New Polycarbonate-Based Thermoplastic Polyurethane Binder for HMX Based Explosives

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New commercially available TPUs may provide improved long-term stability over current TPUs

Advantages:

- More thermally and hydrolytically stable than Estane 5703
- Lower density compared to fluoropolymers – more desensitizing

Disadvantages:

- Limited solubility in solvents of interest
- Tm for hard segments tend to be above the traditional maximum temperatures pressing HMX-based formulations

Before we can test these properties of interest, we need to determine if it is feasible to formulate with these new materials.

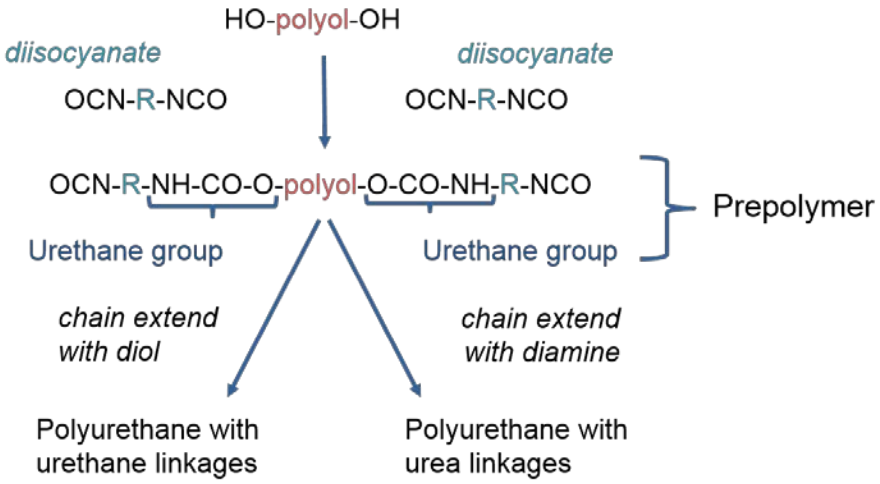
New TPUs are attractive but need to be tested for feasibility first

Selected 3 PC-TPU as binders of interest

Thermoplastic polyurethanes are classified by polyol and isocyanate type.

Urethanes have 3 basic building blocks:

1. Isocyanate (rigid)
2. Polyol (flexible)
3. Chain extender (rigid or flexible)



Known material – Estane

Estane 5703 (used in LX-14 and 9011) is an aromatic polyester-based TPU

Potential new binders – PC-TPUs

Polycarbonate as the polyol

- Excellent hydrolysis and chemical resistance at elevated temperatures
- Low compression set
- *No documented use in explosives*

Aliphatic and aromatic as the isocyanate

- Aliphatic have excellent adhesion
- Aromatic are known for toughness

Selected 3 PC-TPU as binders of interest

3 commercially available PC-TPU were purchased.

Type	Polyurethane	Manufacturer	Durometer (Shore Hardness)	Specific Gravity
Aliphatic Polycarbonate-based Polyurethane	Chronoflex AL 75A-Q	AdvanSource	75A	ca 1.10*
Aliphatic Polycarbonate-based Polyurethane	Quadrathane ALC-75A	Biomerics	75A	1.14
Aromatic Polycarbonate-based Polyurethane	Quadrathane ARC-75A	Biomerics	75A	1.17
Aromatic Polyester-based Polyurethane	*Estane 5703P [now Pearlstick 5703]*	*Lubrizol*	*70A*	*1.19*
Fluoroelastomer	*Viton A-100*	*Chemours*	*79A*	*1.82*

*TSD gives a large range of properties

Selected PC-TPUs with hardness values similar to Estane 5703

First concern – Is it safe?

A. Compatibility test of PC-TPUs with HMX

Determined by gas evolution using Chemical Reactivity Test (CRT).

Binder	Explosive	CRT Total gas release, 22 h @ 120 °C
Chronoflex AL 75A	HMX	0.01 cc g^{-1}
Quadrathane ALC-75A	HMX	0.05 cc g^{-1}
Quadrathane ARC-75A	HMX	0.08 cc g^{-1}

Measuring gas produced by the mixture of HMX and polyurethane and comparing it to the sum of the gas evolved the individual components.

(explosive + binder) ≤ 0.75 cc g^{-1} + explosive + binder

All three mixtures produced < 0.75 cc g^{-1} – considered compatible

All three binders are compatible with HMX

First concern – Is it safe?

B. LLNL's 5 small scale safety testing of 95 wt% HMX: 5 wt% binder.

Binder	Impact Height for 50% Reaction (DH50), cm	BAM Friction	Spark	CRT Total gas release, 22 hrs @120 °C	DSC Onset/Peak Temperature @ 5 °C min^{-1}, °C (ΔH, J g^{-1})
Chronoflex AL 75A	66	1/10 @ 36.0 kg	0/10 @ 1.0 J @ 510 Ω TIL = 0.19 J @ 0 Ω	0.05 cc g^{-1}	Closed: 272.6/278.1 (1722) Pin Hole: 274.0/278.8 (1734)
Quadrathane ALC-75A	49	1/10 @ 32.4 kg	0/10 @ 1.0 J @ 510 Ω TIL = 0.19 J @ 0 Ω	0.04 cc g^{-1}	Closed: 276.6/279.9 (1783) Pin Hole: 278.2/281.4 (1741)
Quadrathane ARC-75A	53	1/10 @ 32.5 kg	0/10 @ 1.0 J @ 510 Ω TIL = 0.15 J @ 0 Ω	0.10 cc g^{-1}	Closed: 279.0/282.1 (1605) Pin Hole: 279.3/282.4 (1624)
LX-14 (95.5% HMX 4.5% Estane 5703)	*69*	*0/10 @ 36.0 kg*	*0/10 @ 1.0 J @ 500 Ω*	*0.03 cc g^{-1}*	*Closed: 276.6/280.7 (1565) Pin Hole: 275.1/279.3 (1740)*

All formulations are in the same general range (which is to be expected). Main variations are in their impact sensitivity.

All three binders register on the same safety scale as LX-14

Second concern – Could we press to high density?

LLNL has a limitation (for safety) of pressing HMX formulations at up to 105 °C with in-die pressures up to 35 ksi

Type	Polyurethane	Tg(SS)	Tg(HS)	Tm(SS)	Tm(HS)	Test Press
Aliphatic Polycarbonate-based	Chronoflex AL 75A	-31.4 °C	NO	68.2 °C	110.5 °C	98.8% TMD
Aliphatic Polycarbonate-based	Quadrathane ALC-75A	-33.3 °C	59.4	118.8 °C	133.3 °C	98.5% TMD
Aromatic Polycarbonate-based	Quadrathane ARC-75A	-27.3 °C	NO	72.4 °C	166.0 °C	98.3% TMD

Estane 5703 has a hard segment melting temperature between 150 °C and 200 °C, depending on the content and perfection of the crystallites[1]

1. Hoffman, D.M., *Dynamic mechanical signatures of a polyester-urethane and plastic-bonded explosives based on this polymer.* Journal of Applied Polymer Science, 2002. **83**(5): p. 1009-1024.

All three binders have melting characteristics similar to Estane 5703 and are capable of pressing to high densities

Third concern – Can we formulate it?

A. Binders need to dissolve in a solvent that does not readily dissolve HMX as well to allow for coating the explosive

LX-14 uses MEK to dissolve the Estane binder.

Polyurethane	Chloroform	Cyclohexanone	50:50 MEK:Toluene	MEK + Benzoflex 9-88 (plasticizer)
Chronoflex AL 75A	Readily dissolves	**Dissolves with minimal heat**	Dissolves with heat	No
Quadrathane ALC-75A	Readily dissolves	**Dissolves with minimal heat**	Dissolves with heat	No
Quadrathane ARC-75A	No	**Dissolves**	Dissolves with high heat	Dissolves with heat
HMX Solubility	0.012 g/ 100 mL @ 20 °C[2]	**1.0 g/ 100 g @ 25 °C[3] 3.06 g/100 g @ 30 °C[4]**	1.403 g/ 100 g @ 30 °C[4] : 0.011 g/ 100 g @ 30 °C[4]	1.403 g/ 100 g @ 30 °C[4] + Unknown

2. Yasuda, S. K. (1968). “Microdetermination of estane in explosive mixtures.”
3. Sitzmann, M. E., et. al. "Solubilities of High Explosives: Removal of High Explosive Fillers from Munitions by Chemical Dissolution.“
4. B. Singh, L. K. C., P.N. Gadhikar (1978). "A Survey on the Cyclotetramethylene Tetranitramine (HMX)."

Cyclohexanone selected for all three to reduce variability going forward

Third concern – Can we formulate it?

B. Slurry coating procedure utilized as it would be the most scalable

Cyclohexanone solubility in water starts out low but increases rapidly with temperature. As such, the lacquer addition must be done at ambient (20–25 °C).

Incorporated HMX in water

Immediately after lacquer addition

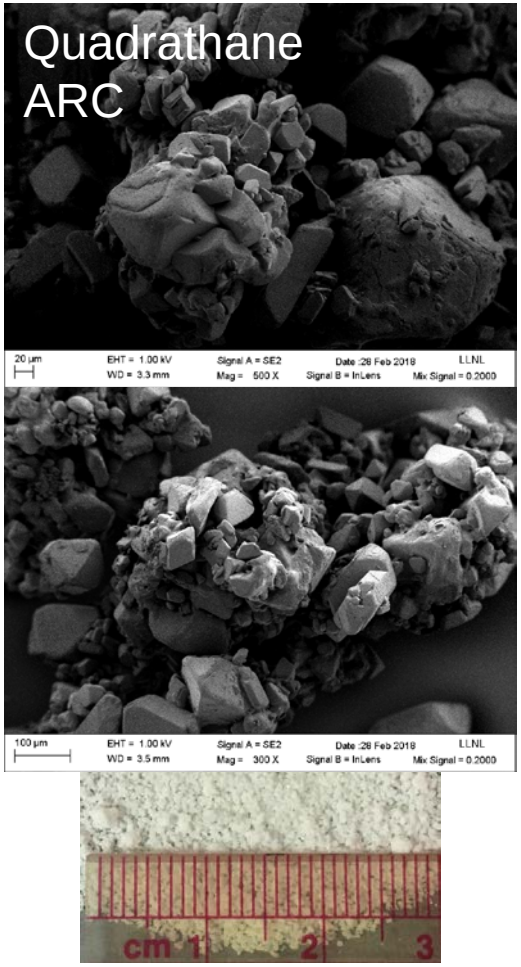
Immediately after water addition

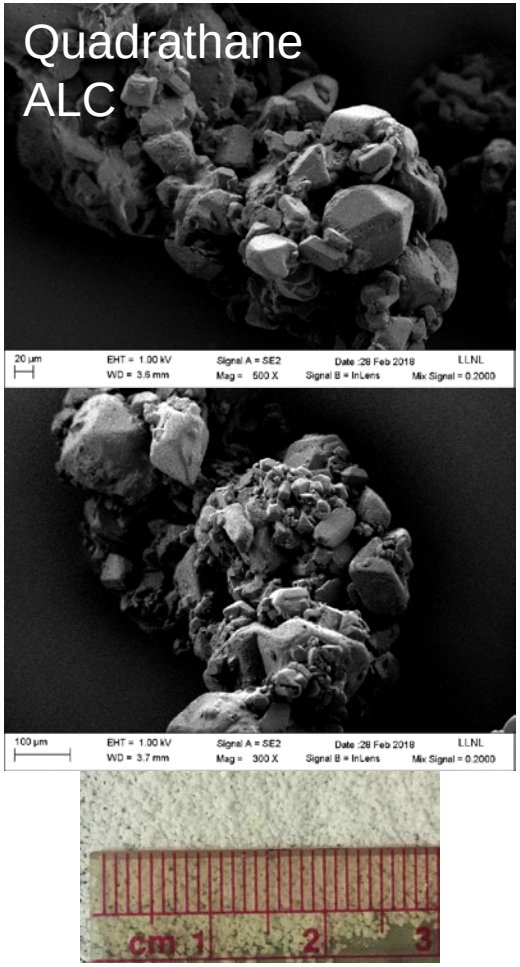
Slurry reached ~80 °C

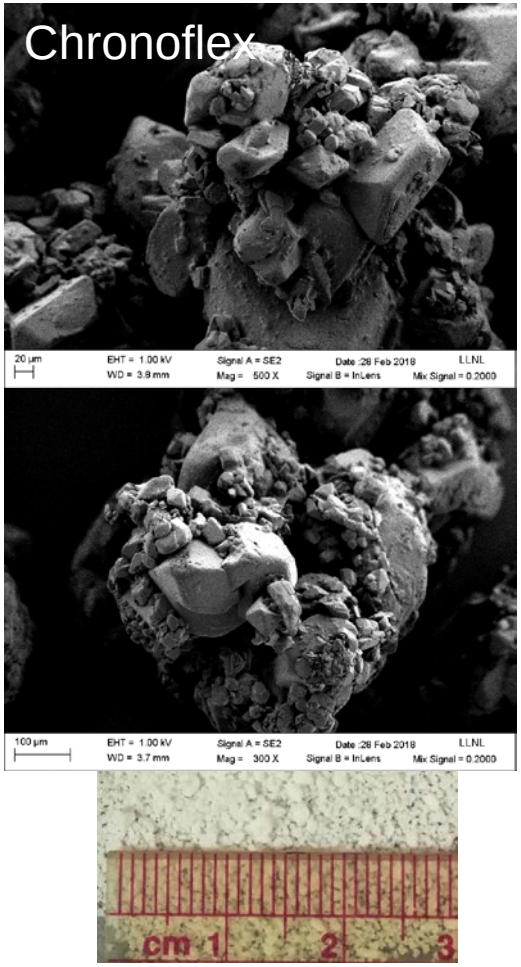
Resulting molding powder

If lacquer was added to a warm (60 °C) slurry, the binder becomes associated with the water phase and coats the vessel rather than forming beads.

Molding powder is binder encapsulated by HMX







All three formed uniform molding powder

How do they measure up?

Type	Polyurethane	Safety	Pressability	Lacquers	Slurry Coating
Aliphatic	Chronoflex AL 75A	Similar	Slightly lower melting point (Tm (HS) 110 °C)	Multiple options to dissolve	Similar
Aliphatic	Quadrathane ALC-75A	Similar	Slightly lower melting point (Tm (HS) 133 °C)	Multiple options to dissolve	Similar
Aromatic	Quadrathane ARC-75A	Similar	Slightly higher melting point (Tm (HS) 166 °C)	Difficult to dissolve	Similar

All three have similar safety and pressability. Molding powders with similar particle sizes are achievable under identical parameters.

The aromatic PC-TPU was very limited in solvents. The aliphatic PC-TPUs were more flexible in their solvent options.

Aliphatic PC-TPUs have benefits over the Aromatic PC-TPUs

Future plans

Thermal characterization

- Coefficient of Thermal Expansion (CTE)
- Softening point

} Thermal Mechanical Anlaysis (TMA)

Explosive Characteristics

- Detonation velocity
- C-J pressure

} Disc Acceleration eXperiment (DAX)

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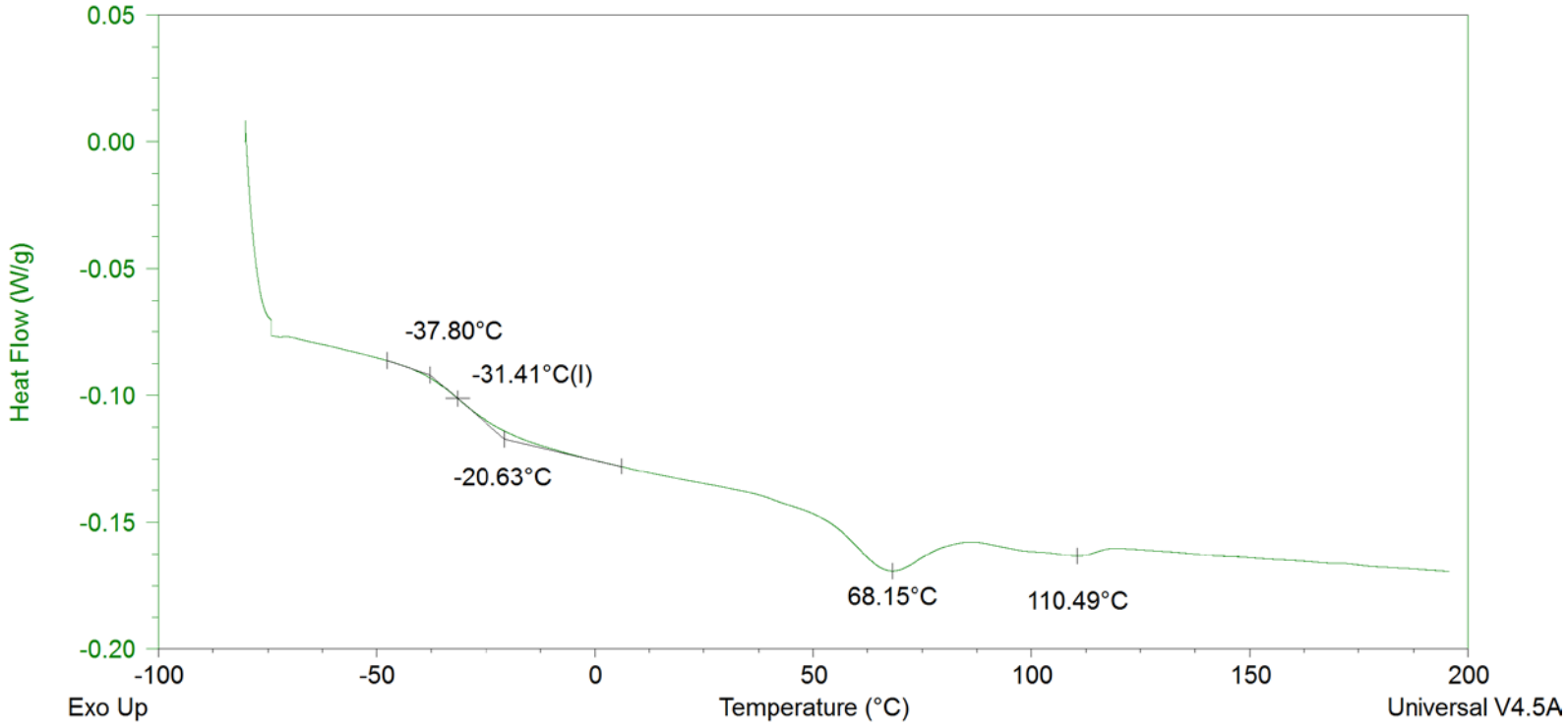
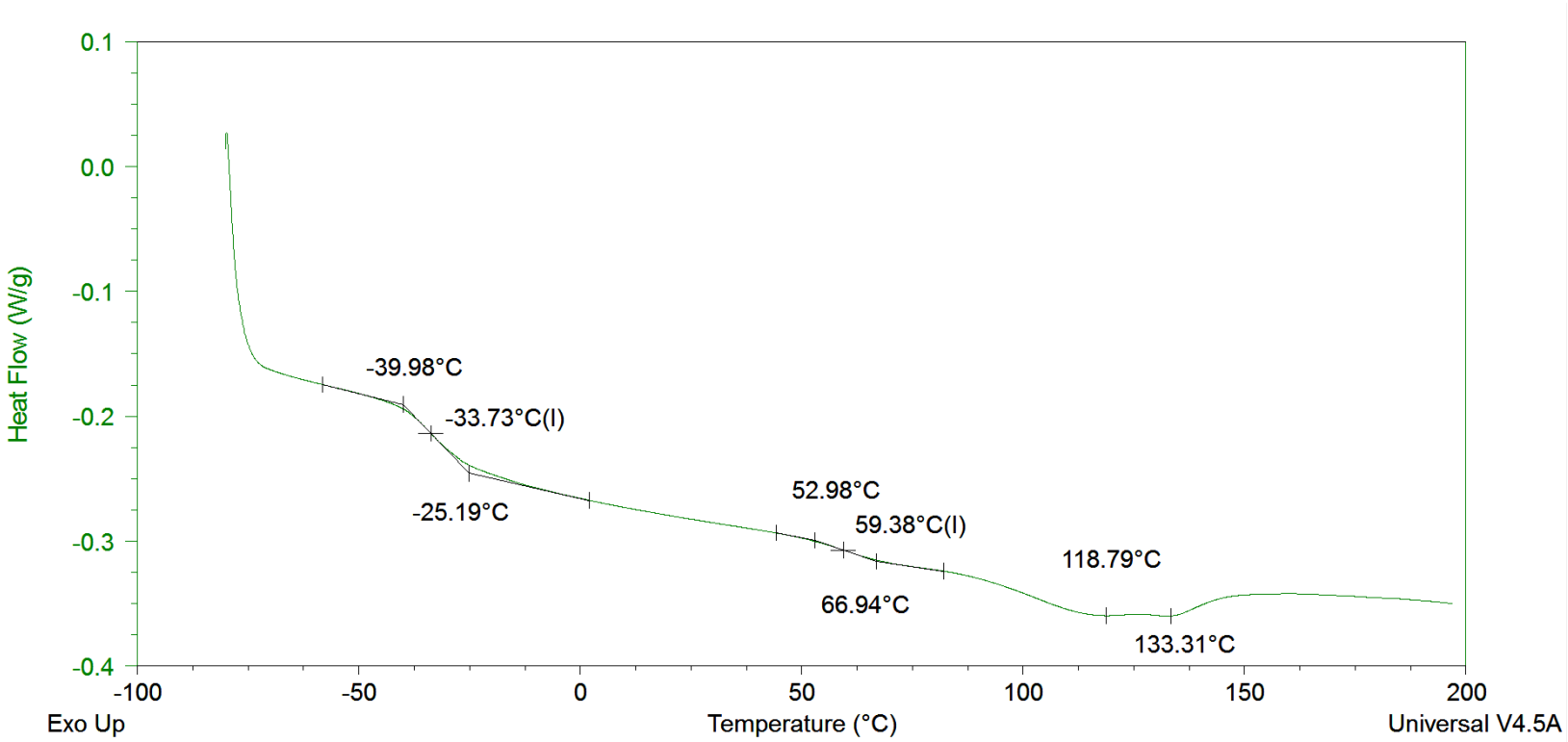
Chronoflex DSC



ChronoFlex AL 75A – aliphatic polycarbonate-based polyurethane.

20 mg tested in a closed hermetic dish from -80 °C to 205 °C at 5 °Cmin^{-1}

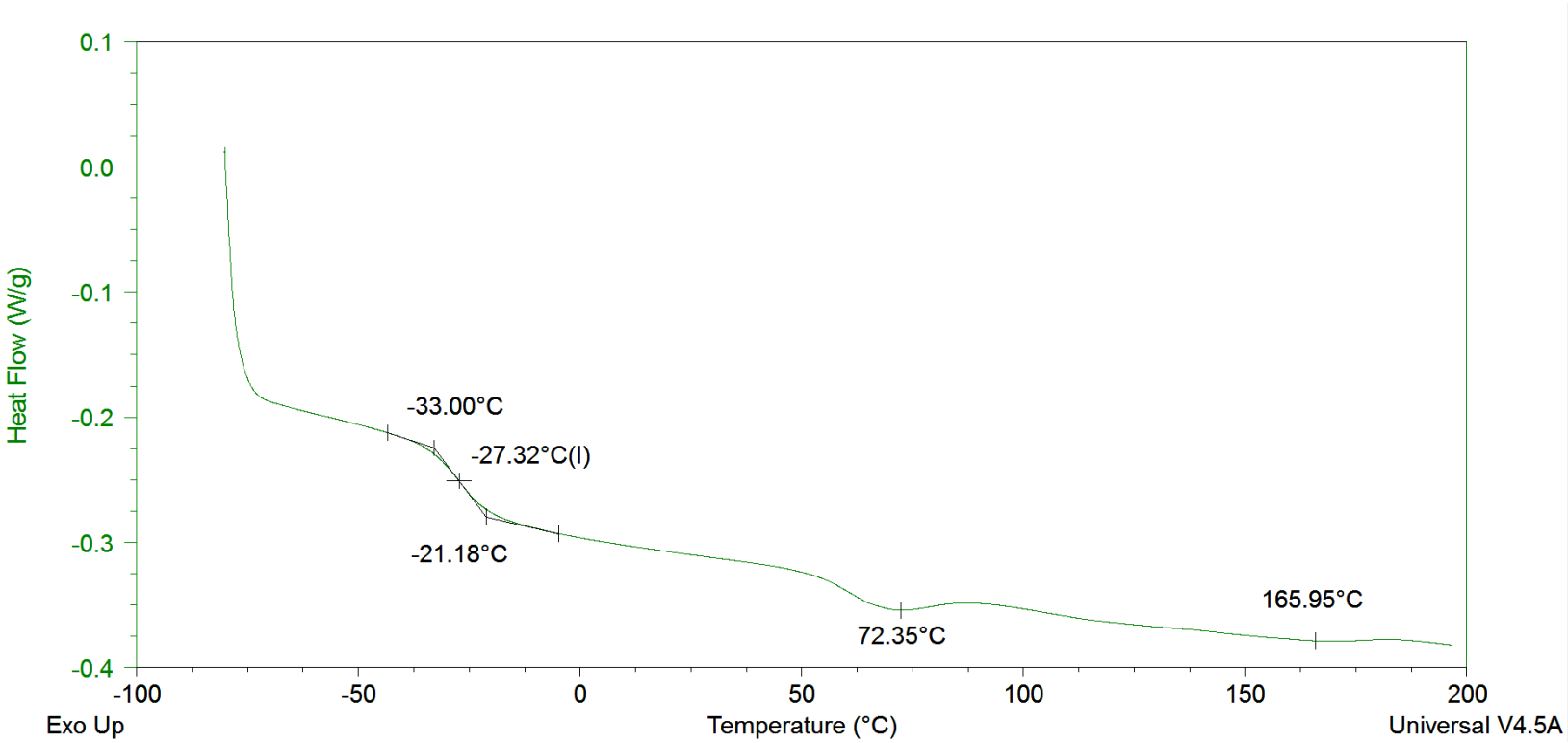
Quadrathane ALC DSC



Quadrathane ALC – aliphatic polycarbonate-based polyurethane.

20 mg tested in a closed hermetic dish from -80 °C to 205 °C at 5 °Cmin^{-1}

Quadrathane ARC DSC



Quadrathane ARC – aromatic polycarbonate-based polyurethane.

20 mg tested in a closed hermetic dish from -80 °C to 205 °C at 5 °Cmin^{-1}