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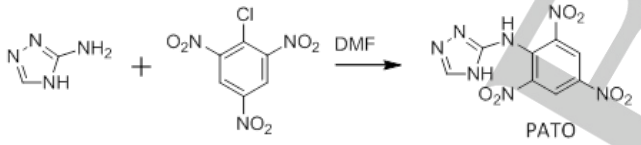
Synthesis and Evaluation of 3-picrylamino-1,2,4-triazole (PATO) formulations

Philip Leonard*[a], Patrick Bowden, Marvin Shorty, and Matt Schmitt

Abstract: 3-Picrylamino-1,2,4-triazole (PATO) is a thermally stable explosive invented at Los Alamos National Laboratory (LANL) almost half a century ago. Despite a rapid and high yielding synthesis, performance data for this promising explosive are scant. We prepared material using Coburn's synthesis, and discovered that the particle size distribution and morphology leads to difficulty in pressing formulations to high density. Three formulations were made using glycidyl azide polymer (GAP), FK-800, and Estane 5703/nitroplasticizer (NP) as binders. The maximum pressed density of these formulations was 89% of theoretical maximum density (TMD). We determined detonation velocity and, for the FK-800 formulation, detonation pressure. The performance of PATO is similar to TATB at equivalent pressed density.

1 Introduction

In 1968, Coburn [1] published the synthesis of 3-picryamino-1,2,4-triazole (PATO) a safe-to-handle explosive with high density, high thermal stability, and a low cost of manufacture. At the time this explosive was neglected while TATB was selected for scale up and utilization [2]. In the context of economic and environmental considerations, PATO may be the superior alternative to TATB in certain applications.



Scheme 1. The synthesis of PATO by nucleophilic aromatic substitution.

PATO is formed in near quantitative yield from 3-amino-1,2,4-triazole, a common herbicide (amitrole), and picryl chloride which is available from conversion of picric acid. Li has shown that tetryl can also be used as a starting material for picryl chloride, allowing for the reuse of outdated ordnance [3]. Substitution is performed at 100 °C in DMF, and achieves near quantitative yield. If the solvent is purified to remove dimethyl amine then the product is free of the ring-N substitution product found by Chioato [4, 5]. PATO has a strong tendency to retain bulk water and needs to be dried at elevated temperature or under reduced pressure if dry material is required. By comparison, the synthesis of TATB using Benziger's methodology requires fuming acids for nitration and a pressure reactor for aminolysis, making the overall effort more hazardous [6]. As described by Bower for TATB, the formulation of a plastic bonded explosive (PBX) can have significant influence over the physical and sensitivity properties of the material [7]. To support the utility of PATO we generated three formulations and measured their performance.

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2 Experimental Section

General: Solvents and 3-amino-1,2,4-triazole were obtained from Alfa Aesar, picryl chloride was produced by Eastman Kodak, FK-800 and glycidyl azide polymer were produced by 3M, and Estane 5703 was manufactured by Lubrizol. Nitroplasticizer (NP) refers to the eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)acetal (BDNPF/A) and was manufactured by Naval Surface Warfare Center-Indian Head. Methyltriacetoxysilane was purchased from Sigma Aldrich and used as received. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at ambient temperature using a Bruker Ascend 400 MHz spectrometer. Chemical shifts (δ) were referenced to the residual solvent signal from DMSO-d_6. FTIR spectra were measured using a Thermo-Nicolet iS5 FTIR spectrophotometer using OMNIC software. IR spectral measurements were made using pressed KBr pellets. The SEM used for this work is a JEOL7000F field emission microscope having a Schottky type (T-FE) gun with a secondary electron (SE) signal optimum resolution of ~ 10 nm. The PATO powder was dispersed using hexane and then placed into a triode type sputter coater wherein a ~ 20 nm sputter coating of Au/Pd was applied. SEM images shown are those of SE emission capture.

Synthesis: 3-Amino-1,2,4-triazole (37.72 g, 0.45 mol) is dissolved in anhydrous *N,N*-dimethylformamide (DMF, 450 mL). Picryl chloride (44.45 g, 0.18 mol) is slowly added to the mixture, while it is chilled in a 1 L flask in an ice-water bath. The reaction mixture is heated to 100 °C for 5 hours, then allowed to cool for 30 minutes before being poured into a 2 L beaker containing 500 g of crushed ice. A yellow precipitate forms which is filtered and allowed to air dry overnight in the hood before being dried at 60 °C in an explosion-proof oven. FTIR and NMR spectra were consistent with literature values [8]. ^{1}H NMR (DMSO-d_6): 8.40 (1), 8.93 (2), 10.48 (1), 13.87 (1) $^{13}C\{^{1}H\}$ NMR (DMSO-d_6): 126.12, 135.93, 137.50, 139.88, 143.47, 157.21. FTIR (KBr): 700, 782, 1027, 1176, 1221, 1322, 1445, 1569, 1616, 3216, 3317 cm^{-1}.

Slurry formulation: PATO is stirred in water at room temperature at a ratio of 10 wt%. The binder is dissolved in ethyl acetate or butanone at 10-20 wt% and added to the stirred suspension creating a bilayer. The suspension is heated with stirring until the organic layer evaporates and the coated PATO precipitates as discussed by Kaspryzk [9]. The solid is isolated from the resulting solution by Buchner filtration and dried in the fume hood, followed by four hours at 60 °C in an explosion-proof oven.

Extrusion: PATO 90 wt% was hand mixed with GAP 9 wt% and methyltriacetoxysilane 1 wt%. The mixture was transferred to an EFP disposable reservoir and a piston was used to mechanically press the formulation into a receiving cylinder where it cured at room temperature over 48 hours, resulting in a hard rubbery solid.

Mechanical pressing: Pressing was accomplished using cylindrical dies applying a maximum of 138 MPa at 60-110 °C during 3-4 minute cycles.

Performance testing: Three formulations of PATO – PATO-GAP, PATO-FK-800 and PATO-Estane/NP – were each fired to determine detonation velocity using shorting wires; additionally, the PATO-FK-800 formulation also utilized a free surface flyer to determine CJ pressure. The PATO-GAP formulation was cast into a 12.6 mm inner diameter, 15.9 mm outer diameter, Lexan tube that was 127.1 mm long (L/D = 10). A mass of 17.830 g of PATO-GAP was placed into the tube giving an average density of 1.125 g/cm^3. Both the PATO-FK-800 and PATO-Estane/NP were die pressed into right circular cylinders. For PATO-FK-800, these cylinders were nominally 12.7 x 12.7 mm and for PATO-Estane/NP these cylinders were 9.5 x 9.5 mm. The average density of the six PATO-FK-800 pellets was 1.709 ± 0.005 g/cm^3 (88% TMD). The average density of the eight PATO-Estane/NP pellets was 1.712 ± 0.009 g/cm^3 (89% TMD). For each shot, an RP-80 (Teledyne RISI) was used to initiate either a C-4 charge (PATO-GAP) or a 12.7 x 12.7 mm pellet of PBX 9407 (94 % RDX, 6 % Exon 461) (PATO-Estane/NP). A copper ground strip was placed along each charge and shorting wires, with sheathing, were either placed on top of the ground strip, or between pellets; PATO-Estane/NP had wires placed between pellets and an additional wire was placed between the end pellet of PATO and an additional 12.7 x 12.7 mm pellet of PBX 9407. In this fashion, 11 wires were used for the PATO-GAP and PATO-FK-800 shots, 8 wires were used for the PATO-Estane/NP shot. A +60 V potential was supplied between the wires and the ground strip. The electrical signals were multiplexed into a single channel to provide timing data that was recorded on a Tektronix DPO4104B oscilloscope. The position of each wire/pellet was measured using a Mitutoyo Absolute Digimatic Height Gage. For the PATO-FK-800 shot, an end-on aluminium (1100 grade) flyer (450 µm thick) was placed on the last pellet and a PDV probe recorded its trajectory for 2 µs. This information allows calculation of CJ pressure following the work of Lorenz [10].

3 Results and Discussion

The largest impediment to the utilization of PATO is the particle size distribution and morphology obtained from precipitation. At the end of the reaction, the solution of PATO is cooled before being poured into water. Rapid precipitation results in a mean particle size which is typically below 10 µm. As shown in Figure 1, although the particle size distribution (PSD) is multimodal, the distribution is strongly skewed toward fine particles with a small standard deviation. This PSD results in a mixture of solids which do not pack optimally, as described by Bierwagen [11].

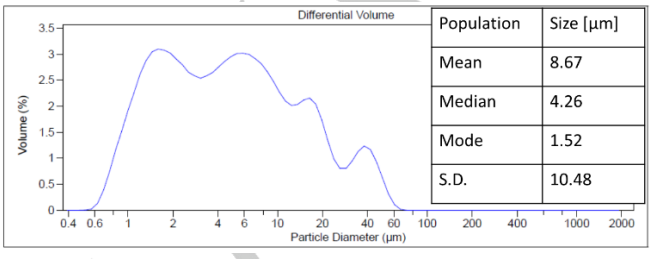

Figure 1. Particle size distribution of PATO as precipitated from DMF/water.

The common morphology for PATO precipitated out of DMF/water is needle-like with an aspect ratio in excess of 10:1 (Figure 2). Without alternative crystallization methods or mechanical size reduction, making a high density formulation with this PSD and morphology is challenging.

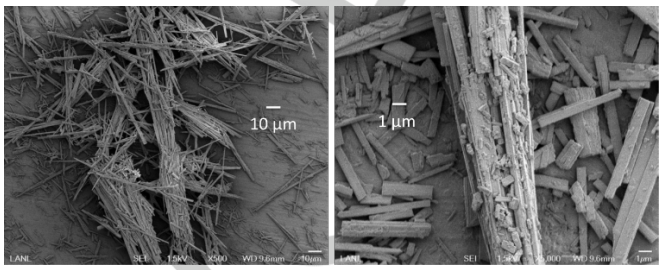

Figure 2. The morphology of PATO is of long flattened needles that are prone to breakage on the long axis.

As a single component, PATO is insensitive to impact and friction but somewhat sensitive to electrostatic discharge (ESD). Formulation with a polymeric binder tends to alter the handling sensitivity of an explosive, and certain physical characteristics recommend different HE/binder combinations [12]. The binder systems we chose were selected due to both familiarity and their differential attributes, these were: 5 wt% FK-800, a high-density thermally stable binder; 5 wt% Estane 5703/NP, a semi-energetic system with high plasticity; 10 wt% GAP, a rubbery energetic binder when cross-linked by methyltriacetoxysilane.

Table 1 lists the measured sensitivity of the PATO formulations to external stimuli. In all cases the formulations maintained the low impact and friction sensitivity of the parent explosive. Both the Estane/NP and GAP formulations showed higher sensitivity to ESD, as can be expected for energetic binders. Vacuum thermal stability is considered to be acceptable if less than two milliliters of gas is generated per gram of material, all formulations passed this criterion by a comfortable margin.

Table 1. Sensitivity properties of PATO-based formulations.

	PATO	PATO FK-800	PATO Estane/NP	PATO GAP	TATB[e]
Impact, type 12 [J] [a]	>78.4	>78.4	>78.4	>78.4	>78.4
Friction, BAM [N] [b]	>360	>360	>360	>360	>360
ESD, [J] [c]	0.0625	0.125	0.0625	0.0625	>0.125
DSC onset [°C]	310	312	293	220	342
DSC peak [°C]	320	319	320	262	385
Vac. Stab. [ml/g] [d]	0.27	0.35	0.18	0.72	<0.50

[a] Drop height 50% threshold using Neyer D-optimal method. [b] Friction force 50% threshold using Neyer D-optimal method. [c] Threshold Initiation Level at 3.4% probability. [d] Gas evolved after 48 hr at 120 °C. [e] Typical values shown for dry-aminated TATB.

Thermal compatibility of PATO with both FK-800 and Estane/NP was good with similar peak exotherm temperatures compared to PATO itself. The cast-cure formulation with GAP showed a reduction in onset and an early exotherm as shown in Table 2 and the supplementary information, Figures S1-S4. Reaction to flame varied from self-extinguishing in the case of the FK-800 formulation to a slow carbon snake burn in the case of GAP (Figure S5).

Both of the binder systems FK-800 and Estane/NP pressed to equivalent density at 5 wt% binder loading. The low pressing densities achieved can be understood as a failure of the solid particles in the system to maximally fill space since these pressings represent only 88% TMD (FK-800) and 89% TMD (Estane/NP). This outcome is not surprising as long particles tend to press poorly, more fine particles require higher binder quantities, and the pressing conditions were not optimized.

As the diameter of a rate stick decreases toward the critical diameter (CD), detonation velocity tends to fall off rapidly until propagation of the shockwave can no longer be maintained. At equivalent density and size the Estane/NP formulation should outperform the FK-800 formulation in detonation velocity due to the energy content of the BDNPF/A. As shown in Table 2, the Estane/NP formulation did exceed the velocity of the FK-800 formulation despite reduced rate stick diameter. This result implies that the critical diameter of PATO is significantly smaller than 9.5 mm, otherwise energy loss from reduced diameter would contravene increased internal energy from BDNPF/A.

According to the work of Phillips, at a density of 1.80 g/cm^3 and a diameter of 5.08 mm ufTATB detonates with a velocity of 7.09-7.14 mm/μs [13]. While these results are not directly comparable to ours due to differences in density, diameter, and binder, they demonstrate that PATO and TATB are roughly equivalent in detonation velocity.

Table 2. Performance of PATO-based formulations

	PATO FK-800	PATO Estane/NP	PATO GAP	ufTATB [12]
Density fired [g/cm^3]	1.709 (0.005)	1.710 (0.009)	1.125 (0.01)	1.80
Diameter [mm]	12.70	9.53	12.70	5.08
Detonation Velocity [mm/μs]	7.016 (0.010)	7.059 (0.004)	4.808 (0.014)	7.09-7.14
Detonation Pressure [GPa]	25.8 (0.1)	-	-	-

In addition to a small critical diameter, PATO has the ability to propagate a detonation at low density in a 10 wt% GAP formulation. The energetic polymer GAP has been used for decades in the development of solid rocket motors due to its mechanical properties and good thermal stability. In explosive formulations we have found that using GAP can improve initiation in composite materials. For a formulation with 10 wt% GAP the TMD calculates to 1.852 g/cm^3. In practice when we cast a slurry of uncured PATO-GAP into a cylinder we achieved a bulk density of only 1.125 g/cm^3. The low density is attributable to entrained air or vapor pockets as the material was extruded under positive pressure into an open cell. Surprisingly the rate stick detonated promptly giving a detonation velocity of 4.8 km/s.

4 Conclusions

PATO has been known for half a century, but until now the detonation performance has been a matter of speculation. In this paper we have shown that this material has facile initiation and good performance for the densities we were able to achieve. The current difficulty in employing PATO is a challenging crystal morphology; efforts are currently underway to improve particle size and shape by selective crystallization. If challenges related to the morphology can be overcome, then PATO would be an attractive alternative to TATB for certain applications as the result of good handling safety, facile detonability, and equivalent performance.

Acknowledgements

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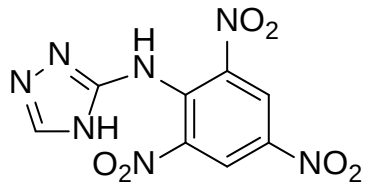

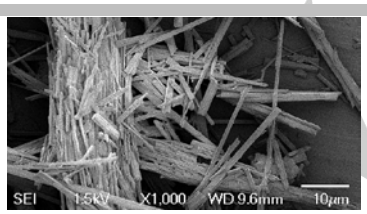

3-Picrylamino-1,2,4-triazole synthesis and performance testing

Philip Leonard,, Patrick Bowden, Marvin Shorty, and Matt Schmitt

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Data for, “Synthesis and Evaluation of 3-picrylamino-1,2,4-triazole (PATO) formulations”

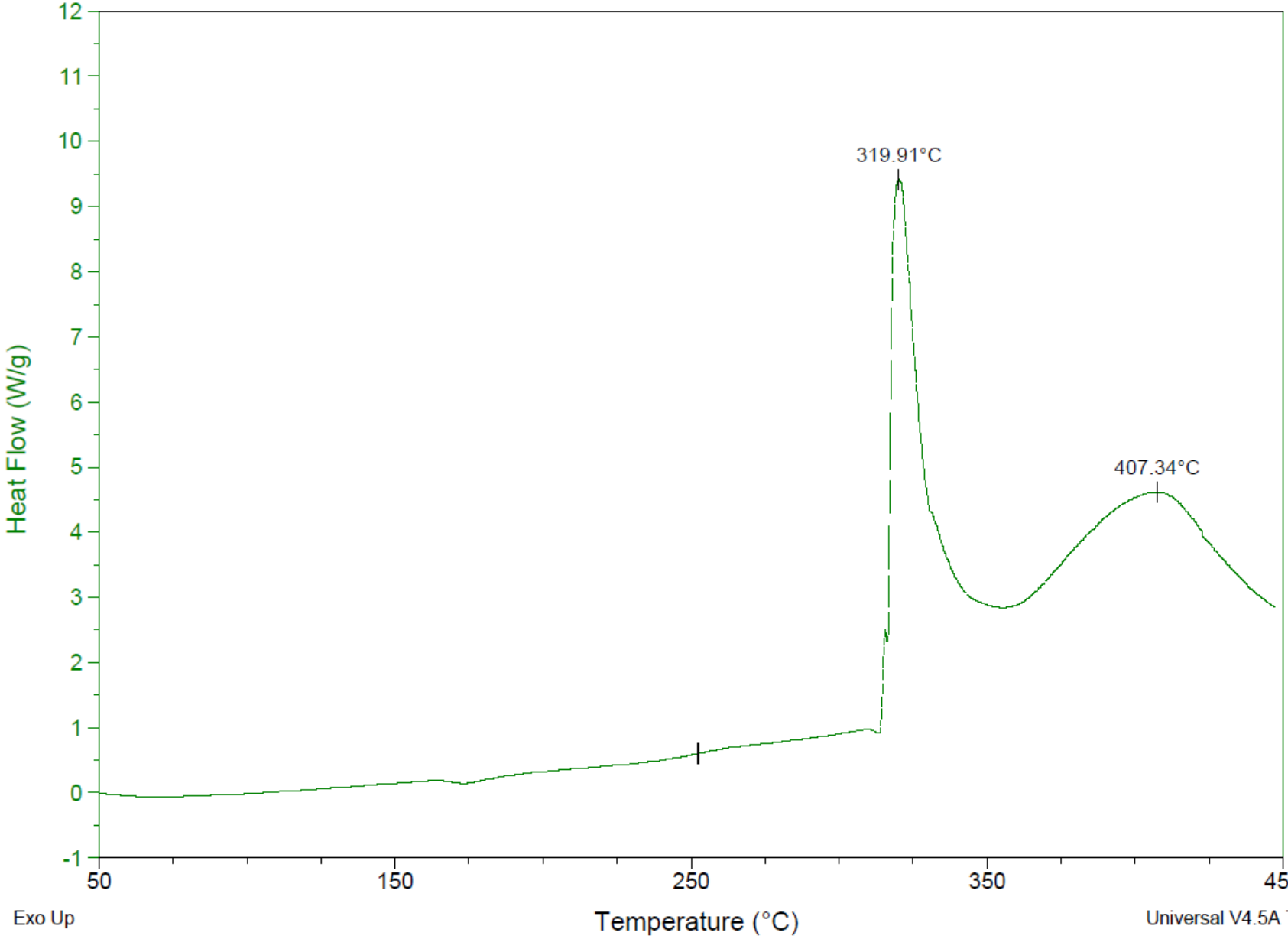
Philip Leonard*[a], Patrick Bowden, Marvin Shorty, and Matt Schmitt

Sample: PATO
Size: 0.6380 mg
Method: 10C Ramp

DSC

Instrument: DSC Q2000 V24.11 Build 124

Figure S1) DSC of PATO

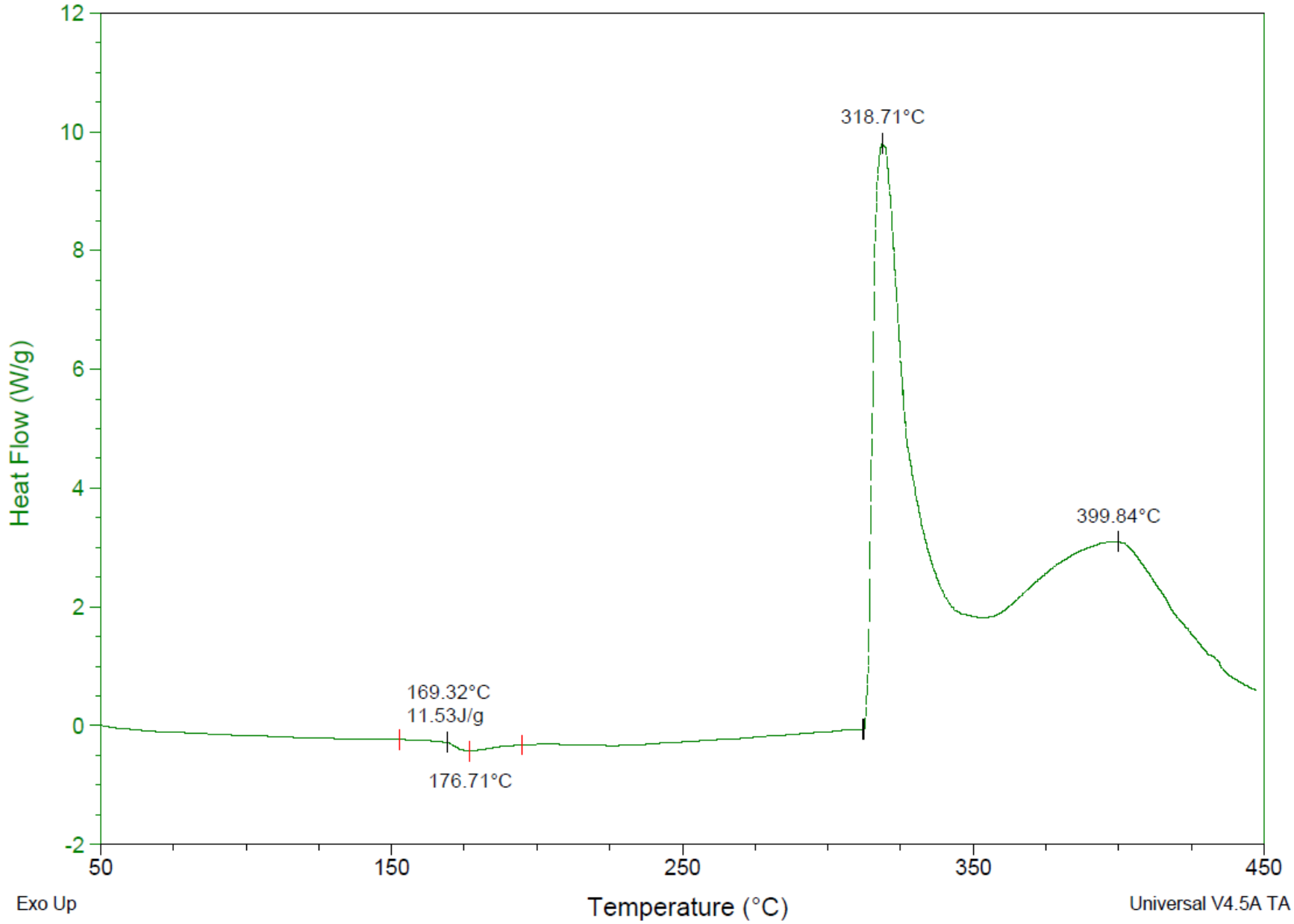


Sample: PATO-FK800
Size: 0.9570 mg
Method: 10C Ramp

DSC

Figure S2) DSC of PATO - FK-800

Instrument: DSC Q2000 V24.11 Build 124



Sample: PATO-Estane-PDNPA-F
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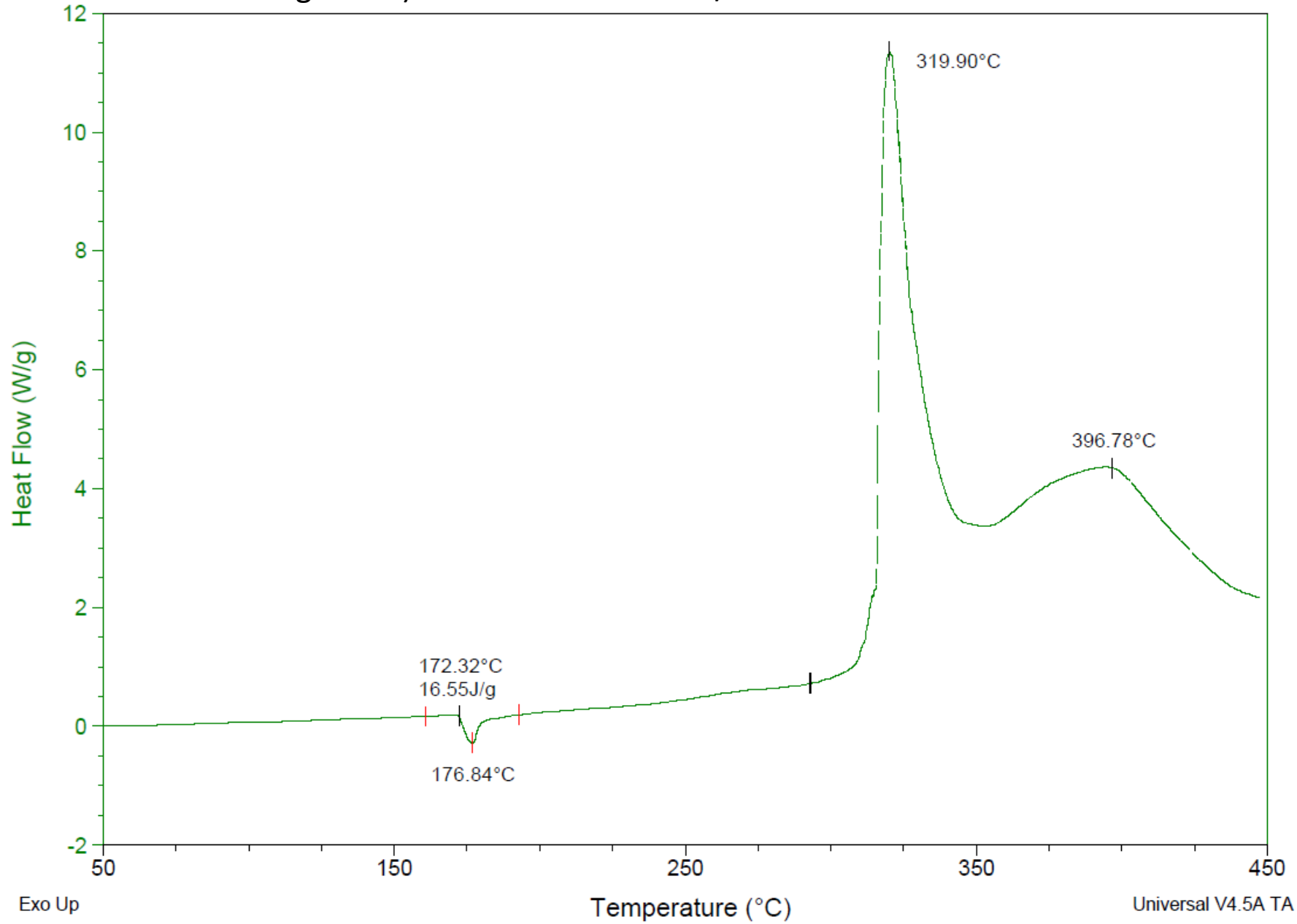
Method: 10C Ramp

DSC

Instrument: DSC Q2000 V24.11 Build 124

Figure S3) DSC of PATO - Estane/NP



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DSC

Instrument: DSC Q2000 V24.11 Build 124

Figure S4) DSC of PATO - GAP

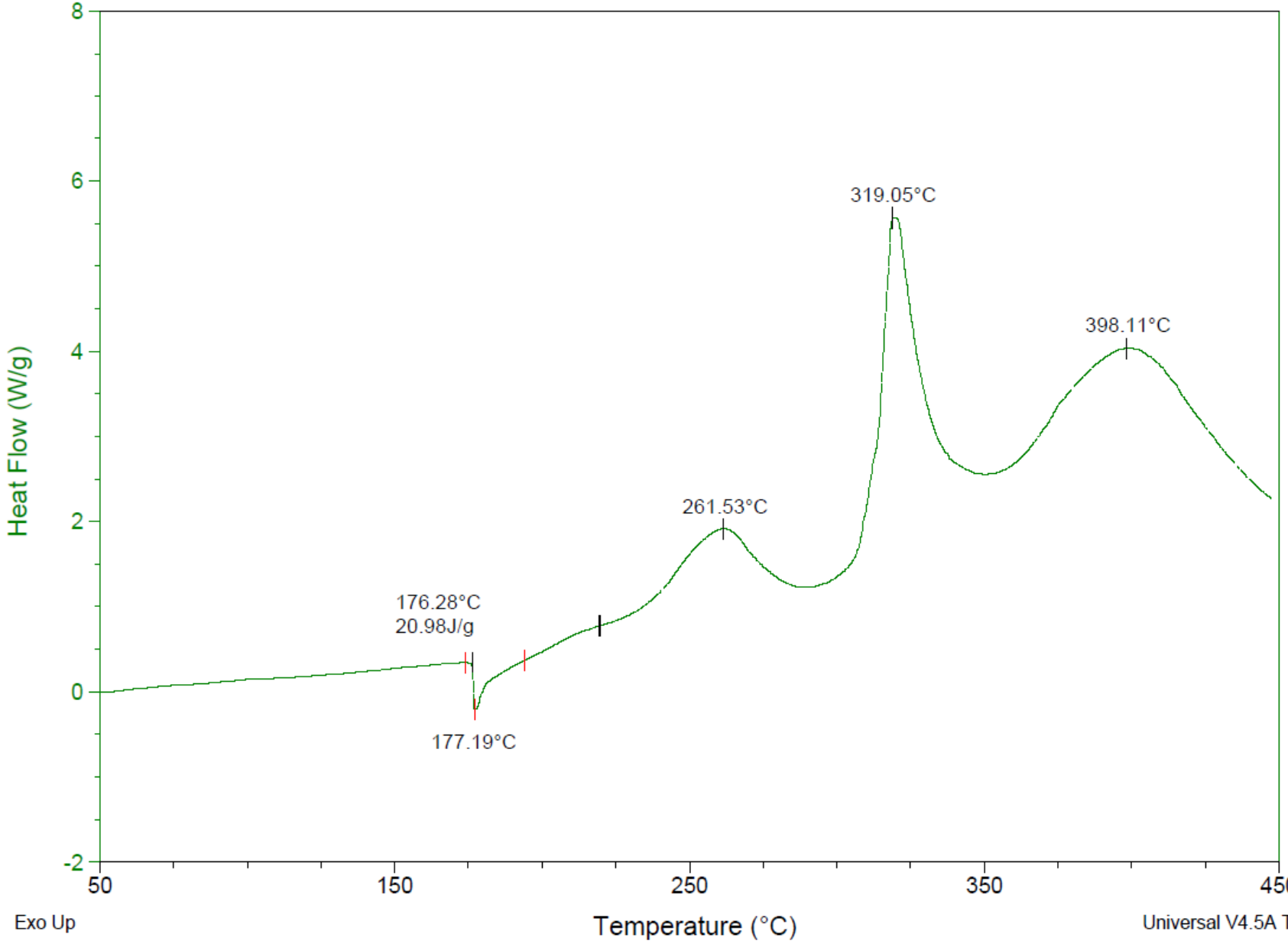

Figure S5) combustion of PATO formulations

PATO - FK-800 PATO - Estane/NP PATO - GAP