression.

The shelf life at ambient temperature (25 °C) of the two PBXs that are summarized in Table 2 is approximately 77 and 67 years, respectively. These results can be compared with Mackarizia's [3] report—computed shelf life of BPXN-5 (95% HMX, 5% viton A or Fluorel FC-2175) is 21 years and computed shelf life of PBXN-301 (80% PETN, 20% silicone Sylgard 182) is 1092 years.

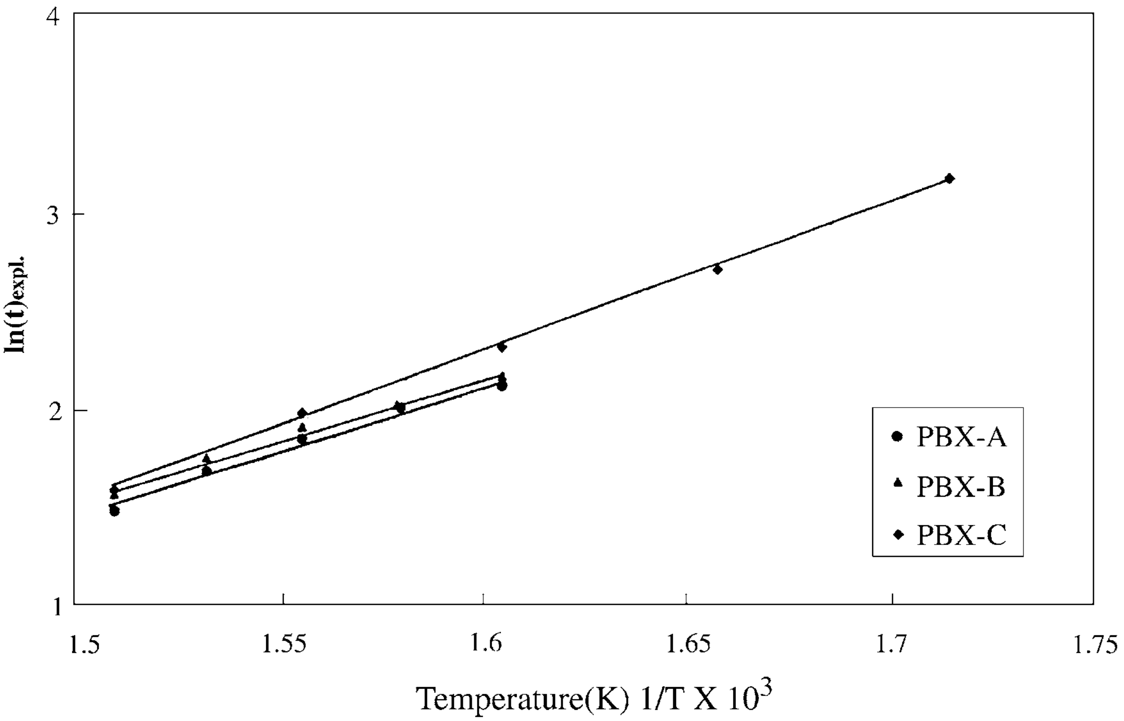

Fig. 1. Plot of $\ln(t)_{\mathrm{expl.}}$ against $1/T \times 10^3$ used to calculation the activation energy, the frequency factor of explosion and the explosion temperature within 5 second of PBXs.

Some thermal properties of PBXs such as glass transition temperature (T_g), specific heat and linear expansion coefficient were also measured by DSC and TMA; the results are summarized in Table 3.

In the analysis of energetic materials such as propellants, pyrotechnics, explosives and many other complicated combustion systems, it is often assumed for purposes of modeling and estimating safety that the combustion reactions are described by a first order Arrhenius equation [4]:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = Z \exp\left(\frac{E}{RT}\right) \tag{5}$$

where $\mathrm{d}Q/\mathrm{d}t$ denotes the heat generation rate of an explosive, Z the frequency factor of the reaction, E the activation energy of the reaction, R the gas constant, and T the absolute temperature of the explosive. In the above equation using the adiabatic assumption [5] the logarithm of the time delay from the moment the energetic material is placed in test equipment until the moment it undergoes rapid combustion can be plotted against the inverse of the temperature. Experimentally, it is found that many materials appear to obey the law except for a region at long ignition delay [6].

$$\ln(t_{\mathrm{ign}}) = \frac{E}{RT} + \ln(Z) \tag{6}$$

Table 4 lists the activation energy, frequency factor and explosion temperature within 5 s and auto-ignition temperature of PBXs, and Fig. 1 shows the relationship between $\ln(t_{\mathrm{ign}})$ and $1/T \times 10^3$, which is used to calculate the kinetic parameters of explosion temperatures of PBXs.

4. Conclusions

Thermal behaviors of three kinds of PBX are studied by some thermal techniques that differ from regular non-isothermal DSC, DTA or TG techniques. In this work the transition temperature of PBXs ranged from -88 to -81 °C and the specific heat (-54–74 °C) and linear expansion coefficient (25–75 °C) of PBXs ranged from 0.93 to 1.3 J/g °C and 9.49×10^{-5} to 9.67×10^{-5} °C^{-1}, respectively. The shelf life at ambient temperature of two PBXs is approximately 77 and 67 years, respectively; these results are comparable to the literature [3].

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