ENERGETICS RESEARCH INSTITUTE

NDIA

2016 Insensitive Munitions & Energetic Materials Technology Symposium

Compatibility Investigations on Novel Energetic Formulations of Nitrogen Rich Azole [Bistetrazolylamine(BTA)]

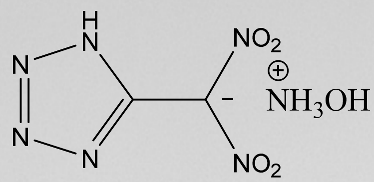
Sasidharan Nimesh*, Pisharath Sreekumar, Zhang Fan and How-Ghee Ang

Energetics Research Institute, Nanyang Technological University, N1-B4a, 50 Nanyang Avenue, Singapore 639798. E-mail: nsasidharan@ntu.edu.sg

Outline

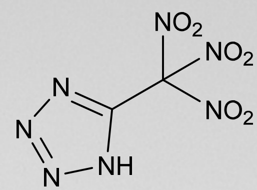
- Background
- Objective
- Bistetrazolylamine and Binders: Synthesis and characterization
- STANAG 4147: Test procedure, criterion.
- Compatibility studies: Results and Discussion
- Activation energy: Comparison with various systems
- Conclusion

High Nitrogen Tetrazole Derivatives as Insensitive High Energy-Density Materials



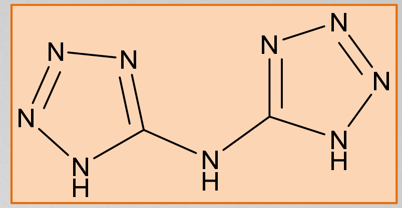
Hydroxylammonium 5-dinitromethyl tetrazolate

HyAmNTz



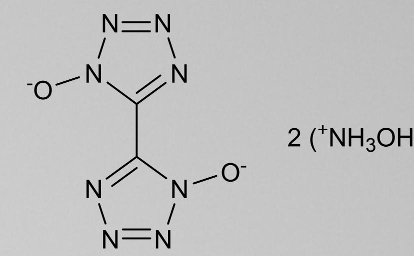
5-trinitromethyl tetrazole

TNMTz



Bistetrazolylamine

BTA



Bis(hydroxylammonium) 5,5'-bistetrazolyl diolate

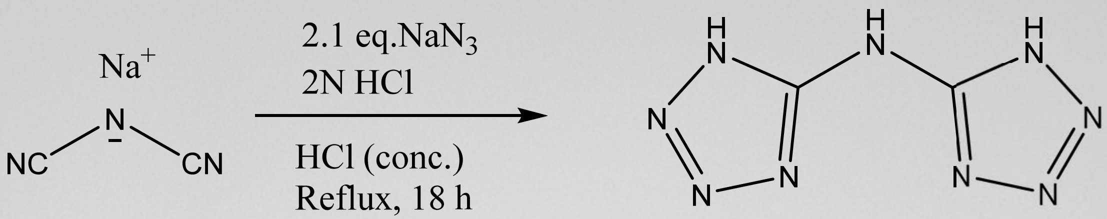
TKX-50

Properties	Tetrazole derivatives				Conventional explosives	
	HyAmNTz	TNMTz	**BTA**	TKX-50	RDX	CL-20
Density, g/cc	1.969	1.918	**1.86**	1.88	1.81	2.03
Thermal stability, $T_{dec.}$ ^{0}C	150	100	**250**	221	210	215
Explosive Performance						
VOD, m/s	-	-	**9120**	9698	8983	9455
$P_{c\text{-}j}$, GPa	-	-	**34.3**	42.4	38.0	46.7
Sensitivity						
Friction sensitivity, N	144	9	**>360**	120	120	48
Impact sensitivity, J	5.5	9	**30**	20	7.5	4
Spark sensitivity, J	-	-	**7.5**	0.10	0.20	0.13

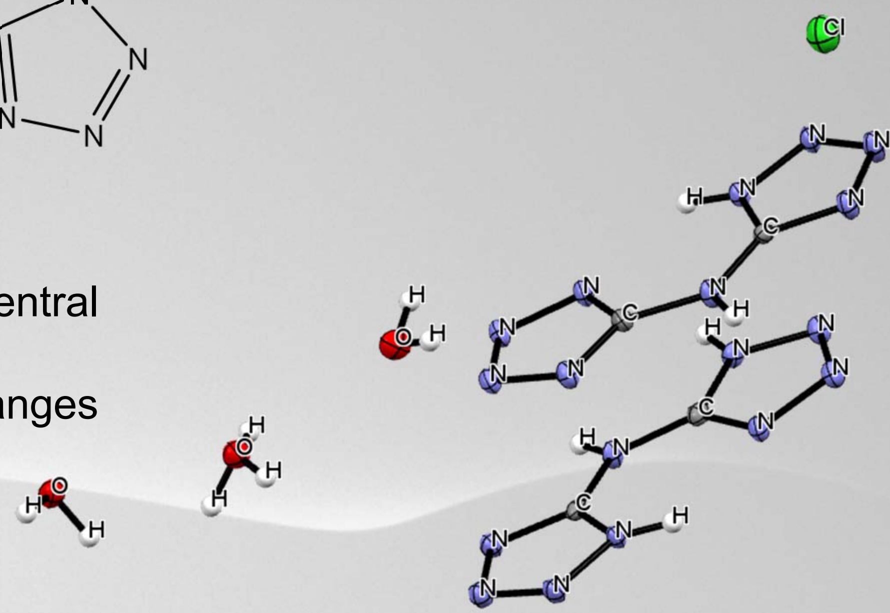
Objective

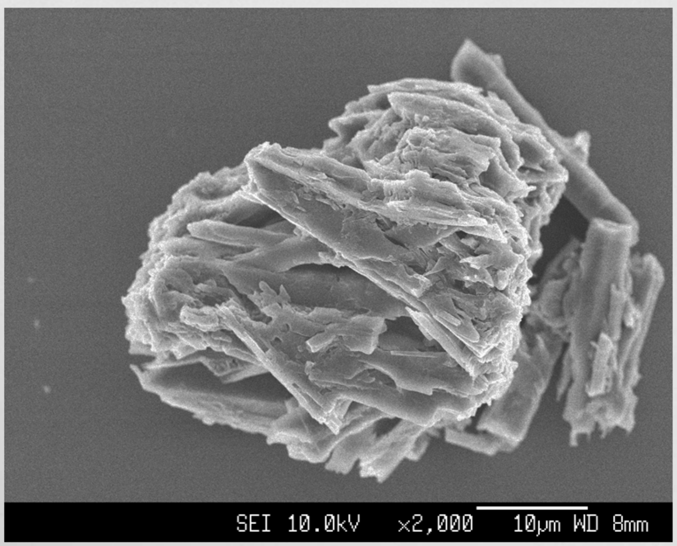
- To investigate the compatibility of binders with Bistetrazolylamine(BTA), in an effort to assess the applicability of the molecule in explosive and propellant formulations.
- BTA represents one of the attractive energetic candidates with high-energy density and insensitivity, a rare combination.
- Although synthesis and characterization of novel high energy-insensitive molecules are reported, very few have been tested for their compatibility with known binders.
- Lack of information on the compatibility and stability of high nitrogen molecules hinders their further development as a formulation.
- The mixtures chosen for our study:
  - **Bistetrazolylamine-Glycydyl azide Polymer (BTA-GAP)**
  - **Bistetrazolylamine-Poly nitratomethyl methyl oxetane (BTA-PNIMMO)**
  - **Bistetrazolylamine-Ethyl cellulose (BTA-EC)**

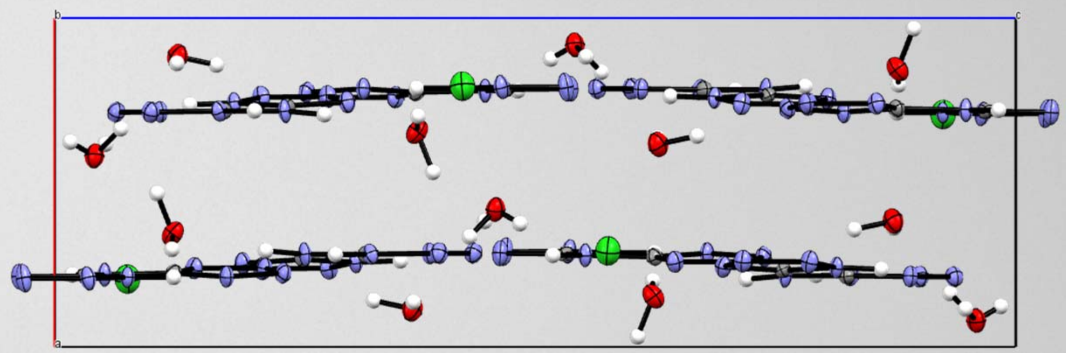
Bistetrazolylamine (BTA)



- High density CHN molecule. (1.86 g/cc)
- Symmetrical tetrazolyl groups on the central nitrogen-high energy system not local minima.
- Presence of substitution and salt formation changes the structure to most stable low energy form.

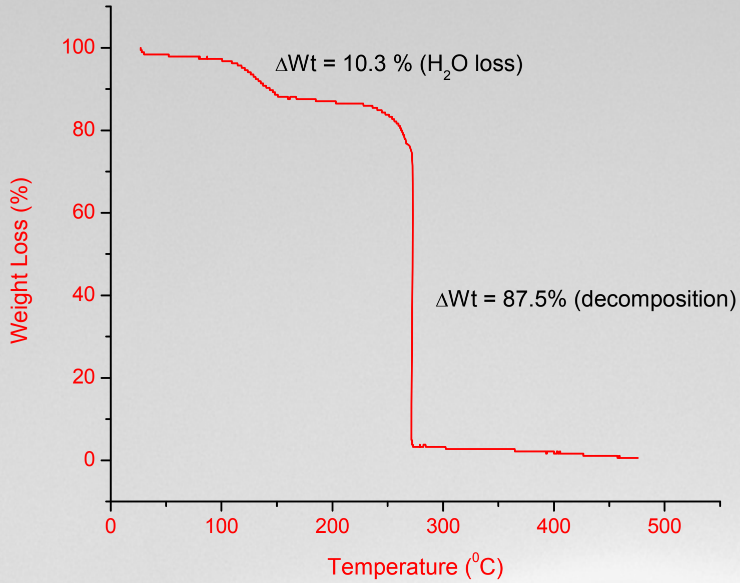


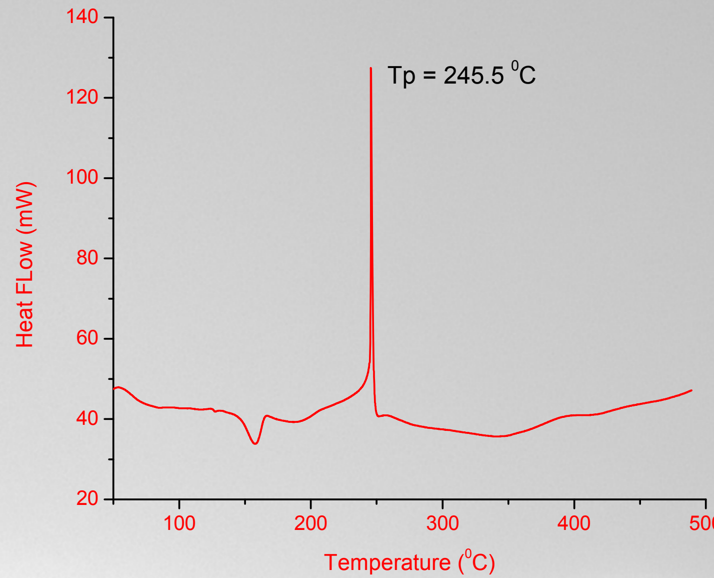


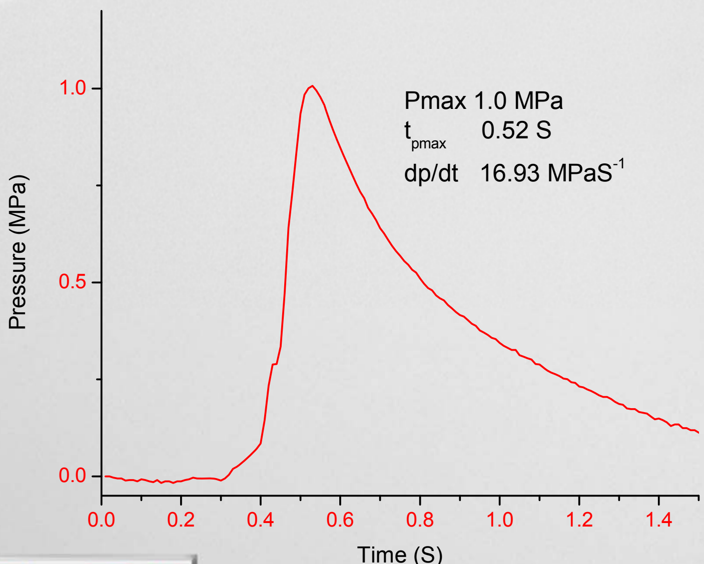


EnRI
ENERGETICS RESEARCH INSTITUTE

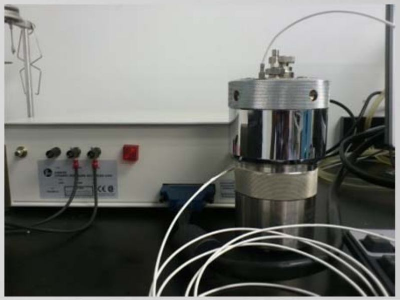
Thermal characterization and P-t studies on BTA





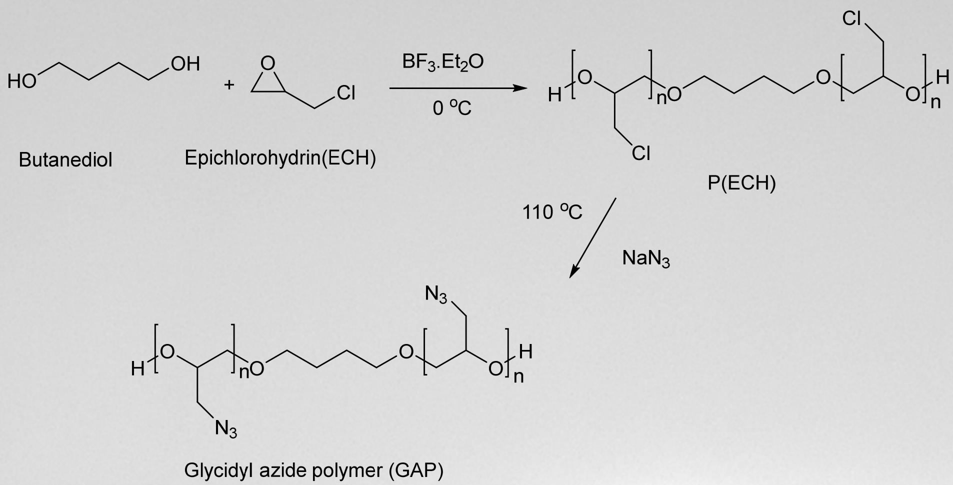


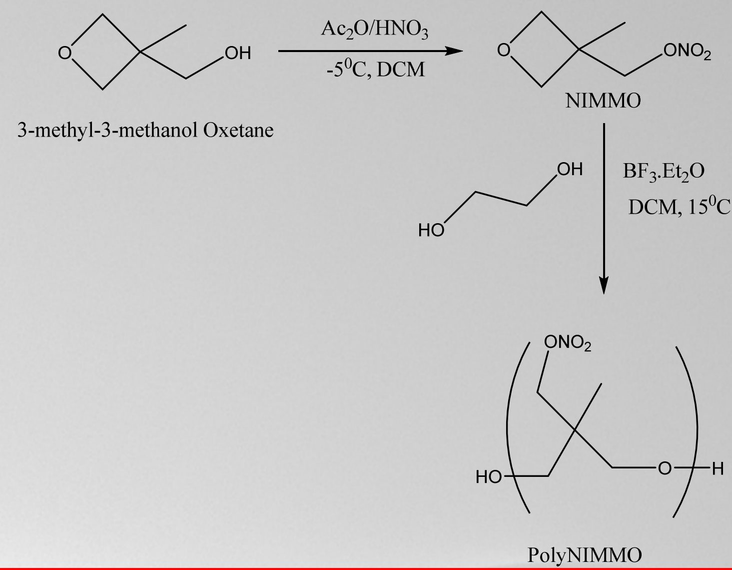
- BTA shows excellent thermal stability up to 240^0C
- DSC curve shows maximum heat release with in a short temperature range.
- P-t curve was measured to understand the ignitability and pressure response of BTA.



EnRI
ENERGETICS RESEARCH INSTITUTE

Energetic binders : GAP & PNIMMO





Binder	Mol. Weight, M_{n}, $gmol^{-1}$	Density, gcc^{-1}	Glass transition, Tg, ^{0}C	Decomposition temperature, T_p, ^{0}C	Heat of decomposition, Jg^{-1}
GAP	2835	1.35	-51.2	241.5	1917
PNIMMO	1295	1.28	-55.5	204.6	1123

EC with 48% ethoxy content was procured from Sigma Aldrich and used as received.

EnRI ENERGETICS RESEARCH INSTITUTE

Importance of Compatibility studies

- Compatibility of novel energetic materials with components of formulations/composites are crucial for their safety and functioning. Ideally compatible materials should not have any chemical interaction with each other over a prolonged period.
- STANAG 4147, MIL-STD-268B and MIL-STD-650 explains the various test procedures and compatibility criteria for energetic materials.VST, IST, TG and DSC analysis includes the various test for determining the compatibility.

Compatibility using micro-calorimetry as per STANAG 4147

- High degree of accuracy in temperature profile and high sensitivity (nW) of micro-calorimeter is advantageous to measure heat flow over a long period. **6 channel TAM III from TA was used**.
- Test measurements:

  1:1 mixture by weight of :
  Energetic material (BTA) + sample(binder)

- Degree of compatibility:

  $$D = 2M/(E+S)$$

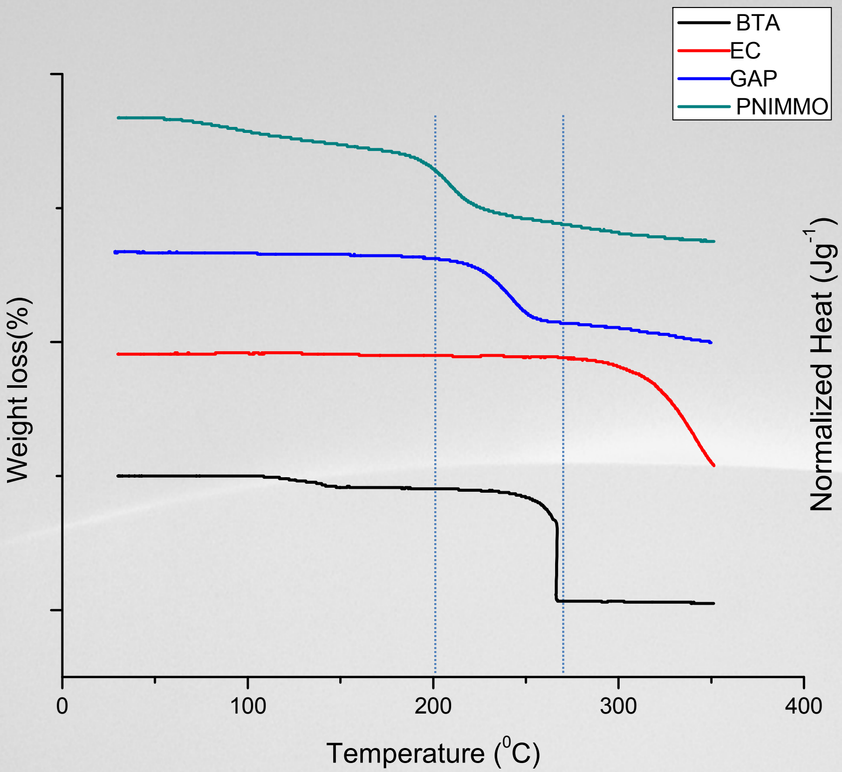
  M = Heat generation for the mixture (J g^{-1})
  E = Heat generation for energetic material(BTA) (J g^{-1})
  S = Heat generation for the sample(binder) (J g^{-1})

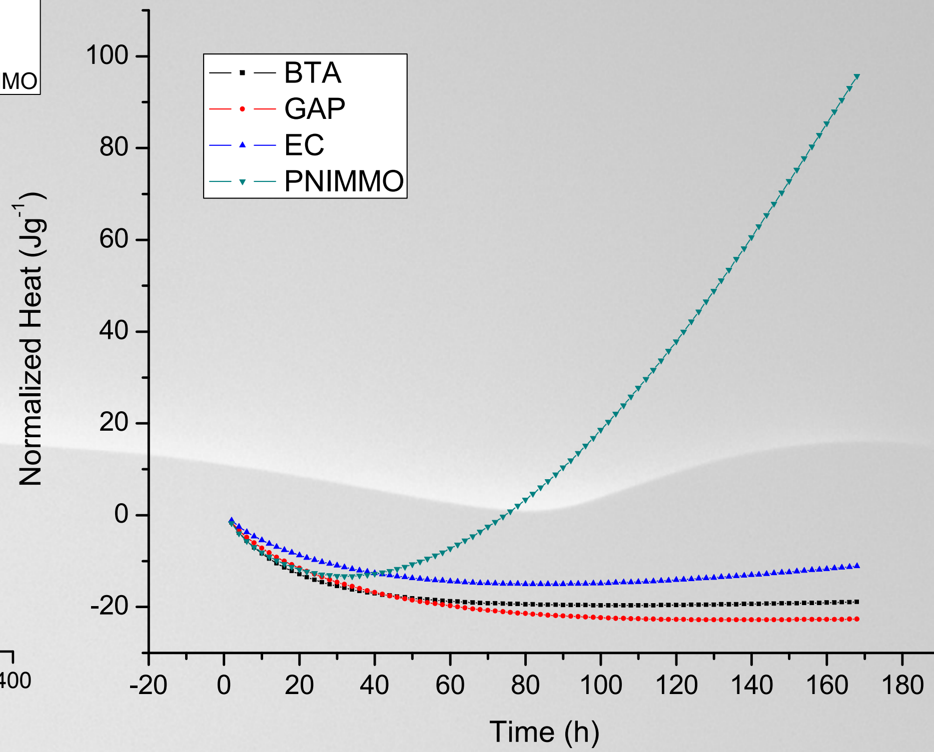
- Acceptance criteria:

  Criteria:
  D > 3 : Incompatible
  2 < D < 3 : Another method should be used

EnRI
ENERGETICS RESEARCH INSTITUTE

Stability and heat flow of BTA and Binders

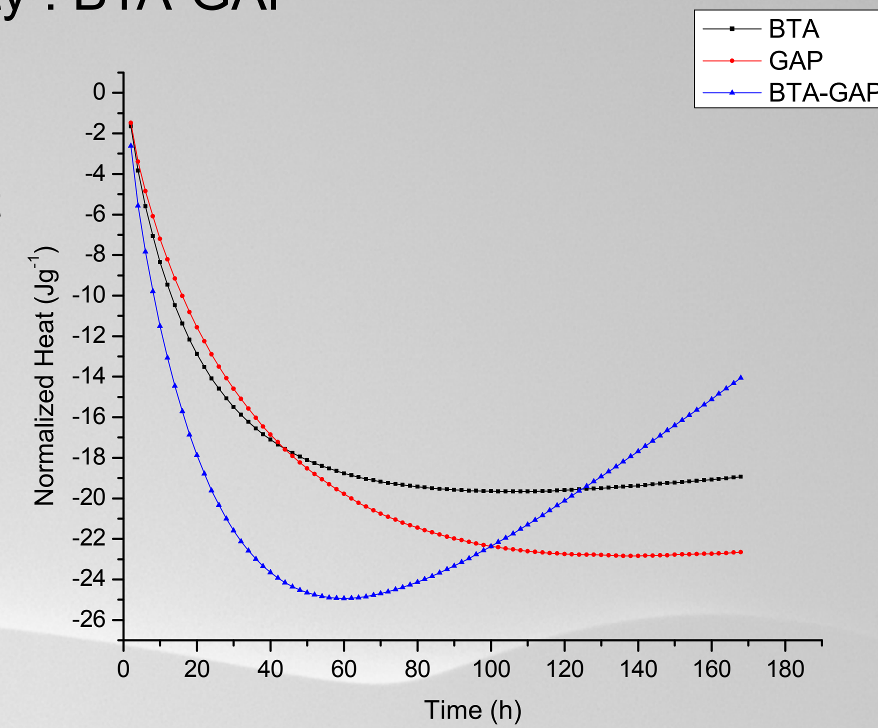


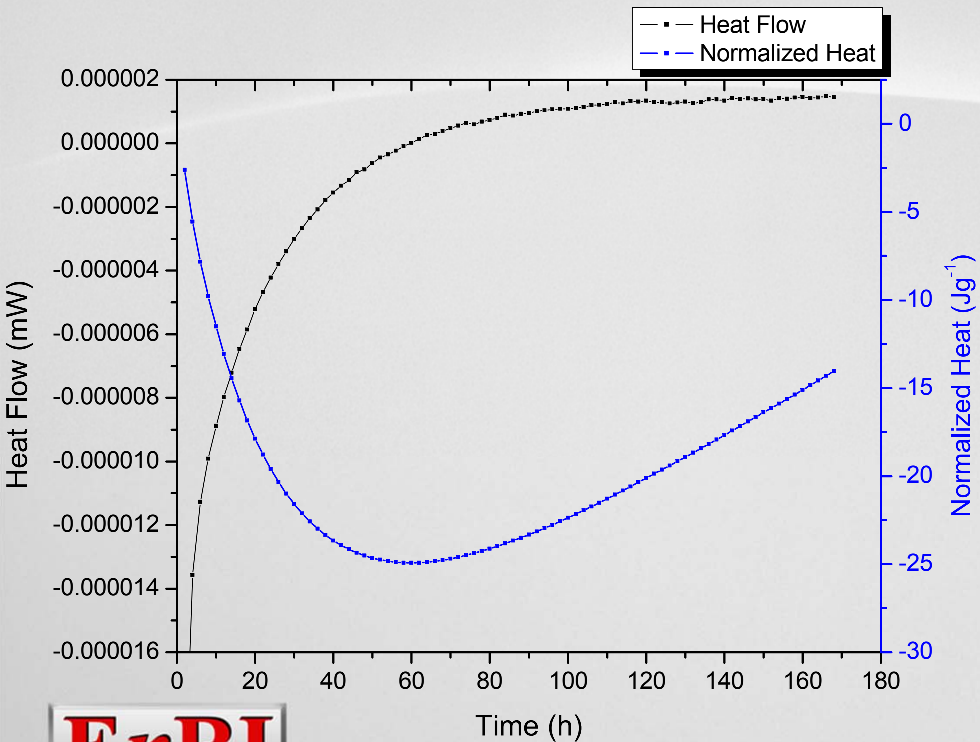


- Thermal decomposition of BTA, GAP and PNIMMO occurs within a closer range of temperature.
- PNIMMO showed a faster heat accumulation rate at 85^0C when compared to the other components

Compatibility : BTA-GAP

- Compared with the individual components, mixture showed increase in heat accumulation after 60 h
- No appreciable heat release rate over 168 h.
- BTA: -18.9 J/g; GAP -22.6; BTA-GAP: -14.05J/g
- D<2



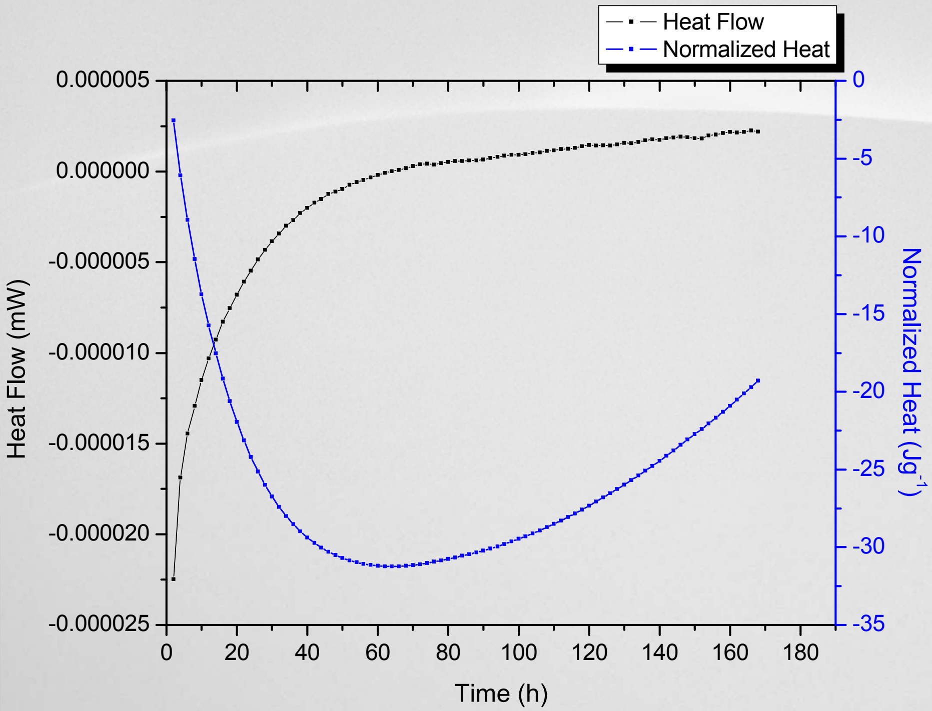


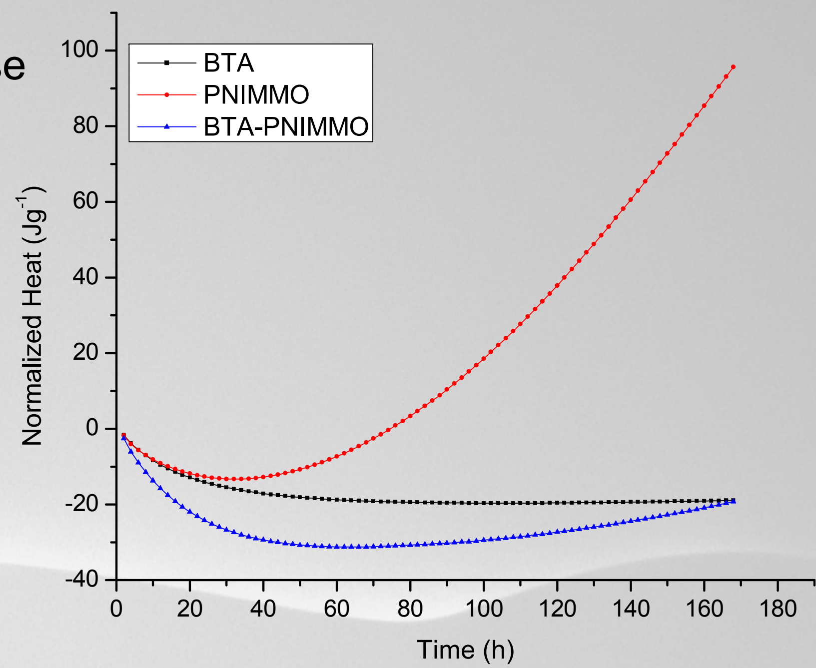
Compatible mixture

EnRI ENERGETICS RESEARCH INSTITUTE

Compatibility : BTA-PNIMMO

- Notably the mixture has lower heat release rate when compared to PNIMMO
- BTA: -18.9 J/g; PNIMMO: 95.6;
  BTA-PNIMMO: -19.3 J/g
- D<2





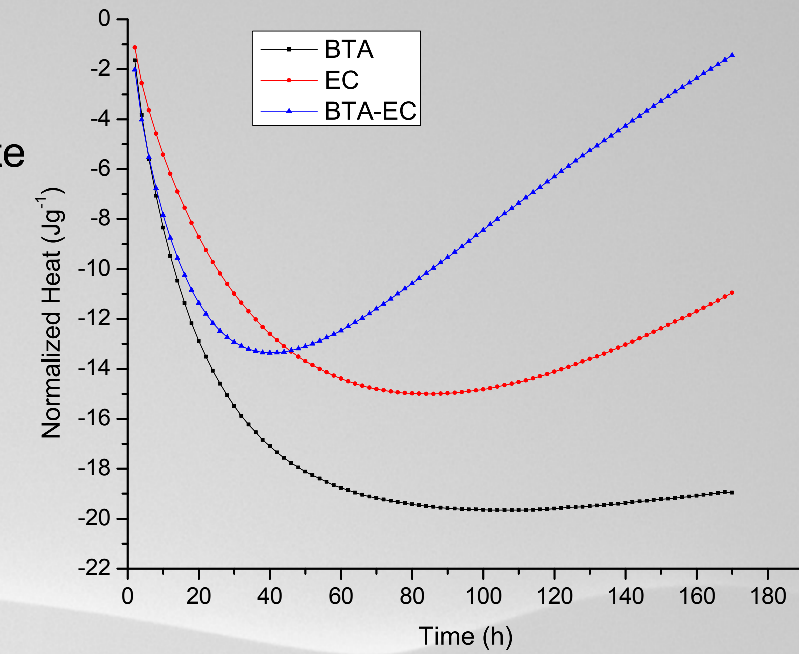
- BTA dilutes the heat release of the mixture by acting as a thermally stable heat sink.
- Exponential increase in heat release rate for PNIMMO after 40 h.

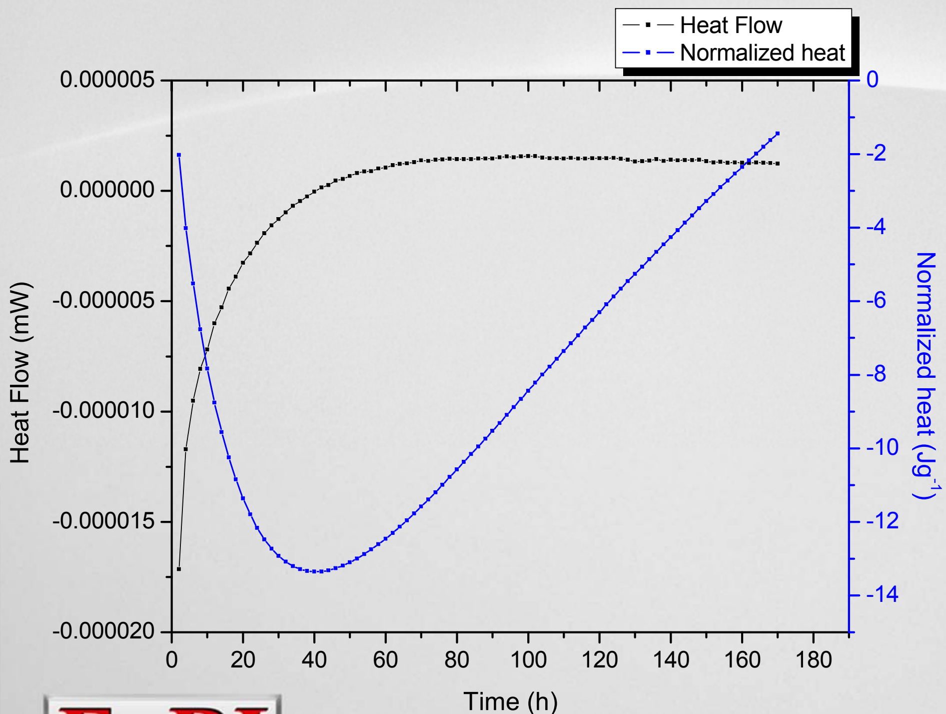
Compatible mixture

ENERGETICS RESEARCH INSTITUTE

Compatibility : BTA-EC

- The mixture has higher heat release rate when compared to components
- BTA: -18.9 J/g; EC: -10.95;
  BTA-EC: -1.4 J/g
- D<2



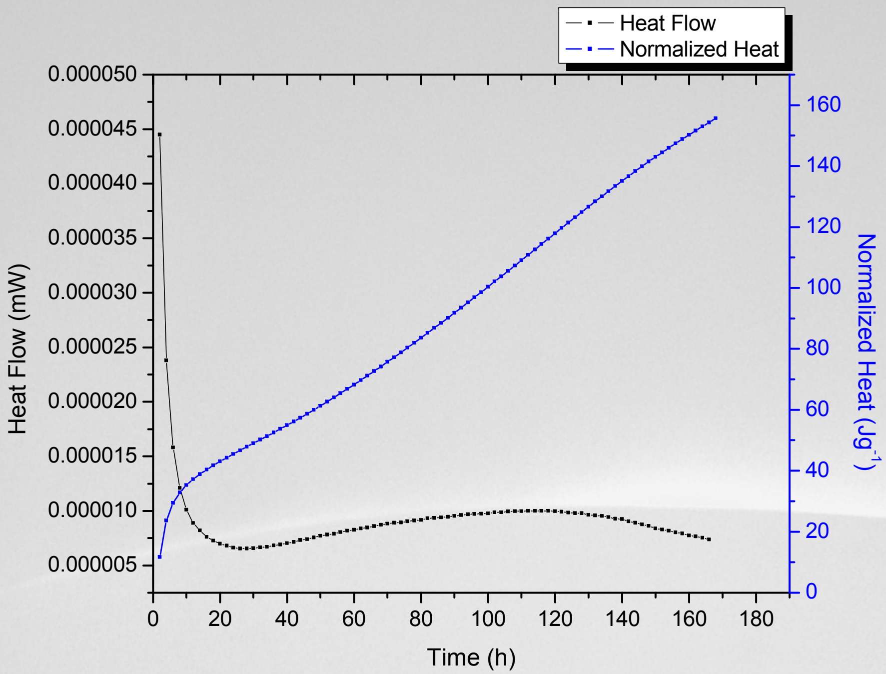


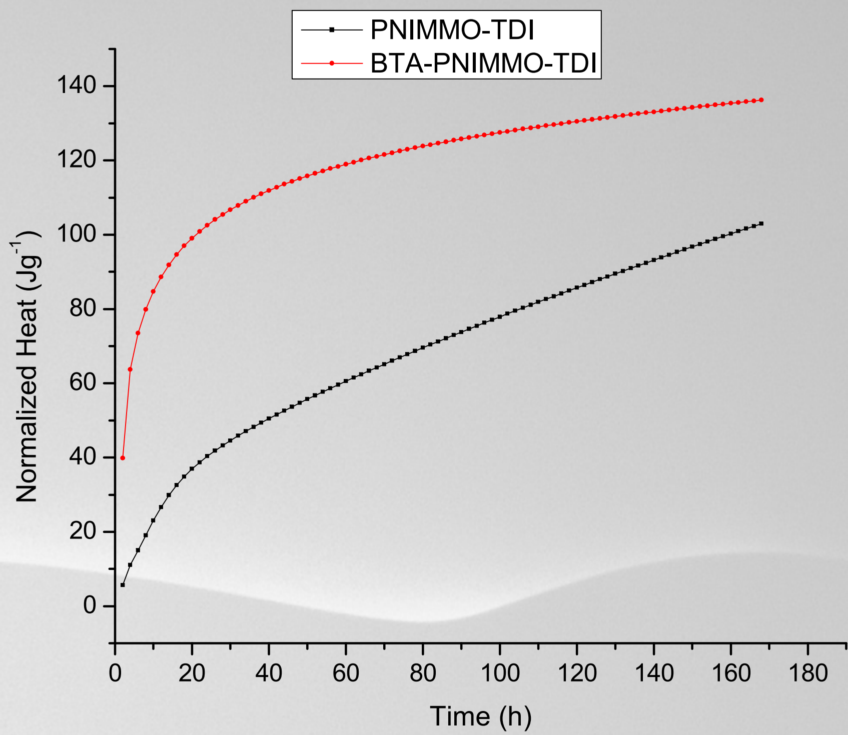
- EC showed an increase in heat release after 80 h.
- Presence of BTA has accelerated the heat release of EC.
- Lewis acid nature of BTA aiding possible hydrolysis of ether linkages ?.

Compatible mixture

ENERGETICS RESEARCH INSTITUTE

Compatibility: BTA-TDI



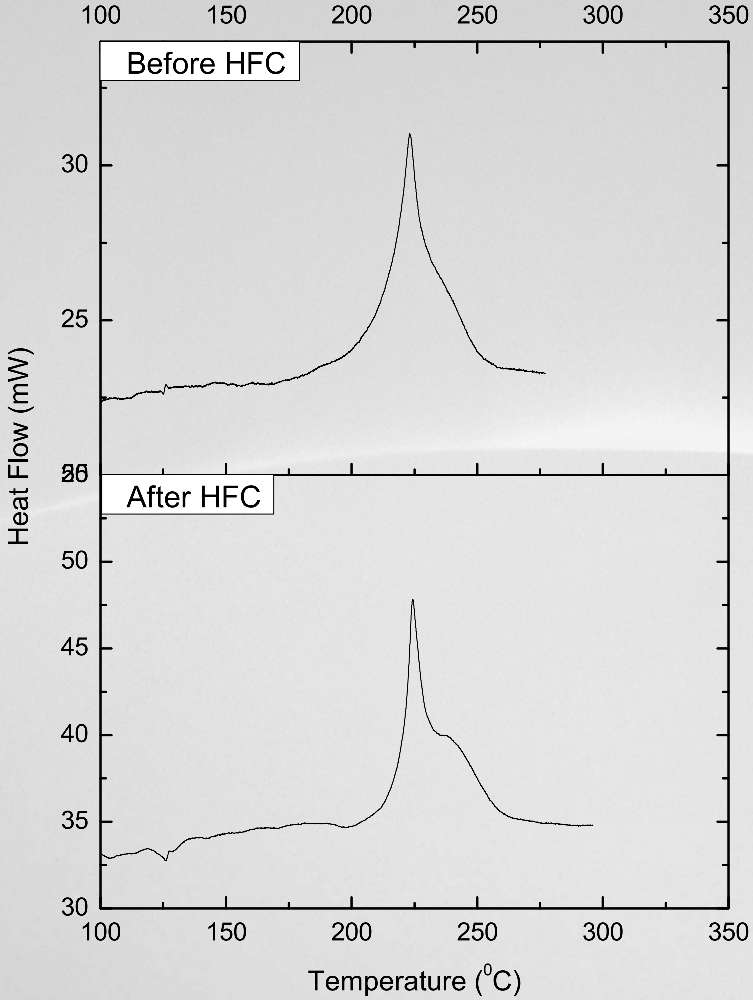


- BTA showed a greater degree of incompatibility with curing agent TDI, indicative of the reaction between the imino hydrogens and iso cyanate group.
- On comparison with the heat release rate of curing reaction with PNIMMO, reaction of BTA with TDI seems to take place at a slower rate.
- The terminal primary hydroxyl groups of PNIMMO will have a preferential reaction with isocyanate compared to that of imino groups in BTA.

EnRI
ENERGETICS RESEARCH INSTITUTE

Comparison of DSC

DSC profiles of BTA/binder mixtures before and after HFC study

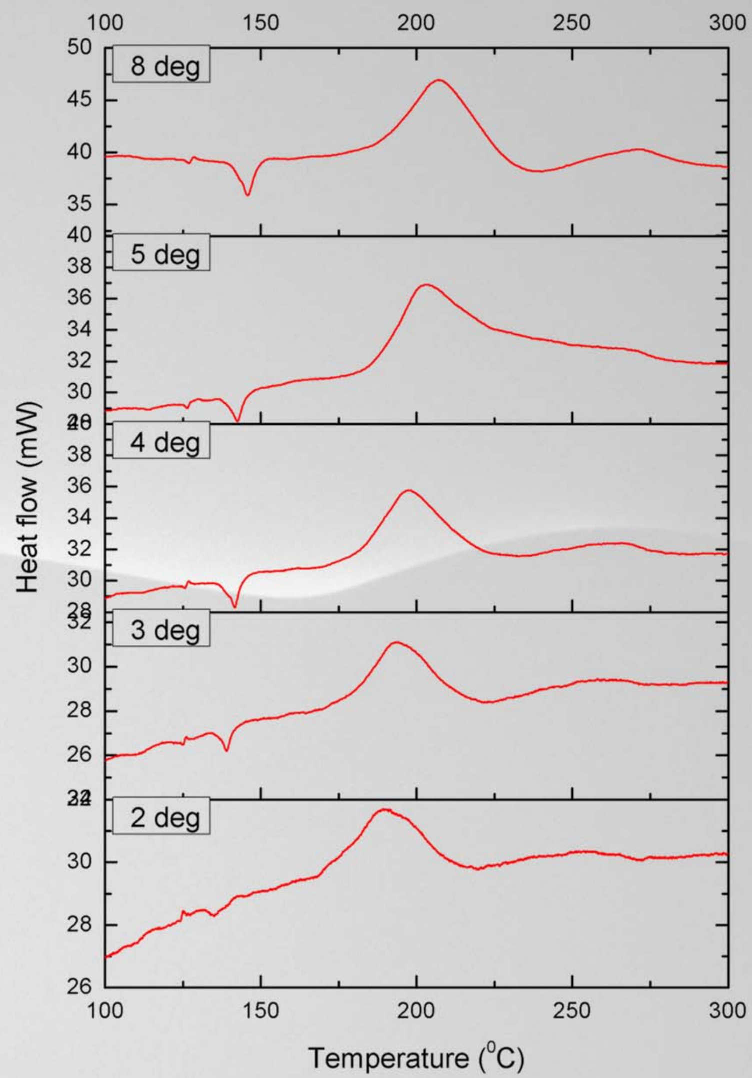


Representative DSC profile of BTA-GAP

- Decomposition characteristics of the formulations are preserved after the compatibility tests with binders.

Activation energy calculations

- Activation energy of decomposition of the energetic mixtures; BTA-GAP & BTA-PNIMMO was calculated.
- Kissinger and Ozawa equations were used for evaluation.
- BTA-GAP E_a - 240±5 kJ/mol
- BTA-PNIMMO E_a - 130± 3 kJ/mol
- BTA-GAP mixture showed a higher activation energy required for decomposition.
- Results indicative of ease of initiation/decomposition for BTA-PNIMMO.



DSC profiles of BTA-PNIMMO

Conclusions

- Compatibility of BTA with common energetic binders(GAP & PNIMMO) as well as with a non energetic binder (EC) were studied as per STANAG 4147.
- Binders showed good compatibility with BTA paving the way to visualize use of BTA as energetic ingredient/fuel.
- DSC analysis on the post experiment samples showed no considerable dilution of energy or change in heat flow profile.

Mixture	Normalized Heat, Jg^{-1}	Degree of compatibility, D	Result
BTA-GAP	-14.05	0.67	Compatible
BTA-PNIMMO	-19.28	0.50	Compatible
BTA-EC	-1.4	0.09	Compatible

Thank You

ENERGETICS RESEARCH INSTITUTE