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A study on the thermal decomposition behaviors of PETN, RDX, HNS and HMX

Jinn-Shing Lee[a,b,c,*], Chung-King Hsu[a], Chih-Long Chang[b,d]

[a]*Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC*
[b]*Department of Chemistry, Chung Yuan Christian University, Chungli, Taiwan, ROC*
[c]*P.O. Box 90008-17-10, Chung Shan Institute of Science and Technology, Lungtan, Taiwan, ROC*
[d]*P.O. Box 90008-15-33, Chung Shan Institute of Science and Technology, Lungtan, Taiwan, ROC*

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Abstract

Pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (RDX), hexanitrostilbene or 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) and cyclotetramethylene tetramine, hexahydro-1,3,5-trinitro-1,3,5-triazine (HMX) are very important high explosives. All are used in a wide variety of military and industrial formulations owing to their suitable properties. Many researchers have demonstrated the usefulness of the above four energetic materials in explosive components. In this work, the thermal decomposition characteristics of PETN, RDX, HNS and HMX were studied using thermal analytical techniques (TG and DSC). Their compatibility with silicone rubber and the kinetic parameters such as decomposition activation energies and the frequency factor of the reaction are also evaluated by non-isothermal differential scanning calorimetry (DSC) techniques.

Keywords: Thermal decomposition; Compatibility; PETN; RDX; HNS; HMX; Silicone rubber

1. Introduction

Energetic materials such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (RDX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (HMX) are the main charge explosives of warheads and are the energetic component of composite propellants. They have recently occupied a key position in the field of explosives and propellants. The kinetics and the mechanism of thermal decomposition are of considerable importance in as much as they relate to the stability of these materials and may also be involved in the combustion processes. Thermal analysis is a useful technique for the characterization of explosives [1–4] and the thermal decomposition studies of the explosives have been reported [5–9]. Differential scanning calorimetry (DSC) gives information about thermal stability, melting, decomposition, etc. In fact, any reaction or transformation involving absorption or release of heat can be detected with this technique. Thermogravimetric analysis (TGA) determines the loss of mass when a sample is heated or when it is maintained at a fixed temperature as a function of time. TGA also gives information about thermal stability and decomposition temperatures and it is a complementary technique of DSC. These thermal

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[*] Corresponding author. Present address: Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC.

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analysis techniques have the advantage of using a small amount of sample, quickly, and frequently yield sufficient information for the accurate determination of kinetic parameters for the reaction. The present work derives the kinetic parameters of the decomposition computed using two equations based on the variable heating rate method, viz. of Kissinger and Ozawa. The Kissinger and Ozawa equation and the thermal behavior of pentaerythritol tetranitrate (PETN), RDX, hexanitrostilbene or 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) and HMX are investigated by DSC. The compatibility of silicone rubber with the above four explosives are also evaluated by comparison of the thermal behaviors between the explosives with silicone rubber and the parent explosives.

2. Experimental

PETN (particle size 100% ≤40 μm, average particle size 15 μm), RDX (particle size 100–800 μm), HMX (100% ≤60 μm, average particle size 19.8 μm), HNS (particle size 74–100 μm) and silicone rubber (Slygard 182) are the raw materials used in this work. PETN, RDX, HNS and HMX composed of silicone rubber with a weight ratio of 4:1, respectively, are also studied. A differential scanning calorimeter (model 910 DSC) and thermogravimetric analyzer (model 951) made by Du Pont were used. The sample weight of the explosives was about 5 mg. To determine the kinetic parameters of the thermal decomposition of the explosives and those containing silicone rubber, heating rates of 5, 10, 15 and 20 °C min^{-1} under a static atmosphere, and not sealed Pt crucible, were employed for the experiments.

3. Results and discussion

DSC curves of PETN, RDX, HNS and HMX can be seen in Fig. 1. In the PETN curve, one sharp endothermic peak is observed at about 143 °C. The decomposition then takes place and a broad exothermic peak with the maximum is observed at 208 °C. In the RDX curves, it shows a sharp endothermic peak with the minimum at 204 °C corresponding to the melting process. Immediately after melting, decomposition occurs and a broad exothermic peak is observed at 237 °C. HNS gave a moderate exothermic peak at 332 °C, before the exothermic peak there is an endothermic peak at 318 °C, which indicates the melting point of HNS. The DSC curve of HMX shows three peaks, the weak endothermic peak at about 195 °C is due to the morphology transformation, after the transformation the sharp endothermic peak at 281 °C corresponds to melting which is followed by strong exothermic peaks, this peak immediately after the melting is due to the self-decomposition of HMX [3,4]. The enthalpy change (Δ*H*, J/g) and the peak temperature for the exothermic peak for PETN, RDX and HMX at different heating rates are shown in Table 1. With increasing heating rate there is an

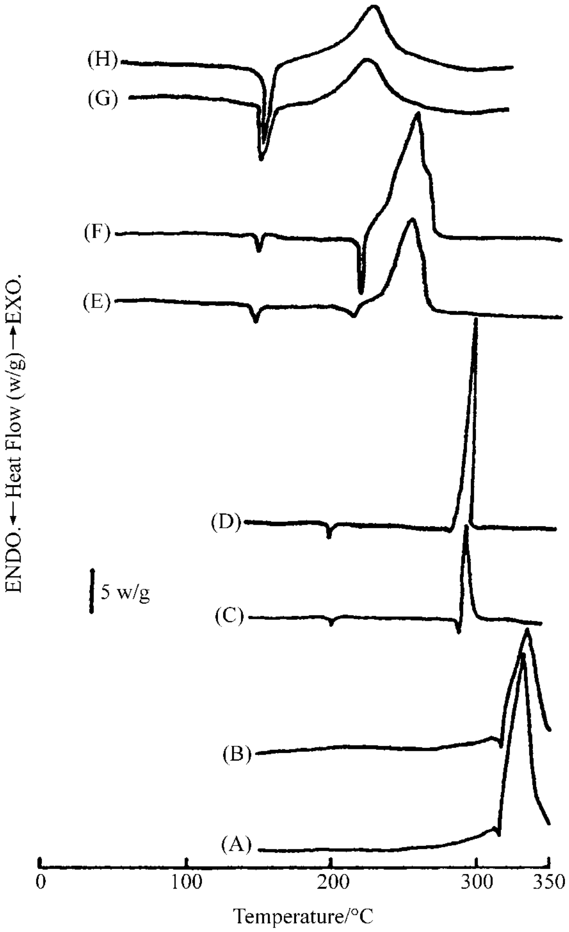

Fig. 1. DSC curves of PETN, RDX, HMX, HNS and PBXs at a 10 °C min^{-1} heating rate under static air atmosphere. (A) HNS (B) HNS/silicone = 80/20 (C) HMX (D) HMX/silicone = 80/20 (E) RDX (F) RDX/silicone = 80/20 (G) PETN (H) PETN/silicone = 80/20.

Table 1
Enthalpy and peak temperatures of exothermic peak for PETN, RDX, HNS and HMX

Heating rate (°C min^{-1})	PETN		RDX		HMX		T_p (°C) for HNS
	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_p (°C)	
5	225	201	707	231	1387	282	325
10	261	208	959	241	1268	285	331
15	362	212	1144	245	1212	288	337
20	403	216	1081	251	1126	290	343

Table 2
Kinetic parameters of thermal decomposition for explosives

Explosives	E_a (kJ mol^{-1})	$-\gamma_b$[a]	A (s^{-1})	Temperature (°C)	Value in the literatures (kJ mol^{-1})	References
PETN	175 ± 3.3	0.998	3.98×10^{15}	201–216	131/117/337/165	[3,5–7]
RDX	144 ± 4.3	0.962	1.11×10^{11}	231–251	134/142	[3,6]
HNS	197 ± 4.0	0.993	7.44×10^{11}	324–343	127	[9]
HMX	444 ± 4.6	0.989	2.04×10^{18}	282–290	611/197	[2,8]

[a] $-\gamma_b$: correlation coefficient for linear regression.

upward shift in the peak temperature of the exothermic peak for PETN and RDX and slight decrease in the ΔH value with an upward shift in the peak temperature of the exothermic peak occurs only for HMX.

The kinetic parameters of decomposition for three explosives were determined via DSC using Kissinger's method (1). The relevant equation is

$$\ln\left(\frac{\phi}{T_p^2}\right) = \ln\left(\frac{AR}{T}\right) - \frac{E_a}{RT_p} \tag{1}$$

where ϕ is the heating rate and T_p is the peak temperature of a DSC scan at that rate. In the experiment, T_p's at various rates were collected, and values of $\ln(\phi/T_p^2)$ were plotted against values of $1/T_p$. A straight line through the data points was obtained by linear regression. The activation energy, E_a, was determined from the slope, and the frequency factor, A, was determined from the intercept. The results are tabulated in Table 2.

Compatibility tests are used to study whether explosives are sensitized by contact material like binders, glues or plastics. Vacuum stability and mass loss test are usually used for this purpose. Compatibility can also be evaluated from DSC and TG curves by studying the effect of the contact material on the exothermic decomposition temperature of the explosives [6–8]. The determination of compatibility is clearly very complicated, and there are many factors that influence the results of thermoanalytical determinations. The compatibility results between the four explosives and silicone rubber are listed in Table 3. By comparing the activation energies of decomposition for the four explosives bonded with silicone rubber and the activation energy of decomposition for parent explosives. The activation energy of decomposition for polymer bonded explosives (PBXs) and parent explosives are closed, and the melting points of four explosives with silicone rubber are not lower by more than 2 °C than

Table 3
Compatibility test between the explosives and contacted materials

Explosives or PBXs	T_m (°C)	T_p (°C)	E_a (kJ mol^{-1})	$-\gamma_a$[a]
PETN	142.6	208.3	175	0.998
RDX	207.2	241.1	144	0.962
HNS	318.0	331.9	197	0.993
HMX	197/281.5	285.4	444	0.989
PETN/silicone	142.8	207.81	153	0.987
RDX/silicone	208.0	242.1	162	0.996
HNS/silicon	318.2	336.2	169	0.998
HMX/silicone	196.3/280	287.8	365	0.987

[a] $-\gamma_a$: correlation coefficient for linear regression.

that of the parent explosives. These systems are, therefore, compatible with silicone rubber.

4. Conclusion

Thermal behaviors of PETN, RDX, HNS, HMX and the four PBXs are studied using DSC. The kinetic parameters of decomposition are also investigated using non-isothermal technique. The results of this study are in agreement with the literature values [2,3,5–8]. By comparing the melting point, peak temperature of exothermic peak and the activation energies between PBXs and parent explosives, silicone was found to be compatible with PETN, RDX, HNS and HMX.

References

[1] H.E. Kissinger, Anal. Chem. 29 (1957) 217.
[2] T. Ozawa, J. Therm. Anal. 2 (1970) 301.
[3] P.G. Hall, J. Chem. Soc., Faraday Trans., Part 2 67 (1971) 556.
[4] M. Herrmann, W. Engel, N. Eisenreich, Propell. Explos. Pyrot. 17 (1992) 190.
[5] Z.R. Liu, C.M. Yin, Ch.Y. Wu, M.N. Chang, Propell. Explos. Pyrot. 11 (1986) 11.
[6] J. Harris, Thermochim. Acta 14 (1976) 183.
[7] M.O. Hemmila, J. Therm. Anal. 25 (1982) 135.
[8] G. Krien, in: Proceedings of the First Symposium on Chemical Problems Connected with the Stability Explosives, 1967, p. 66.
[9] D. Skinner, D. Olson, A. Block-Bolten, Propell. Explos. Pyrot. 23 (1997) 34.