

Compatibility Assessment of Thermoplastic Formulations

Daniel McAteer, Matthew Weaver, Lisa H. Blair, Nathan Flood
and Sally E. Gaulter

Centre for Defence Chemistry, Cranfield University, Defence Academy of the United Kingdom,
Shrivenham, SN6 8LA, UK

d.mcateer@cranfield.ac.uk

Abstract: Prior to the large-scale preparation of any new chemical formulation an assessment of the potential reactivity between the components must be carried out. This practice, which is common to many fields including pharmaceutical science, is particularly essential in the case of energetic formulations whose chemical incompatibility may result in an unexpected and potentially explosive decomposition. The common method used to investigate incompatibility is to heat 1:1 (w/w) formulations and evaluate the variation in their thermal stability with respect to the neat, pristine explosive. The techniques used are: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), vacuum stability and heat flow calorimetry. As trends in energetics move towards safer formulations the components are more commonly selected for their high thermal stability and low sensitivity to initiation. However, recently prepared thermoplastic formulations which incorporate a thermally stable explosive, 2,2',4,4',6,6'-hexanitrostilbene (HNS II), and a selection of high-melting-point thermoplastics produced anomalous results during their compatibility assessment leading to the suggestion that historical tests originally devised for less thermally stable materials, such as N,N',N''-trinitro-1,3,5-triazacyclohexane (RDX), may not be directly transferable to the newer generations of insensitive explosive formulations.

Keywords: formulation; compatibility; differential scanning calorimetry; thermoplastic

1 Introduction

The development of an explosive formulation is a process of compromise, which seeks to modify the physical properties of an energetic material for a particular application. By incorporating a polymeric binder with an explosive it is possible to produce a less hazardous composition. However, the addition of a binder may also dilute the energetic content of a formulation and, as a result, a “trade-off” must be reached between the desired performance and the required physical, chemical and hazard properties.

Thermally-extruded polymer-bonded explosive (PBX) formulations have been investigated as potential developments in the field of explosives research [1]. In a recent project between Cranfield University and African Explosives Limited (AEL), an investigation was made into the development of a thermally-extrudable PBX formulation utilising commercially sourced thermoplastics as the polymeric binder. The tested formulations were based on the thermally stable explosive hexanitrostilbene (HNS, Figure 1).

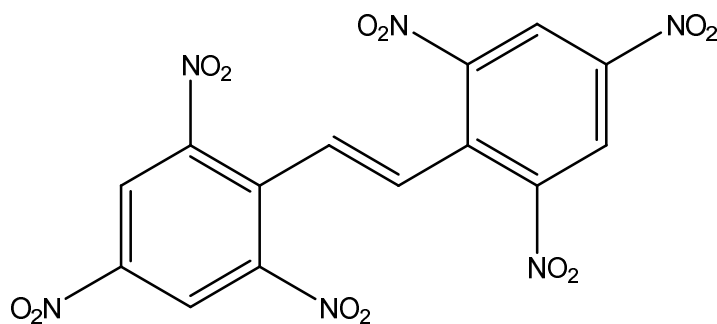


Figure 1: 2,2',4,4',6,6'-Hexanitrostilbene (HNS)

An initial assessment was made of the chemical compatibility of each of the sourced polymers with HNS. Assessment of chemical compatibility is an essential practice in the development of any PBX formulation. The tests utilised for compatibility assessment seek to elucidate whether the explosive and the additives (polymeric binder, plasticiser, etc) react to compromise either the physical, chemical or hazard properties of the components [2].

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and vacuum stability are among the most common techniques used to assess compatibility [3-6]. Furthermore these techniques have been outlined in the North Atlantic Treaty Organisation (NATO) standardisation agreement (STANAG) 4147, which is often cited in research of PBX formulations as the guideline on compatibility [6-7]. Essentially the procedure described is designed to assess compatibility between energetic compositions and the materials that they may be exposed to during their storage and use over the materials lifetime [8]. Nonetheless, the tests and their pass/fail criteria have been reported in assessments of the potential reactivity between components of formulations.ⁱ

Each of the aforementioned techniques (DSC, TGA and vacuum stability) enables the researcher to probe the potential reactivity between PBX components however each of the techniques is limited.ⁱⁱ The recommended tests are capable of detecting thermal events and variations in mass/gas generation which, although useful, do not probe the chemistry between the formulation components as would be possible if modern hyphenated techniques such as thermogravimetric analysis – mass spectrometry (TGA-MS) were used [9]. As a result, it is prudent to assess compatibility by utilising multiple tests. This paper presents the DSC, TGA and vacuum stability assessment results gathered from the investigation of a selection of thermoplastic PBX formulations.

1.1 Thermoplastic Formulations

Thermal extrusion is commonplace in industrial manufacturing of plastics and therefore a large number of potential polymeric binders were considered for the thermoplastic formulation. From the outset it was considered prudent that the temperature at which the formulation would be thermally extruded should be far below the temperature of decomposition of the composition. As a result, polymers with a melting point of <150 °C were researched. The polymers selected for use were polyolefin and ethylene vinyl acetate copolymers (EVA) sourced from Dow and DuPont respectively.

ⁱ The STANAG provides detailed description of compatibility tests but it also emphatically states that it should not be used as a guideline for PBX formulation compatibility but rather compatibility of explosives with ammunition component materials, “The STANAG is not concerned with compatibility between ingredients in explosive compositions and the consequent stability of such compositions” [7].

ⁱⁱ “A major weakness of these tests is that they provide no indication of the type of reaction occurring, or of the reaction products formed” [2].

2 Experimental

2.1 Materials

The polyolefin polymers, Engage 8401 and 8402, were purchased from Resinex, a UK distributor of Dow™. The ethylene vinyl acetate copolymers (EVA), Elvax 40W, 210W, 240A and 250A, were provided by DuPont™. The HNS II (II indicates the particle size grade) was purchased from Chemring Energetics UK.

2.2 Preparation of Thermoplastic Formulations

A known mass of powdered explosive (X mg) was suspended in a solution containing a known mass of dissolved polymer (Y mg) in a nickel crucible; the masses are shown in Table 1. The suspension was agitated with a bone spatula until the solution had evaporated to dryness. The resultant polymer/explosive composition was allowed to dry at room temperature (20°C) for 24 h prior to further drying at 3 h under vacuum over silica.

Table 1: Small-scale 1:1 thermoplastic formulations with HNS II

Polymer	Explosive Mass (X mg)	Polymer Mass (Y mg)
Elvax 40W	100	110
Elvax 210W	100	103
Elvax 240A	110	111
Elvax 250A	110	108
Engage 8401	105	102
Engage 8402	102	102

2.3 Analytical Methods

2.3.1 DSC

Each HNS II formulation was investigated in duplicate using a Mettler-Toledo differential scanning calorimeter instrument, model DSC1 STARe System, equipped with a liquid nitrogen low temperature attachment and an autosampler (heating rate ranged between 2 – 20°C/min; flow rate of nitrogen gas: 80 ml/min; sample size: 1-10 mg in 40 µl aluminium dishes). All crucibles were sealed with a pierced lid. All data was interpreted using STARe Software version 10.00 (Build 2480).

2.3.2 TGA

A Mettler Toledo M3 TG50 with a Mettler TA4000 interface was used with N₂ flowing through the instrument (200 ml/min flow rate). Samples weighing between 1 – 15 mg were placed into alumina oxide crucibles and their weight loss was examined by carrying out both dynamic and isothermal temperature programs. The dynamic temperature program remained the same for each formulation (30 – 400°C) whereas the isothermal program varied in response to the position of the decomposition onset recorded within the dynamic results. The isothermal datasets were collected over a period of 900 mins at 20°C below the recorded decomposition onset temperature for each formulation. All TGA collections were run at 2°C/min. Data interpretation was performed using STARe Software version 10.00 (Build 2480).

2.3.3 Vacuum Stability

A vacuum stability assessment (STANAG 4147 test 1b) was carried out on 2 x 2.5 g 1:1 formulations of Elvax 40W and HNS II. This test involves heating the 1:1 compositions within evacuated glass vials for 40 h at 100°C. The volume of gas which evolves from the sample under heat is measured and compared to control samples of the neat explosive and pristine polymeric binder. The materials are deemed to be chemically compatible when the volume of gas that is generated is less than 5 ml after 40 h.

3 Results and Discussion

In each of the assessed DSC heating rates it was evident that the variation in the peak decomposition temperature of the formulation varied significantly from that of the neat explosive, HNS II. The variation was such that in most cases it would be a clear indication of chemical incompatibility.

Tables 2, 3 and 4 show the DSC results attributed to the HNS II formulations collected at 2, 10 and 20°C/min respectively. Elvax 40W displayed the greatest effect upon the decomposition temperature of HNS II. A 1:1 formulation with Elvax 40W was shown to shift the decomposition temperature by approximately 17% or more than 50°C (with respect to the decomposition temperature of the neat explosive). In general any variation in decomposition temperature of 20°C or more is taken as an indication of chemical incompatibility according to the STANAG guideline [8].

Table 2: HNS II Formulations DSC results (2°C/min)

Polymer	Average Onset (°C)	Average Peak (°C)	Deviation (°C)	Deviation (%)
Neat Explosive	321.5	333		
Elvax 40W	271	278	55	17
Elvax 210W	272	280.5	52.5	16
Elvax 240A	271.5	281	52	16
Elvax 250A	274	283	50	15
Engage 8401	281.5	291	42	13
Engage 8402	282	290.5	42.5	13

Table 3: HNS II Formulations DSC results (10°C/min)

Polymer	Average Onset (°C)	Average Peak (°C)	Deviation (°C)	Deviation (%)
Neat Explosive	325	354.5		
Elvax 40W	289.5	295.5	59	17
Elvax 210W	291.5	299.5	55	16
Elvax 240A	299	309	45.5	13
Elvax 250A	296.5	310	44.5	13
Engage 8401	299	315	39.5	11
Engage 8402	306.5	320.5	34	10

Table 4: HNS II Formulations DSC results (20°C/min)

Polymer	Average Onset (°C)	Average Peak (°C)	Deviation (°C)	Deviation (%)
Neat Explosive	349.5	365.5		
Elvax 40W	296.5	304.5	61	17
Elvax 210W	302	314	51.5	14
Elvax 240A	304	314.5	51	14
Elvax 250A	304.5	313.5	52	14
Engage 8401	311.5	322.5	43	12
Engage 8402	311	318	47.5	13

The DSC measurements were complimented with the DSC measurements of the pristine polymers as shown in Tables 5, 6 and 7. In each of the EVA based polymers (Elvax 40W, 210W, 240A and 250A) two endothermic peaks were observed and recorded. As with all thermoplastics an endothermic peak would be expected this corresponds to the melting point of the polymer. In each of the polymers the first endotherm observed is approximately equivalent to the melting point quoted in the commercial data sheet. In the case of the EVA polymers the second endotherm was initially believed to be a second melt prior to decomposition of the material. However, upon assessment of one of the neat polymers (Elvax 40W) by dynamic TGA (30 - 400°C) it was observed that this melting point corresponded to a significant mass loss and that the second endotherm may be attributed to decompositionⁱⁱⁱ. This would suggest that while the decomposition temperature of HNS II was compromised by incorporation with Elvax 40W, it was not due to the reaction between the explosive and polymer. Instead the results might indicate that decomposition of the formulation was caused by the reaction of the explosive with the decomposition products of the polymer.

This observation was difficult to prove due to the broad nature of the decomposition endotherm peak in the Elvax DSC's, as a result the true onset temperature of the decomposition was not found and thus a correlation between the temperature of decomposition of the formulation and the decomposition of the polymer could not be made.

Accordingly the formulations were assessed by TGA and vacuum stability to qualify the observations of the DSC. In the case of Elvax 40W/HNS II the 1:1 formulation displays good thermal stability at 100 and 200°C. This is observed in the vacuum stability result for the formulation which shows the generation of 0.15 ml of gas from the composition after 40 h at 100°C and the isothermal TGA experiment which displays mass loss of approximately 2% at 200°C. When the temperature of the isothermal experiment was increased to 245°C the mass loss of the Elvax 40W/HNS II formulation was observed to increase to approximately 25%.

Table 5: Pristine polymers DSC results (2°C/min)

Polymer	Endotherm 1 Peak (°C)	Endotherm 2 Peak (°C)
Elvax 40W	X	323
Elvax 210W	X	326
Elvax 240A	X	327
Elvax 250A	X	326
Engage 8401	X	-
Engage 8402	100	-

ⁱⁱⁱ Many EVA materials are recommended for use at temperatures over 200-230°C although no formal decomposition temperature has been found in the literature [10].

Table 6: Pristine polymers DSC results (10°C/min)

Polymer	Endotherm 1 Peak (°C)	Endotherm 2 Peak (°C)
Elvax 40W	50	348
Elvax 210W	49	349
Elvax 240A	47	352
Elvax 250A	48	352
Engage 8401	84	-
Engage 8402	101	-

Table 7: Pristine polymers DSC results (20°C/min)

Polymer	Endotherm 1 Peak (°C)	Endotherm 2 Peak (°C)
Elvax 40W	52	360
Elvax 210W	54	364
Elvax 240A	51	363
Elvax 250A	51	364
Engage 8401	85	-
Engage 8402	100	-

When DSC and TGA are used to assess chemical compatibility, the sample mass is necessarily limited to the mg scale. However, it is suggested by the results obtained herein that slight variations in sample mass have the potential to significantly affect the values recorded. This was observed when the analyses of 1.5 mg and approximately 5 mg of the Elvax 40W/HNS II formulation were compared. These results are highlighted in Table 8 and Figure 2, and show a variation in the initial mass loss, between 30-280°C, of 4% to 17% depending on the sample size. Figure 3 shows the dynamic TGA results associated with the Elvax 40W/HNS II formulation as well as its associated DSC results compared to the DSC results of the neat HNS II explosive.

Table 8: HNS II/Elvax 40W formulation TGA mass losses recorded (2°C/min)

Sample	Mass (mg)	Mass Loss Between 30-280°C (%)	Mass Loss Between 280-400°C (%)
1	1.4567	17.00	47.00
2	4.3569	4.00	44.00
3	5.0312	3.44	42.00

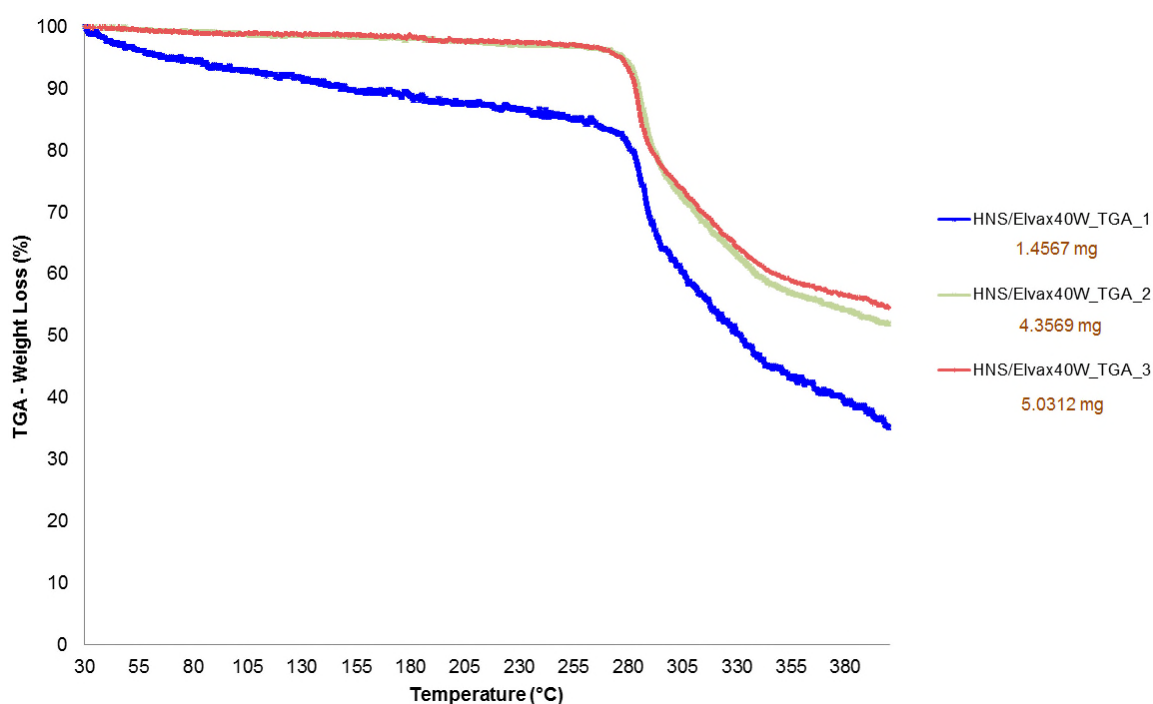


Figure 2: HNS II/Elvax 40W formulation TGA sample overlay (2°C/min)

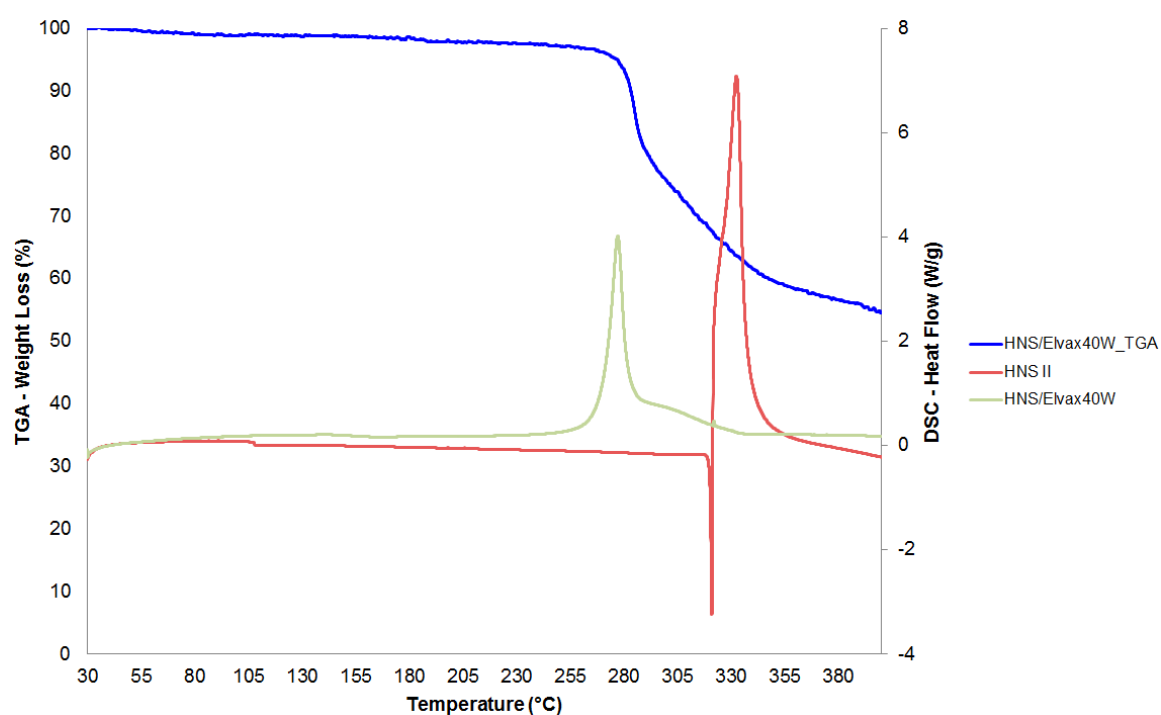


Figure 3: HNS II/Elvax 40W formulation DSC and TGA results (2°C/min)

In the case of the polyolefin materials Engage 8401 and 8402 the early onset of decomposition in their formulations with HNS II is not understood. At all heating rates (2, 10 and 20°C/min) the decomposition temperature of the HNS II/Engage 8401 and HNS II/Engage 8402 formulations were observed to be approximately 40°C lower than that of the neat explosive as can be seen in Figures 4 and 5. Unlike the EVA polymers there was no obvious indication of decomposition when the DSC thermograms of the pristine polymer were assessed.

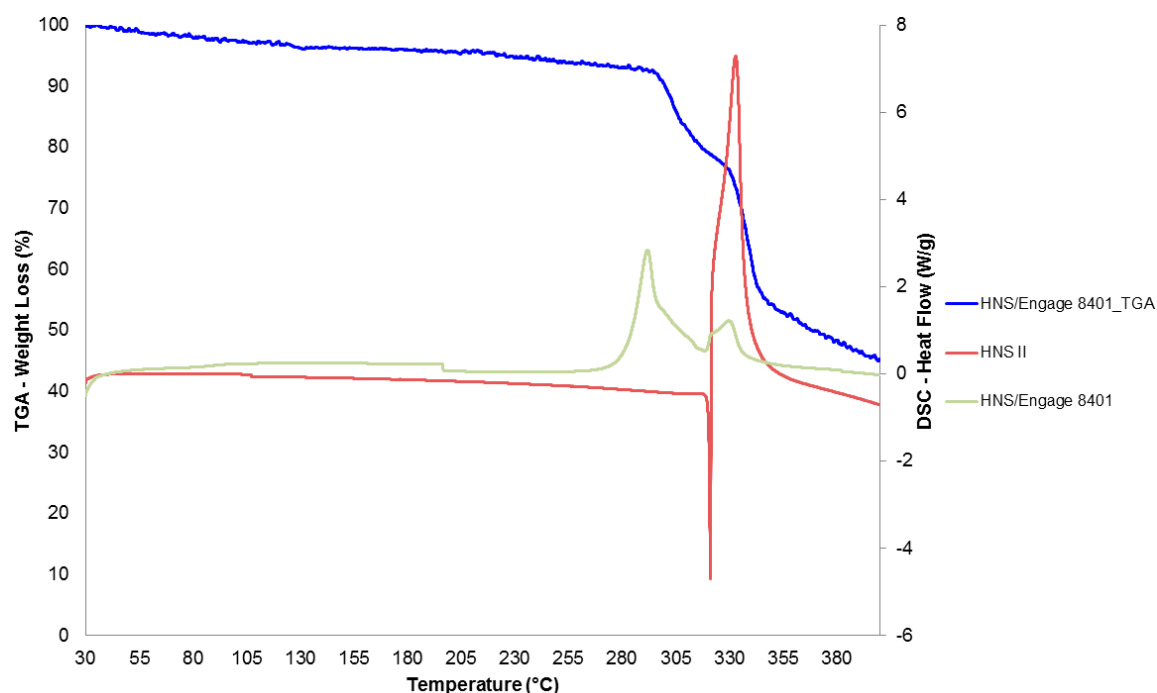


Figure 4: HNS II/Engage 8401 formulation DSC and TGA results (2°C/min)

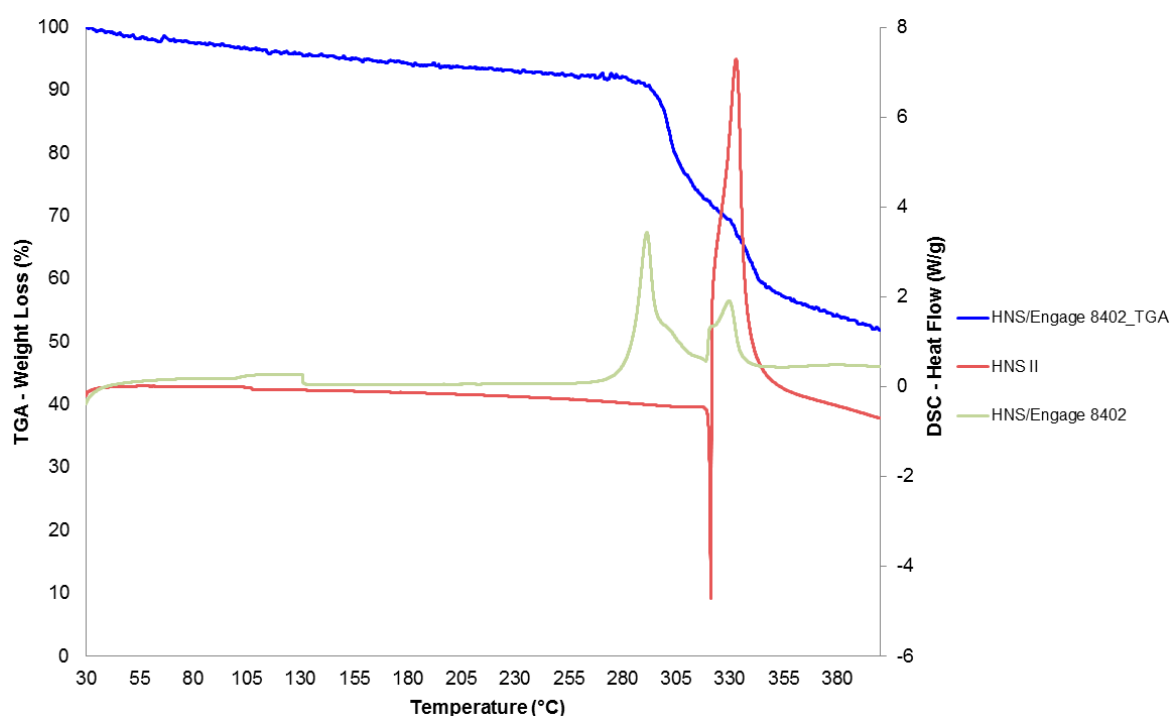


Figure 5: HNS II/Engage 8402 formulation DSC and TGA results (2°C/min)

4 Conclusions

The formulations of HNS II and a selection of thermoplastic polymers have been evaluated by DSC, TGA and vacuum stability. The chemical compatibility of the formulations has been investigated but insufficient evidence has been gathered to allow for judgement on the compositions assessed. A further study will be conducted utilising modern hyphenated analysis techniques such as TGA-MS, which may provide additional data on the nature of the thermal events observed. The current techniques used in chemical compatibility assessment may be improved by further development of chemical analyses, which validate the endothermic and

exothermic events observed in DSC, the mass loss observed in TGA and the gas evolution in vacuum stability. With this improved understanding it may be possible to better judge the stability and compatibility of explosive formulations and allow the advances in modern chemical analyses to progress the development of safe and stable energetic compositions.

Acknowledgments

This work was developed from a two year project funded by African Explosives Limited (AEL).

Thanks go to Dr Karlheinz Hausmann (DuPont) for the provision of thermoplastic polymer samples and Mr Anjum Agha for overseeing the vacuum stability tests. A particular debt of gratitude is owed to Dr Matthew Andrews (MSIAC) and Dr Philip Gill (Cranfield University) for their helpful discussions on the topic of chemical compatibility assessment.

References

- [1] J. E. Kowalczyk , M. Malik , D. M. Kalyon , H. Gevgilili , D. F. Fair , M. Mezger, M. Fair safety in design and manufacturing of extruders used for the continuous processing of energetic formulations, *Journal of Energetic Materials*, 25(4), p. 247-271, **2007**.
- [2] L. Malotky, H. Heller, Explosive compatible polymers for defense application, *Journal of Hazardous Materials*, 2(2), p. 189-195, **1978**.
- [3] Q.-L. Yan, S. Zeman, T.-L. Zhang, A. Elbeih, Non-isothermal decomposition behavior of Fluorel bonded explosives containing attractive cyclic nitramines, *Thermochimica Acta*, 574, p. 10-18, **2013**.
- [4] S. Zeman, A. Elbeih, Q.L. Yan, Notes on the use of the vacuum stability test in the study of initiation reactivity of attractive cyclic nitramines in the C4 matrix, *Journal of Thermal Analysis and Calorimetry*, 112(3), p. 1433-1437, **2013**.
- [5] S. Ek, K. Dudek, J. Johansson, N. Latypov, Scale-up and characterization of 3(5),4-dinitropyrazole (DNP) for its use as a melt-cast matrix, in proc. *New Trends in Research of Energetic Materials*, Pardubice, April, **2014**.
- [6] M. A. C. Mazzeu, E. da Costa Mattos, K. Iha, Studies on compatibility of energetic materials by thermal methods, *Journal of Aerospace Technology and Management*, 2(1), p. 53-58, **2010**.
- [7] STANAG 4147 (Ed. 2), Chemical compatibility of ammunition components with explosives (non-nuclear applications), **2001**.
- [8] A. Myburgh, Standardization on STANAG test methods for ease of compatibility and thermal studies, *Journal of Thermal Analysis and Calorimetry*, 85(1), p. 135-139, **2006**.
- [9] J. C. Oxley, J. L. Smith, M. A. Donnelly, K. Collizza, S. Rayome, Thermal stability studies comparing IMX-101 (dinitroanisole/Nitroguanidine/NTO) to analogous formulations containing dinitrotoluene, *Propellants, Explosives, Pyrotechnics*, 41(1), p. 98-113, **2016**.
- [10] R. J. Koopmans, R. van der Linden, E. F. Vansant, Quantitative determination of the vinylacetate content in ethylene vinylacetate copolymers – a critical review, *Polymer Engineering and Science*, 22(14), p. 878-882, **1982**.



DSPACE

<https://dspace.org/>

Compatibility assessment of thermoplastic formulations

McAteer, Daniel; Weaver, M.; Blair, L. H.; Flood, Nathan; Gaulter, Sally E.

2016-07-01

<http://dspace.lib.cranfield.ac.uk/handle/1826/10056>