Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 2, 463–467

THERMAL DECOMPOSITION PROPERTIES AND COMPATIBILITY OF CL-20, NTO WITH SILICONE RUBBER

J.-S. Lee[1*] *and K.-S. Jaw*[2]

[1]Department of Chemistry, Chung Yuan Christian University, Chungli, 320, Taiwan, R.O.C., P.O.Box 90008-17-17, Chemical Division, Chung Shan Institute of Science and Technology, Lungtan, 325, Taiwan, R.O.C.
[2]Department of Chemical Engineering, Northern Taipei University of Technology, Peitao, Taiwan, R.O.C.

The new polycyclic nitramine 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW) has been focused as a considerable amount of research recently on investigating its polymorphs, relative stability, and respective reaction chemistry. It is known as CL-20 popularly, CL-20 is a very high-energy and relatively high oxygen balance value crystalline compound whose method of synthesis and detailed performance data are still classified. 5-oxo-3-nitro-1,2,4-triazole (NTO, or nitrotriazolone) was an insensitive molecule comparison general explosives, and the NTO based polymer bonded explosives (PBX) was a low vulnerability explosive. Both energetic materials are all very important high explosives, which is used in a variety of military formulations widely owing to the properties of high energy and desensitization of PBX, many researchers have demonstrated the usefulness of above two energetic materials in explosive component. In this work, the thermal decomposition characteristics of explosives CL-20 and NTO were studied using thermal analytical techniques (TG, DSC), then the compatibility of above two explosives with silicone rubber, and the decomposition kinetic parameters such as activation energies of decomposition, the frequency factor of the decompose reaction are also evaluated by non-isothermal DSC techniques.

Keywords: *CL-20, compatibility, DSC, NTO, polycyclic nitramine, silicone rubber, TG*

Introduction

CL-20 is the highest energy molecular explosive has known to human, with a chemical formula of $C_6H_6N_{12}O_{12}$ and the basic structure consists of a rigid isowurtzitane cage with a nitro group attached to each of six bridging nitrogens within the cage. HNIW have an oxygen balance value of –11% (the oxygen balance value of RDX and HMX is –21.6%), which is higher than the current explosive such as RDX (Hexogen, cyclotrimethylenetrinitramine, Research Development Explosive) and HMX (cyclotetramethylenetetranitramine, nomenclature by Great Britain, high melting point Explosive, and named Octogen by Germany). The potential military applications for CL-20 include minimum-signature tactical propulsion for strategic missiles or space launches, and special warheads for 'smart' or light weapons [1]. The potential non-military applications include charge and explosives for construction and structure demolition. CL-20 was first synthesized in 1987 by chemist Nielsen, at the Naval Weapons Center, China Lake. Two synthetic routes to the compound from a precursor are used currently. Both syntheses were designed to introduce the compound's high-energy nitramine functional groups at the last step in the process, a nitration, because of safety concerns. CL-20 is currently in the pilot-plant stage both at Thiokol and Aerojet. Applications for the high-energy compound are under development, and several commercial and military products based on CL-20 are planned. In the same way, maximum performance in the field of explosive compounds for military warheads has been known as a driving force behind research.

A part of their effort involves research on the explosive itself in order to develop stable explosive formulations which best utilize the properties of CL-20, particularly interested in extrudable CL-20 formulations. Paste extrudable Explosive (PEX) [2] formulations are gelled materials which are designed to remain extrudable throughout their stockpile lifetime. Maintaining the particle size distribution of the crystalline explosive contained within these formulations is critical to the stability of those materials as their age. In order to avoid changes in particle size distribution and develop stable explosive in polymer binder systems is quite important.

On the other side, although intensive research was pursued to find the higher performance molecule, the problem of warhead vulnerability has become acute more and more over the past twenty-five years or so. New PBX compositions were possible to resist the aggressive phenomena (namely, immunity to fire and to bullet impact) considered, which consist of 3-D

* marble.lee@msa.hinet.net

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

polymer matrix encasing a granular explosive. NTO is one of products of relatively low sensitively compared to conventional secondary explosives. Their performance levels are not as high, though NTO's is higher in detonation velocity (8510 m s^{-1}, density is 1.91 g cm^{-3}), and as a raw material for use in formulating composite explosives, only NTO can easily be obtained in particle size.

Energetic materials such as high performance but low vulnerability are the main charge explosives of warhead and as an energetic component of composite propellants, have recently occupied a key position in field of explosive and propellants. The kinetic and mechanism of its thermal decomposition are 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 [2–7] and the thermal decomposition studies of the explosives have been reported [8–12]. 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 [13–17]. The present work derives the kinetic parameters of the decomposition were computed using two equations based on variable heating rate method viz., Kissinger and Ozawa equation, and the thermal behavior of CL-20 and NTO are investigated by DSC/TG. The compatibility of silicone rubber with above two explosives are also evaluated by comparison the thermal behaviors between the explosives with silicone rubber and the parent explosives.

Experimental

NTO supplied by S.N.P.E, France, CL-20 supplied by U.S.A., and silicone rubber (Slygard 182) are the raw materials in this work, CL-20 and NTO composed of silicone rubber in a mass ratio of 4:1, respectively. A Differential Scanning Calorimetry (model 910 DSC) and Thermogravimetry (model 951), made by Du Pont Ltd. were used. The sample mass of explosives was about 5 mg and aluminum crucible with closed vessel was used in DSC analysis, but opened vessel with aluminum pan was used in TG analysis. To determine the kinetic parameters of the thermal decomposition of explosives and PBX those containing silicone rubber, the heating rates are from 2 to 30°C min^{-1} under a static atmosphere were employed for these experiments. In order to study the fully decomposition process and avoid evaporation, closed vessels and high pressure version was suggested the best option in measurement.

Results and discussion

DSC curves of CL-20, NTO and two different explosives based PBX can be seen in Fig. 1. In the CL-20 curve, one small endothermic peak appears at about 165–170°C. Then the decomposition of explosive takes place and a sharp exothermic peak with the maximum is observed from 236 to 263°C with different heating rate. The onset temperature of exothermic peak were 208, 220, 228, 236°C, respectively for 2, 5, 10 and 20°C min^{-1} heating rate. These results were agreed with Foltz [13]. But in CL-20/silicone traces, a small endothermic peak also observed from 165 to 179°C from 2 to 20°C min^{-1} heating rate, then accomplished a sharp exothermic peak with the maximum from 237 to 264°C with 2 to 20°C min^{-1} heating rate, the relatively high and sharp exothermic decomposition peaks of explosive always found in DSC/DTA curves, because the fast propagated reaction occurs in explosive, and the maximum decomposition temperatures of CL-20/silicone explosive slightly shift to the higher temperature than that of CL-20 explosive. In

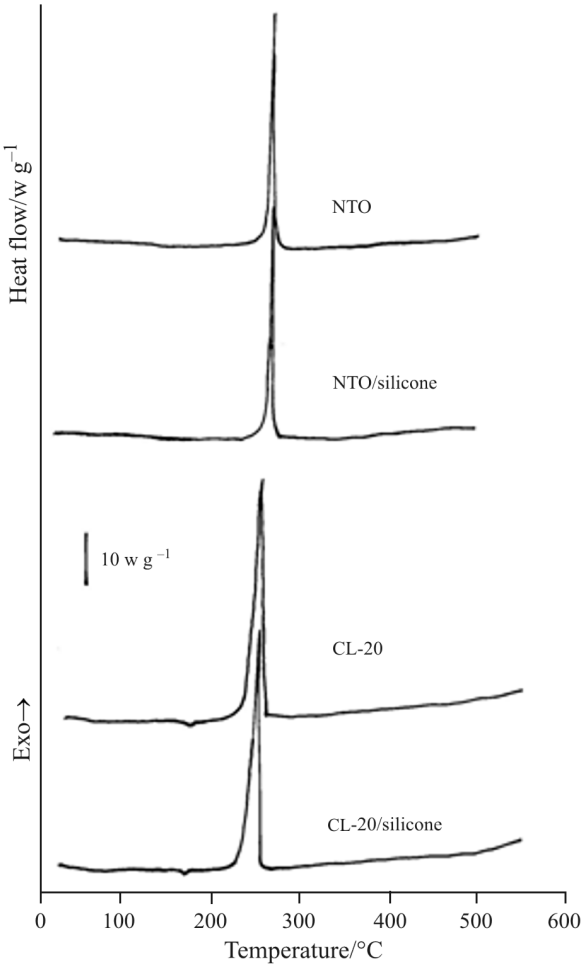

Fig. 1 DSC curves of NTO, CL-20 and two PBXs with a 10°C min^{-1} heating rate, under a static air atmosphere

Table 1 Kinetic parameters of thermal decomposition for explosives

Explosives	E/kJ mol^{-1}	$-\gamma_b$	A/s^{-1}	T/°C
CL-20	191.7±3.5	0.9975	$2.08\cdot10^{21}$	236–263
CL-20 (under 44 μm)	160.88	0.9884	$2.54\cdot10^{13}$	241–265
CL-20 (under 246 μm)	226.83	0.9995	$2.28\cdot10^{24}$	238–253
NTO	352.7±4.0	0.9983	$9.85\cdot10^{35}$	274–288
CL-20/silicone	177.7±5.6	0.9965	$6.29\cdot10^{19}$	237–264
NTO/silicone	258.7±3.4	0.9980	$1.71\cdot10^{27}$	267–283

$-\gamma_b$: correlation coefficient for linear regression

the NTO curves, it showed no endothermic peak at lower temperature region before decomposition, but accomplished a sharp exothermic peak from 274 to 288°C with 5 to 30°C min^{-1} heating rate. The onset temperature were 265, 270, 275 and 278°C for 5, 10, 20 and 30°C min^{-1} heating rate, respectively. And in the NTO/silicone curves, it also no endothermic peak before decomposition but accomplished a sharp exothermic peak from 267 to 284°C with 5 to 30°C min^{-1} heating rate. The onset temperature were 251, 253, 261 and 267°C for 5, 10, 20 and 30°C min^{-1} heating rate, respectively. The maximum decomposition temperatures of NTO/silicone explosive are shift to lower temperature than that of NTO explosive. According DSC traces in this work, no matter what, NTO and NTO/silicone explosives always show higher decomposition temperature than that of CL-20 and CL-20/silicone explosives, and the onset temperature of exothermic peaks of NTO are almost 50°C higher than that of CL-20, this indicate that the thermal resistivity of NTO was higher than that of CL-20.

The kinetic parameters of two energetic materials are listing in Table 1. The kinetic parameters of decomposition for four explosives and two different particle sizes of CL-20 were determined via DSC using Kissinger method [2]. Large particle size of CL-20 explosive gave higher activation energy of decomposition and a narrow peak temperature range than that of small particle size of CL-20 explosive. This result was usually found in DSC/DTA traces with different size sample (Fig. 2) and the relevant equation of kinetic analysis is:

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

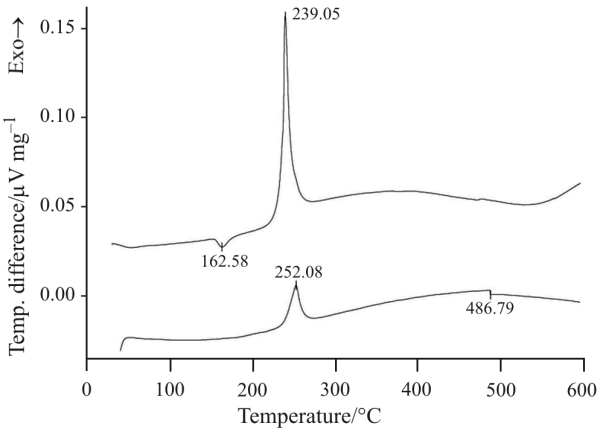

Fig. 2 DTA curves of two different sizes for CL-20, the particle size of upper curve was passed 60 mesh sieve, and the low curve was passed 325 mesh sieve

where ϕ is heating rate and T_p is 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 *vs.* values of $1/T_p$. A straight line through the data points was obtained by linear regression. The activation energy, E, was determined from the slope, and the frequency factor, A, was determined from the intercept.

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

Table 2 Compatibility test between the explosive and contacted material

Explosives or PBXs	T_m/°C	T_p/°C	E_a/kJ mol^{-1}	$-\gamma_a$
CL-20	165–170	236–263	191.7	0.9975
NTO	NA	274–288	352.7	0.9983
CL-20/silicone	165–179	237–264	177.7	0.9965
NTO/silicone	NA	267–283	258.7	0.9980

$-\gamma_a$: correlation coefficient for linear regression

clearly very complicated, and there are many factors that influence the results of thermoanalytical determinations. The compatibility results between the two explosives and silicone rubber are listing in Table 2. By comparing the activation energies of decomposition between two explosives with silicone rubber to parent explosives, for NTO and its PBX, the activation energy of decomposition for PBX and parent explosive are not closed, this indicates that NTO is not compatible with silicone rubber. But the difference on melting points and the maximum decomposition temperature of CL-20 explosive and CL-20 explosive with silicone rubber are not more than 2°C, and the activation energies of CL-20 and its PBX are very closed, CL-20 and silicone rubber system are therefore considered compatible.

TG curves of CL-20, NTO and two PBXs are shown in Fig. 3, the mass loss percentage of CL-20 and its PBX is so large within a quite narrow temperature range, so that the dynamic TG data is not able to calculate the kinetic parameters. But it is easier to evaluate the decomposition kinetic parameters from the dynamic TG data of NTO and NTO based PBX, because the relation between mass loss percentage and temperature are good, then the decomposition kinetic parameters of NTO and NTO based PBX can be obtained from non-isothermal TG technique, the result are listing in Table 3. The activation energy of NTO is slightly lower than NTO/silicone, it is suggested that NTO is easy to decomposition than that of NTO based PBX. In TG analysis, although the activation energy of decomposition for NTO and NTO/silicone are very closed, but the difference of maximum decomposition temperature of NTO and NTO/silicone are larger than 2°C in DSC analysis, we still suggest that NTO explosives are not compatible with silicone rubber.

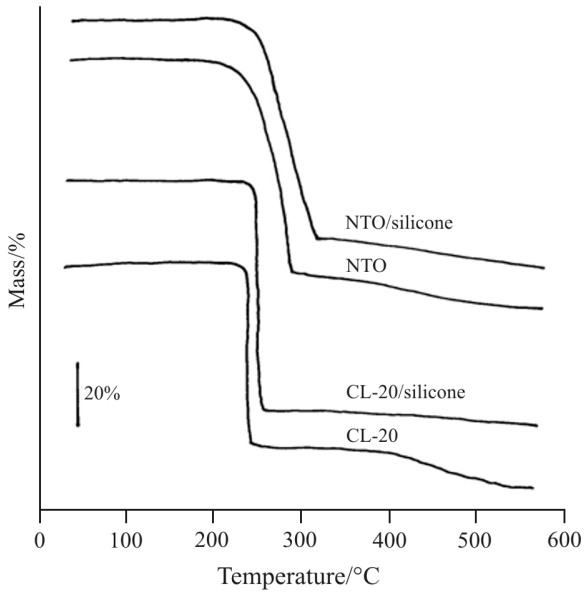

Fig. 3 TG curves of NTO, CL-20 and two PBXs with a 10°C min^{-1} heating rate, under a static air atmosphere

Table 3 Kinetic parameters of NTO and NTO/silicone

Mass loss/%	NTO		NTO/silicone	
	$-\gamma_a$	E_a/kJ mol^{-1}	$-\gamma_a$	E_a/kJ mol^{-1}
1	0.986	106.9	0.999	109.6
3	0.979	108.4	0.998	115.8
5	0.982	110.4	0.996	112.8
7	0.986	111.6	0.996	112.8
9	0.988	110.8	0.999	114.5
15	0.992	110.7	0.997	118.6
20	0.994	110.0	0.998	117.8

γ=correction coefficient for linear regression analysis of Kissinger plot, b=log$P$ (E/R_{Ti})–log$P$(E/RT_{i-1})

There are many routes to synthesis HNIW, benzylamine and glyoxal are always the raw materials for preparation HBIW, then TADB will be the intermediate product, finally HNIW was obtained by nitration TADB with nitrosodium tetrafluoroborate ($NOBF_4$) and nitronium tetrafluoroborate (NO_2BF_4). Figure 4 shows two magnifications of SEM photo-

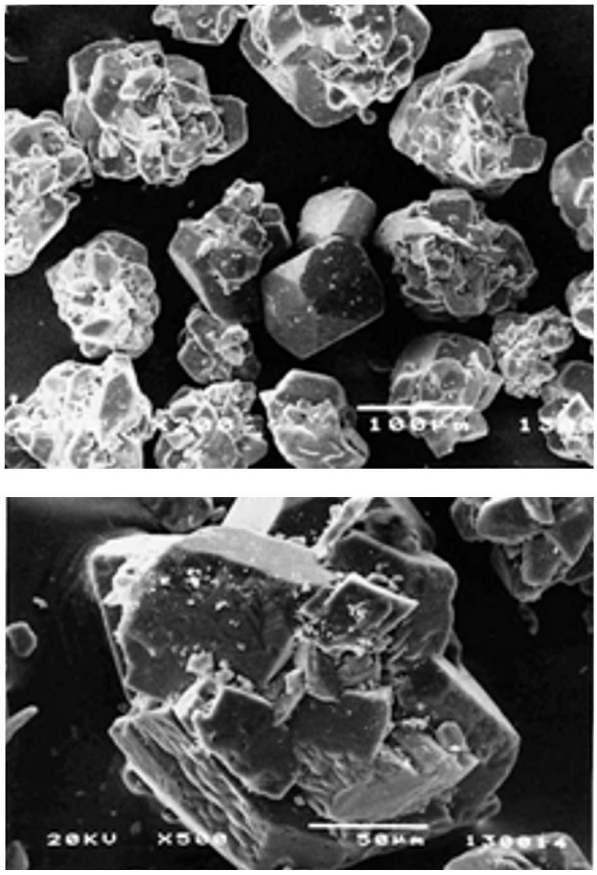

Fig. 4 Two magnifications of SEM photographs of alpha phase crystals used in this experiment

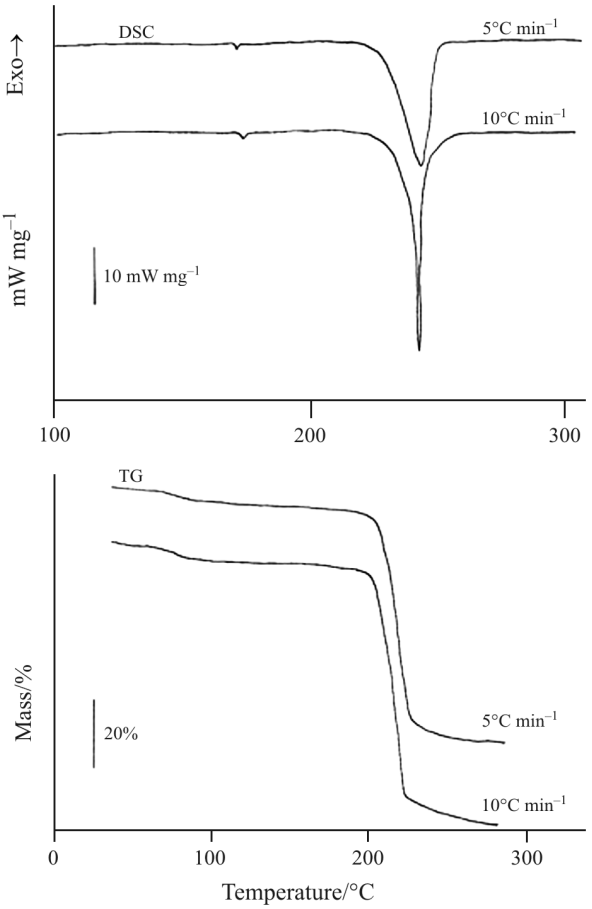

Fig. 5 DSC and TG curves of HNIW

Table 4 Maximum endothermic peak and exothermic peak response as a function of different heating rates

Scan rate/ °C min^{-1}	Foltz results Endotherm T_{max}/°C/ Exotherm T_{max}/°C	Thermal experiments Endotherm T_{max}/°C/ Exotherm T_{max}/°C
10	172/247	172.1/243.3
5	169/244	169.5/241.3

graphs of HNIW crystals used in the experiments, this morphology of crystal is the alpha phase crystals, these results are in agreement with Foltz [18]. And the thermal properties of HNIW that synthesis by Chung Cheng Institute, Taiwan, R.O.C. were also characterized by DSC/TG technique (shown in Fig. 5). On the DSC curves the maximum endothermic peak and the maximum exothermic peak are closed to Foltz's [19] results. According TG analysis, some water was absorbed by HNIW. Table 4 listed the data different between literature and this work.

Conclusions

Thermal behaviors of CL-20, NTO and two PBXs are studied using DSC and TG. The kinetic parameters of decomposition are also investigated using non-isothermal technique. The results of this study are in agreement with the literature values [19]. By comparing the melting point, temperature of exothermic peak and the activation energies between polymer bonded explosives and parent explosives, silicone was found to be compatible with CL-20 explosive but not for NTO explosive.

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Received: September 22, 2005
Accepted: May 25, 2006

DOI: 10.1007/s10973-005-7325-0