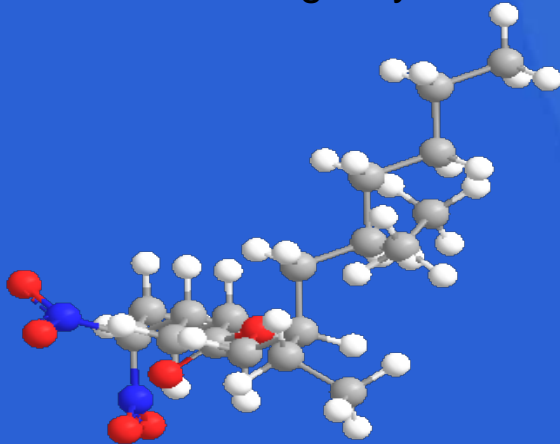




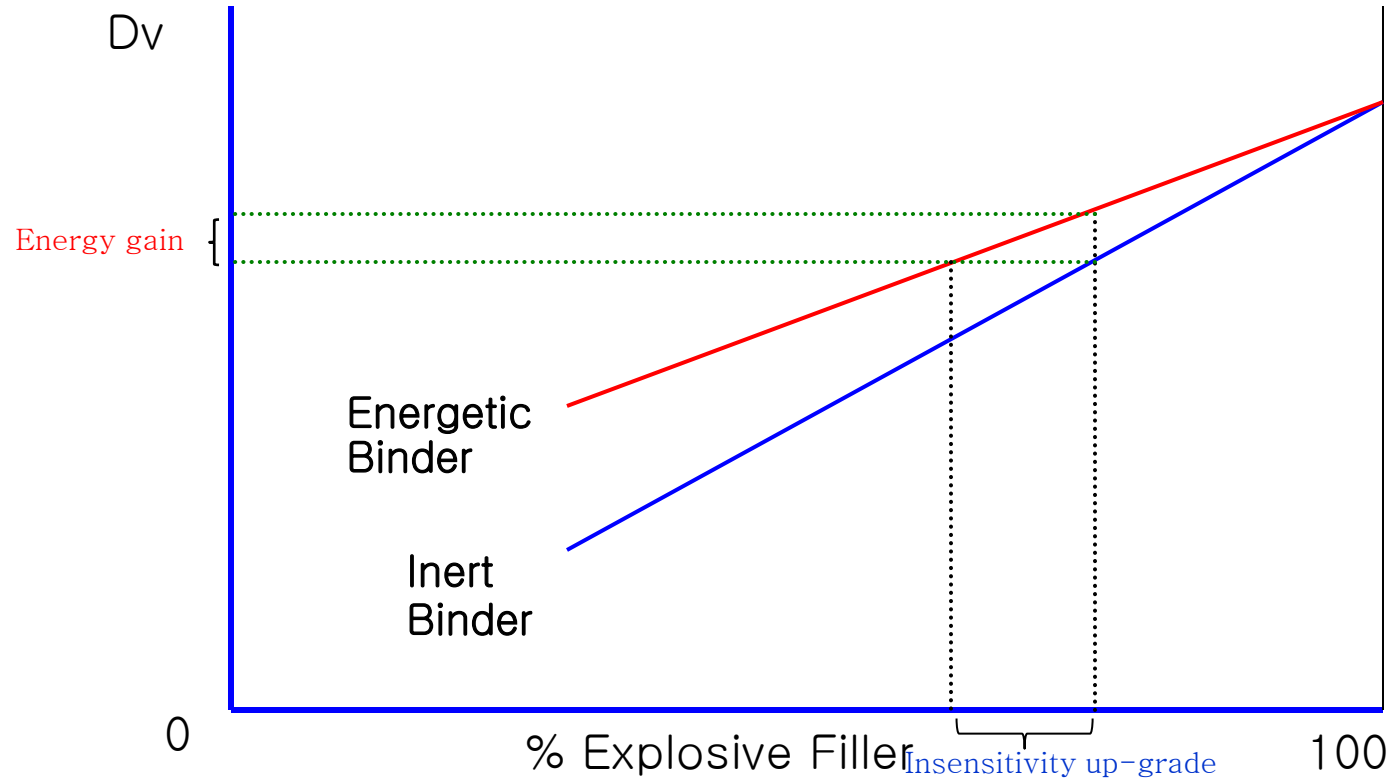
Design of New Insensitive Energetic Plasticizers for HTPB

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High Explosives Group
Agency for Defense Development, Korea



INTRODUCTION



Energetic Plasticizer

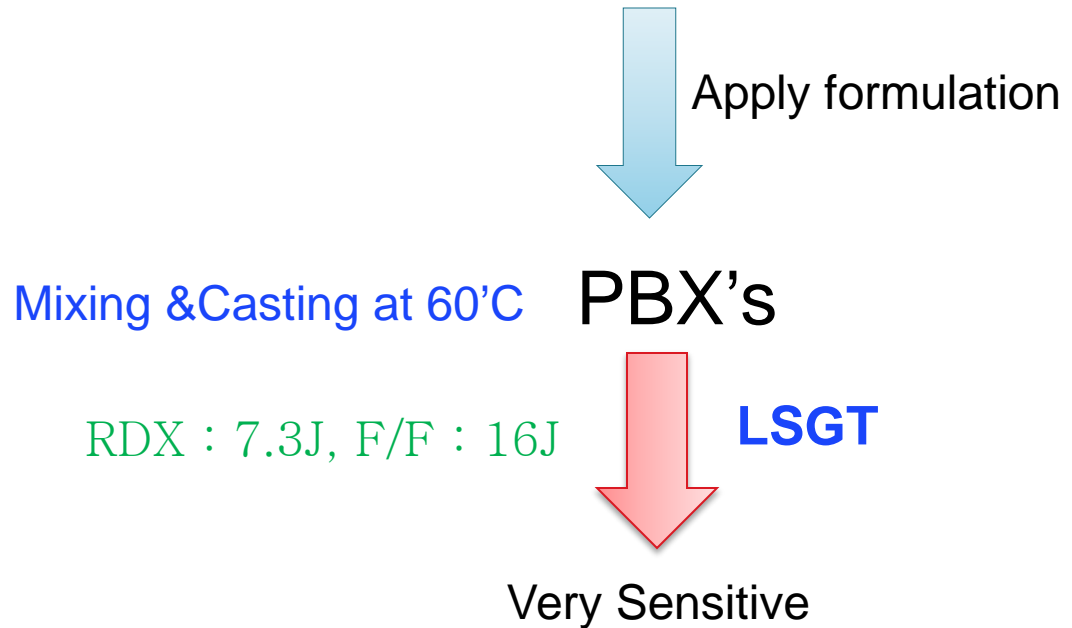
BTTN

TMETN

F/A

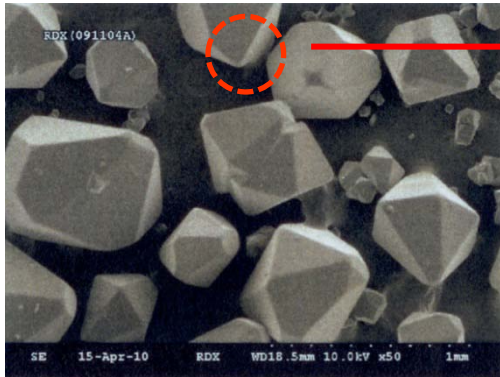
F/F

Formulation & Gap Test



Gap Test with Different Crystal Shape

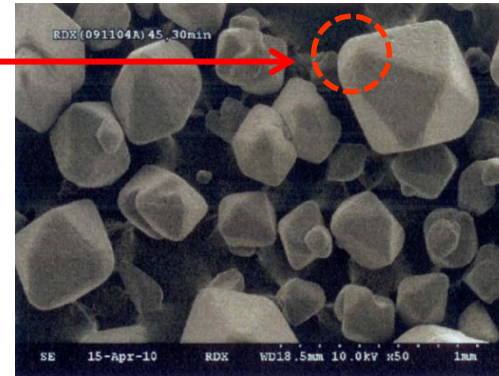
Before etching



CL-3

No. of Card Gap : 138.8

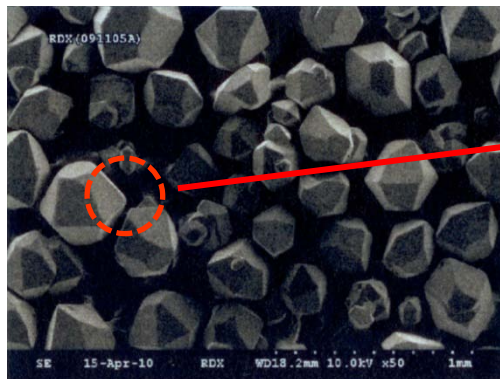
After etching



No. of Card Gap : 119.5

Remove sharp edge

RDX (091105A)



CL-1

No. of Card Gap : 147.7

H1-RDX091105A(55/30)



No. of Card Gap : 125.5

Remove sharp edge

Why this formulation is sensitive ?

Solubility of RDX

plasticizer	solubility(g/cc)	
	25°C	60°C
DOA	0.07	0.13
IDP	0.06	0.10
F/F	3.15	6.05



Solubility Gap change
: Driving force of Change of Crystal Shape



Increase Sensitivity

Preparing RDX Sample from PBX Processing

Plasticizer ; DOA or Mixed Formal

Typical Processing of Castable PBX

Mixing at
Mixer

@ 60'C



Store at Oven w/o
Curing agent

@ 60'C



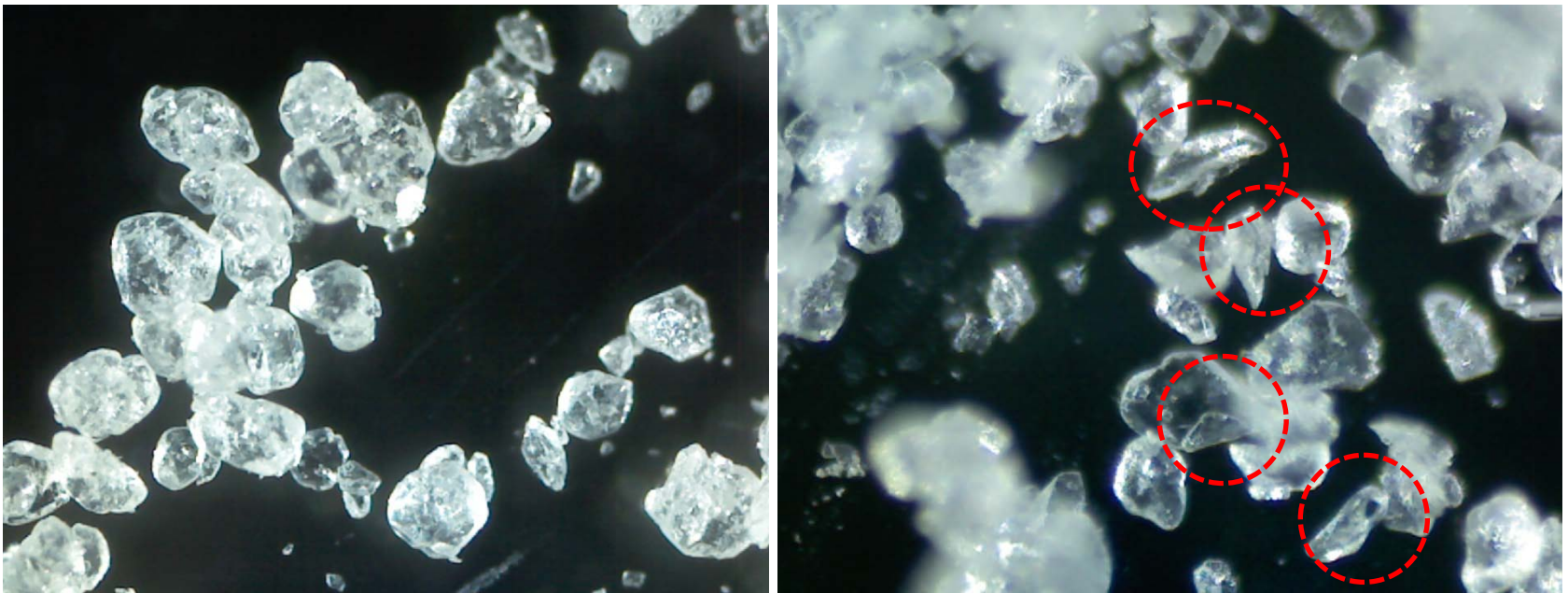
Cool Down
To RT



Collect RDX to investigate Crystal Shape

Optical Microscopy of Recoverd RDX

➤ Recovered RDX Sample from Plasticizer



From DOA

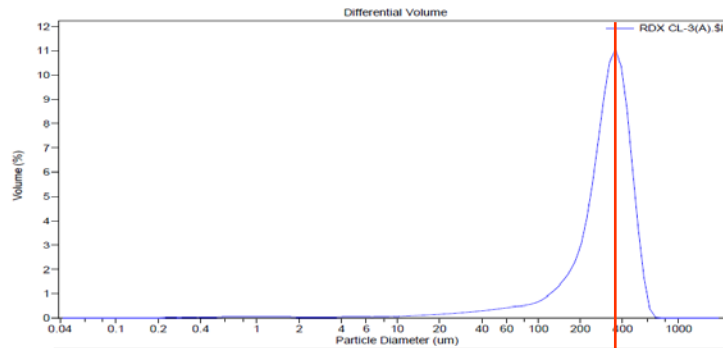


From F/F

Changed crystal shape

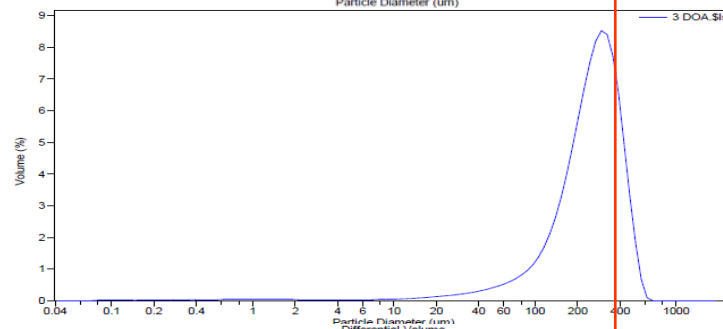
Particle Size Distribution of Recovered RDX

Original
RDX



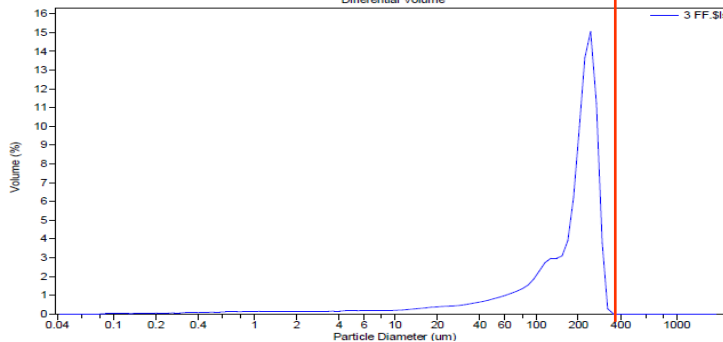
Mean diameter : 306μm

From
DOA



Mean diameter : 257μm

From
F/F



Mean diameter : 175μm

Hydroxyl Terminated Poly(Butadiene)

HTPB

DOA

IDP

HTPB : miscible with only **non-polar plasticizer**.

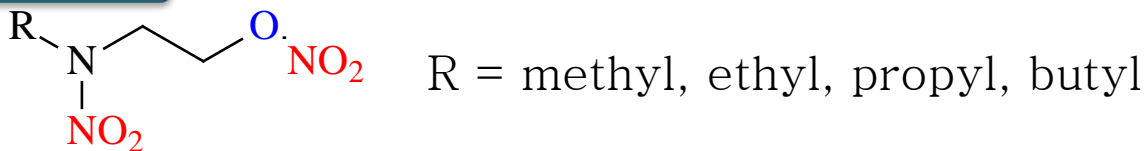
very important prepolymer

Basic Concept for Design of New Plasticizer

- Miscible with HTPB
- Mild Energetic
- Low Solubility with RDX or molecular explosives
- Low Glass Transition Temperatures
- Low Viscosity
- High Thermal Stability
- Economical

Design of Low Energy Plasticizer Like BUNENA

BUNENA



NitratoEthyl NitaAmine

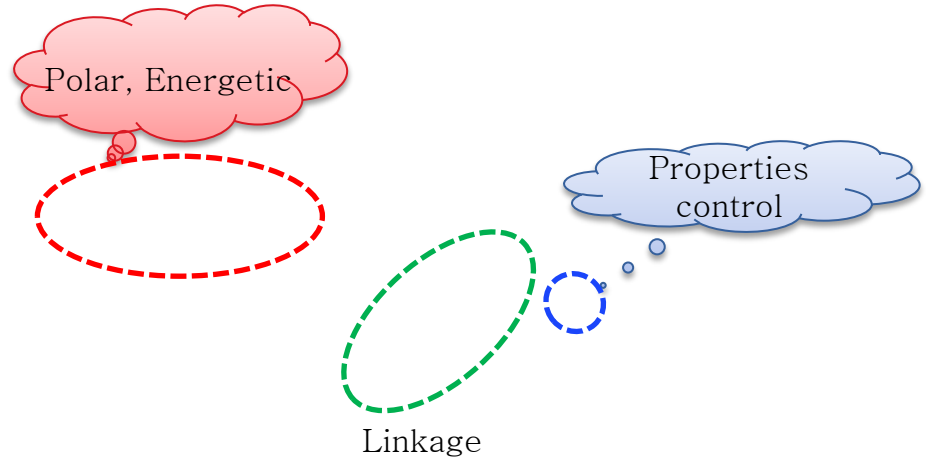
Commercially

Available in Korea



New Plasticizer Like BUNENA

➤ Michael addition



R = butyl, hexyl, heptyl, ethylhexyl

Synthetic Results by Michale Addition

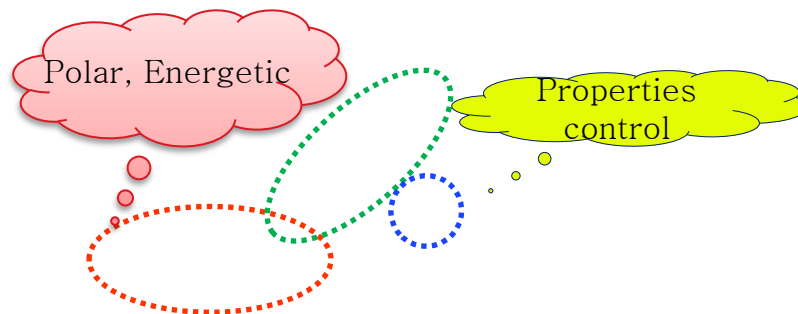
R	Yield(%)	T _g (°C)	T _d (°C)	¹ H NMR (CDCl ₃ -d ₆ , ppm)
Butyl	52	-96.07	262.83	4.12(t,2H), 2.87(t,2H), 2.48(t,2H), 2.15(s,3H), 1.63(m,2H), 1.40(m,2H), 0.95(t,3H)
Hexyl	36	-94.28	262.67	4.10(t,2H), 2.85(t,2H), 2.45(t,2H), 2.13(s,3H), 1.62(m,2H), 1.34(m,6H), 0.90(t,3H)
Heptyl	32	-94.84	260.33	4.11(t,2H), 2.86(t,2H), 2.45(t,2H), 2.13(s,3H), 1.63(m,2H), 1.30(m,8H), 0.90(t,3H)
-Ethylhexyl	33	-90.65	257.33	4.04(dd,2H), 2.86(t,2H), 2.46(t,2H), 2.14(s,3H), 1.55(m,1H), 1.31(m,8H), 0.89(t,3H)

- Low Yield
- Low Reproducibility

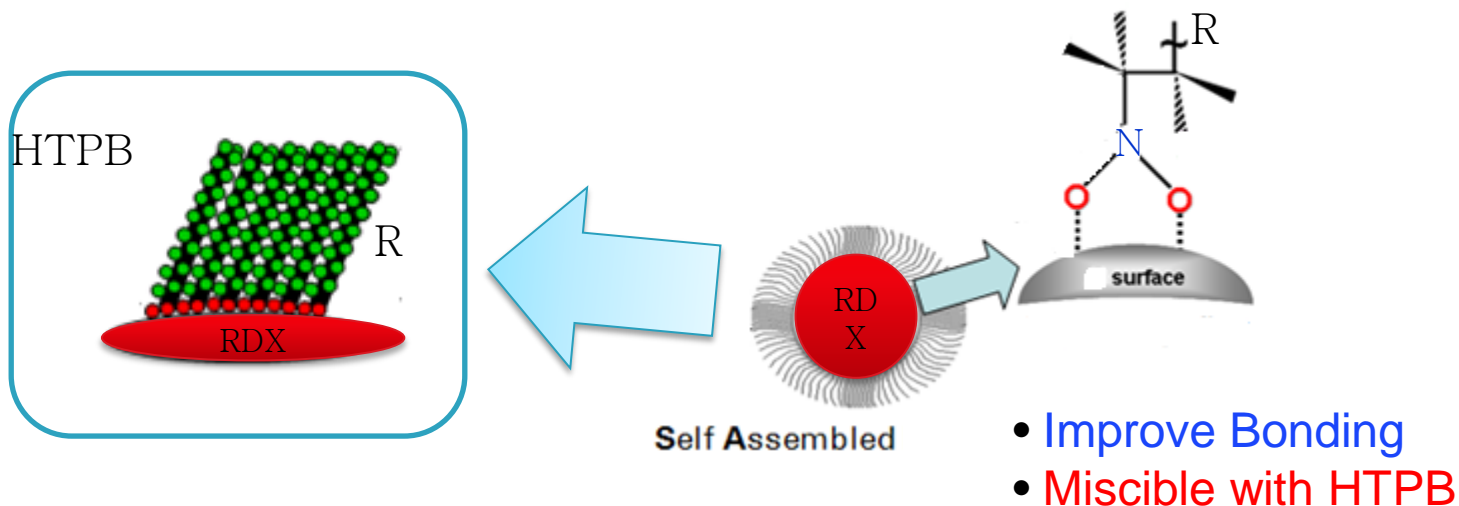
Change Starting Material



cat



R= -hexyl, -octyl, -ethylhexyl, -dodecyl, -butyloctyl, -hexyldecyl

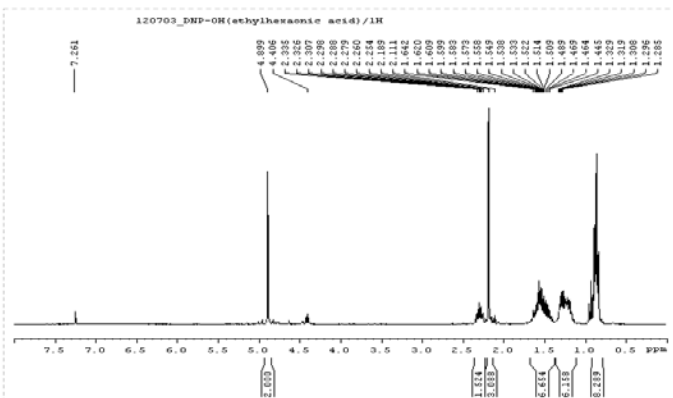


Select Catalyst

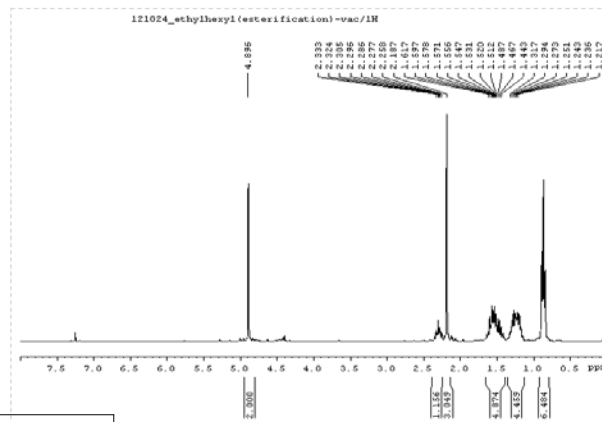
cat

Cat : p-TSA, TFAA, PPA

TFAA



PPA



	Integration ratio
Predicted	2:1.0:3.0:4.0:4.0:6.0
TFAA or p-TSA	2:1.5:3.0:6.6:6.1:8.3
PPA	2:1.2:3.0:4.9:4.6:6.5

Integration mismatched

Synthetic Results by Esterification

-R	Yield(%)	T _g (°C)	T _d (°C)	¹ H NMR (CDCl ₃ -d ₆ , ppm)
Hexyl	83	-101.99	268.00	4.88(s, 2H), 2.32 (t, 2H), 2.08 (s, 3H), 1.58 (m, 2H), 1.28 (m, 4H), 0.87 (t, 3H)
2-Ethylhexyl	77	-96.96	245.67	4.90 (s, 2H), 2.30 (m, 1H), 2.19 (s, 3H), 1.55 (m, 4H), 1.23 (m, 4H), 0.89 (m, 6H)
Octyl	80	-99.15	260.83	4.88 (s, 2H), 2.35 (t, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 1.58 (m, 2H), 1.25 (m, 8H), 0.86 (t, 3H)
Dodecyl*	78	-30.27*	257.00	4.90 (s, 2H), 2.35 (m, 2H), 2.18 (s, 3H), 1.60 (m, 2H), 1.26 (m, 16H), 0.88 (t, 3H)
2-Butyloctyl	64	-93.72	260.83	4.90 (s, 2H), 2.37 (m, 1H), 2.19 (s, 3H), 1.53 (m, 4H), 1.28 (m, 12H), 0.89 (t, 6H)
2-hexyldecyl**	56	-92.57	253.33	4.91 (s,2H), 2.40 (m, 1H), 2.20 (s, 3H), 1.57 (m, 4H), 1.31 (m, 22H), 0.89 (t, 6H)

* T_m

** Scale-up 15kgs

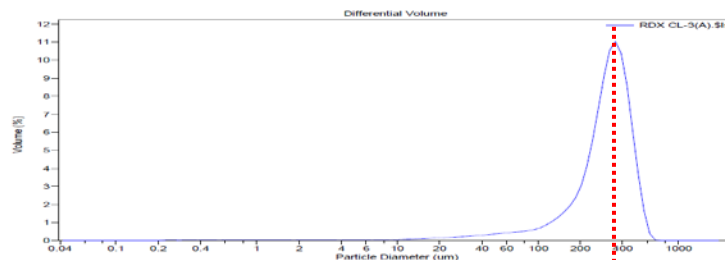
Solubility & Miscibility of IEP

plasticizer	Miscibility with HTPB	solubility(g/cc)		
		25°C	60°C	Solubility Gap
DOA	immiscible	0.07	0.13	0.05
IDP	immiscible	0.06	0.10	0.04
F/F	miscible	3.15	6.05	2.90
-IEP	miscible	0.30	0.86	0.56

Particle Size of Recovered RDX

Original

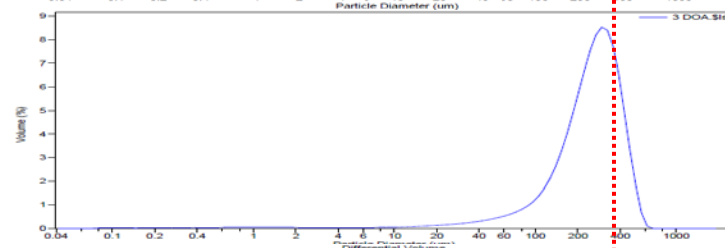
RDX



Mean diameter : 306μm

From

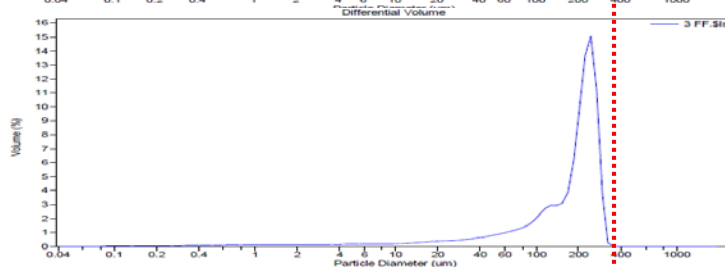
DOA



Mean diameter : 257μm

From

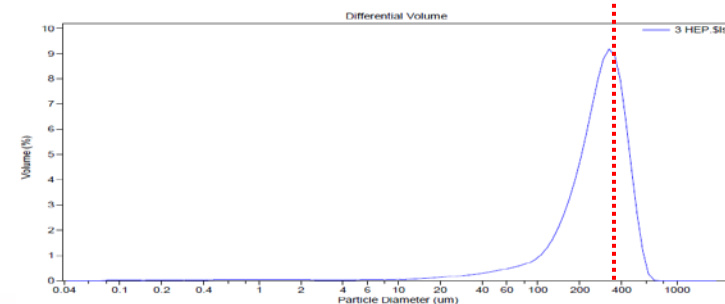
F/F



Mean diameter : 175μm

From

-IEP



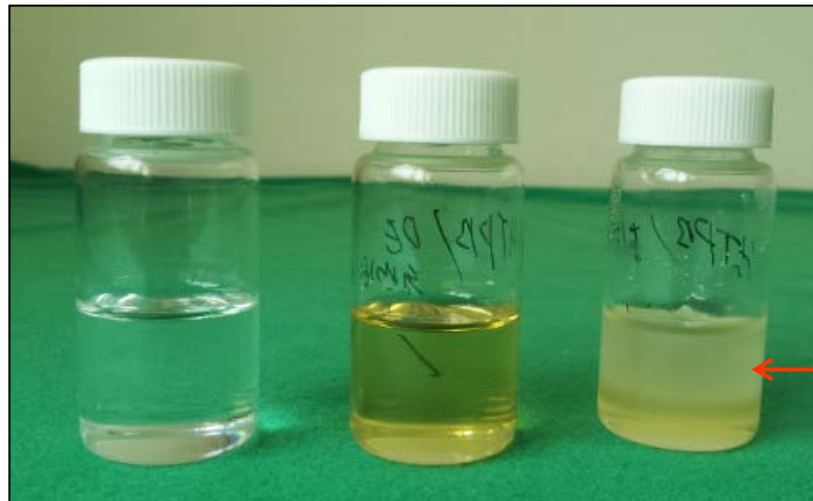
Mean diameter : 279μm

Solubility & Miscibility of IEP

Plasticizer	Miscibility with HTPB	Solubility(g/cc)		
		25°C	60°C	Solubility Gap
DOA	Miscible	0.07	0.13	0.05
IDP	Miscible	0.06	0.10	0.04
F/F	Immiscible	3.15	6.05	2.90
IEP	Miscible	0.45	0.67	0.22

Miscibility with HTPB

➤ Miscibility



← Immiscible

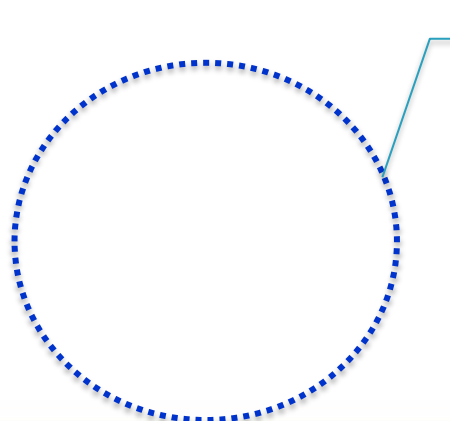
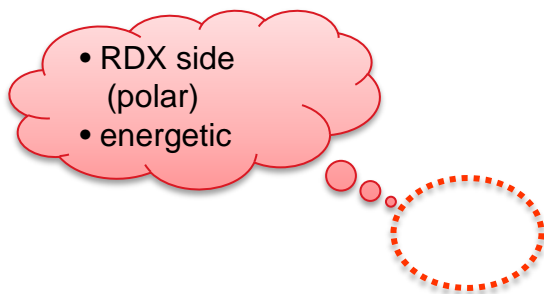
HTPB+DOA HTPB+IEP HTPB+FF

❖ IEP : Miscible with HTPB

Viscosity

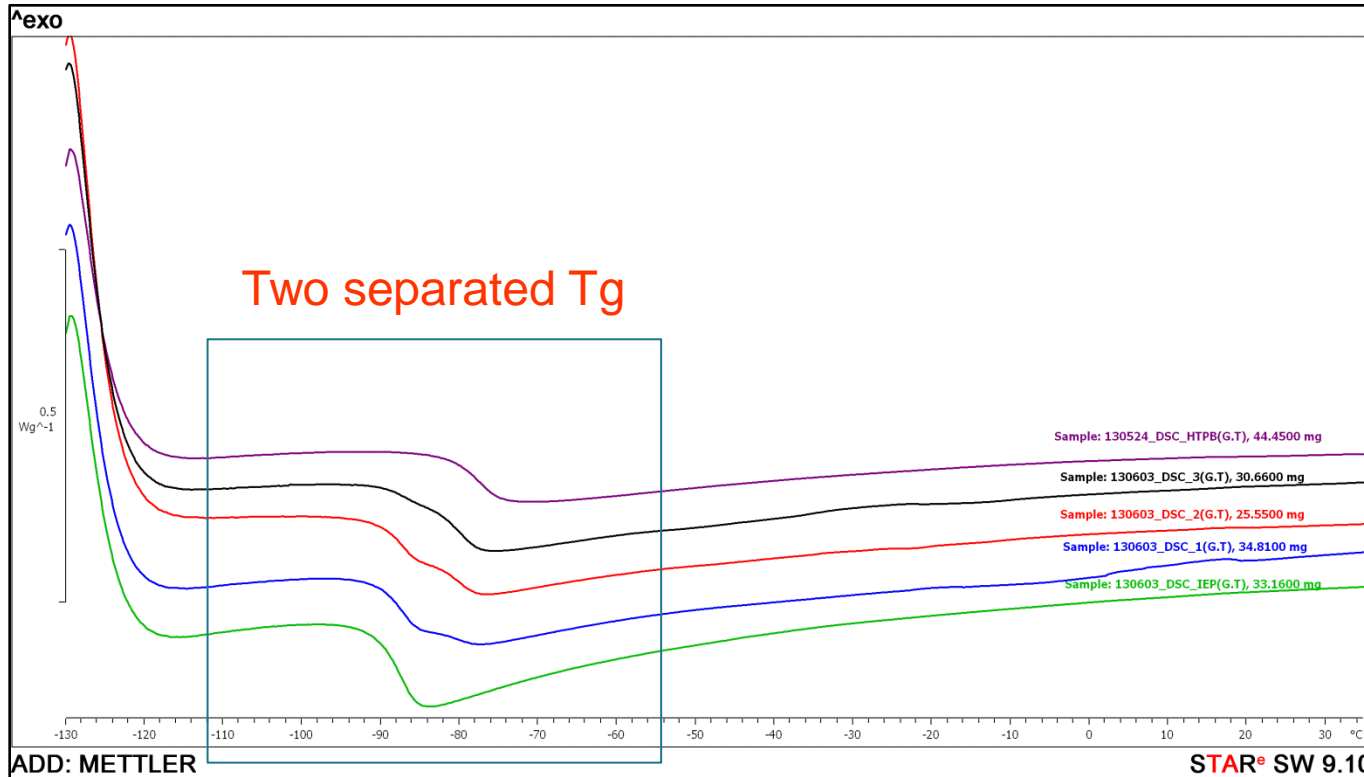
Temp	Viscosity (cp)					
	HTPB	DOA	DOA/HTPB =1/1	F/F	IEP	Mixture (IEP/HTPB=1/1)
30°C	3455	9.3	300	405.0	22.5	135.6
40°C	1967	8.2		261.2	16.3	77.5
50°C	1230	7.5		177.5	13.8	46.3
60°C	806.3	6.9	82	128.8	12.5	32.5

Good Plasticizing
Effect



• Miscible with HTPB (none polar)
• Plasticizing

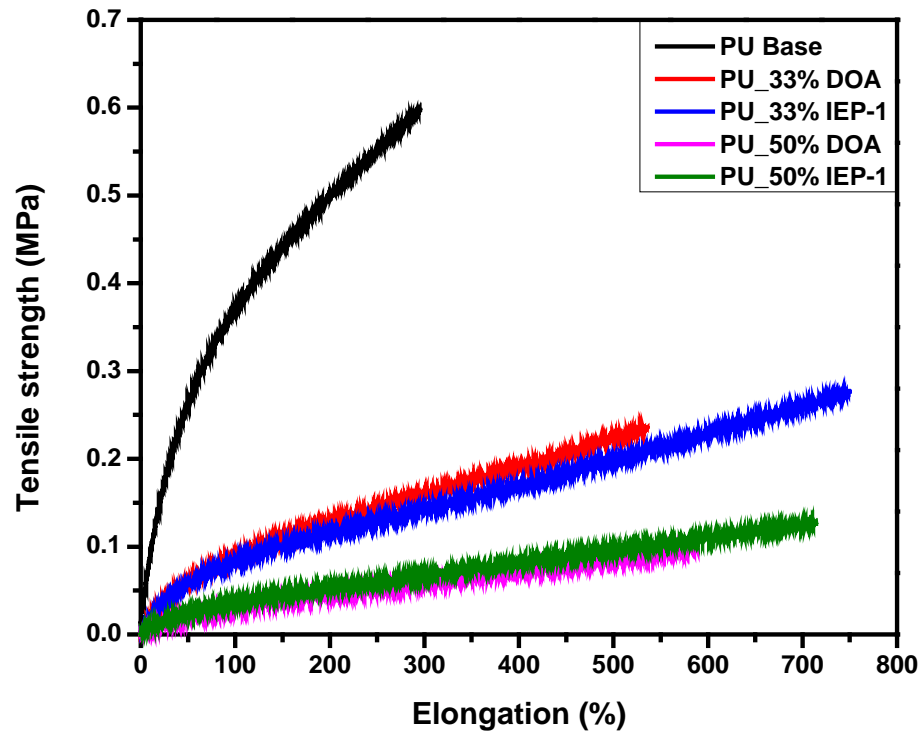
Glass Transition Temp. with HTPB



Pure HTPB
HTPB : IEP = 3 : 1
HTPB : IEP = 1 : 1
HTPB : IEP = 1 : 3
Pure IEP

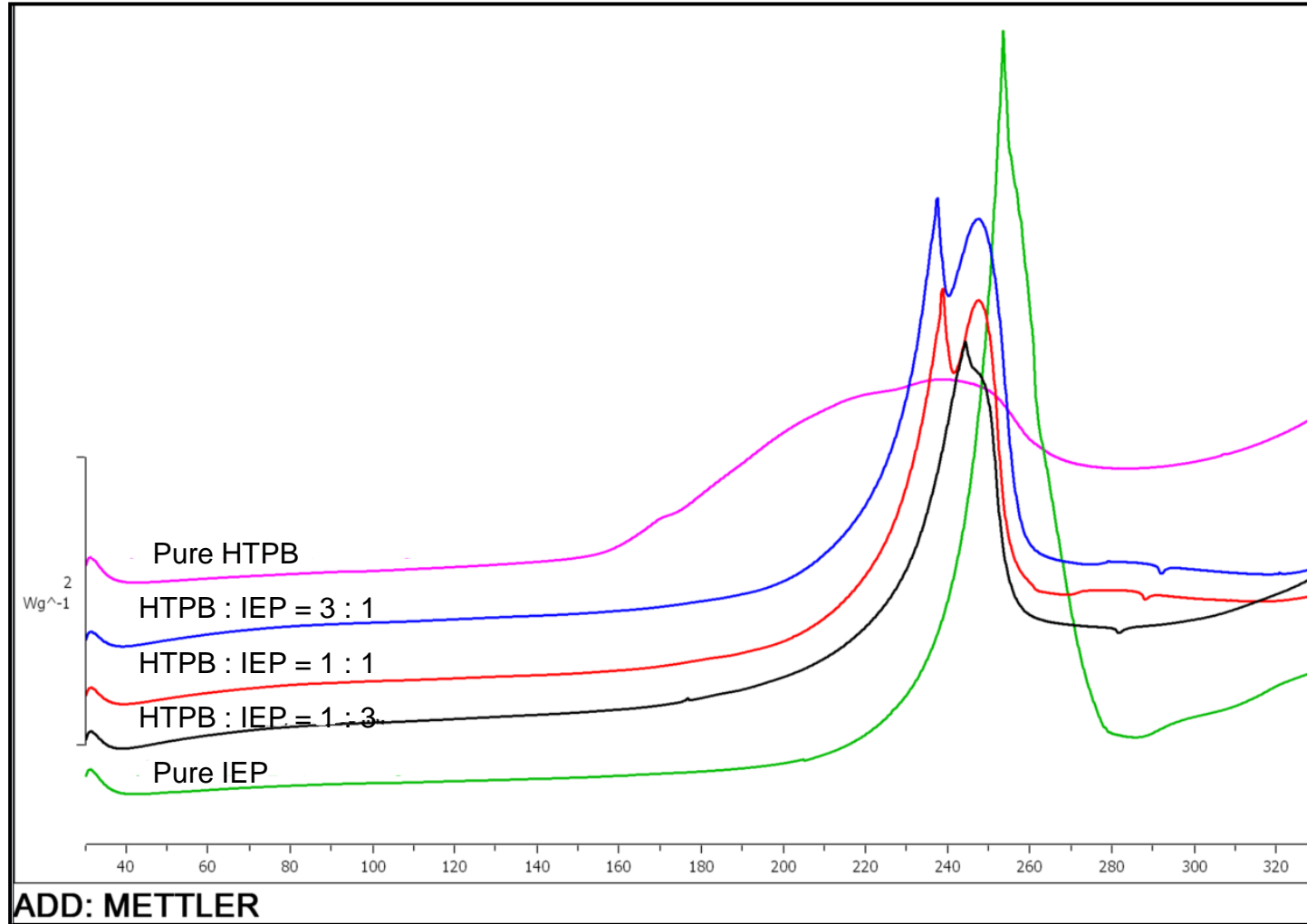
- Evidence of existing of very small domain

Mechanical Properties of PU

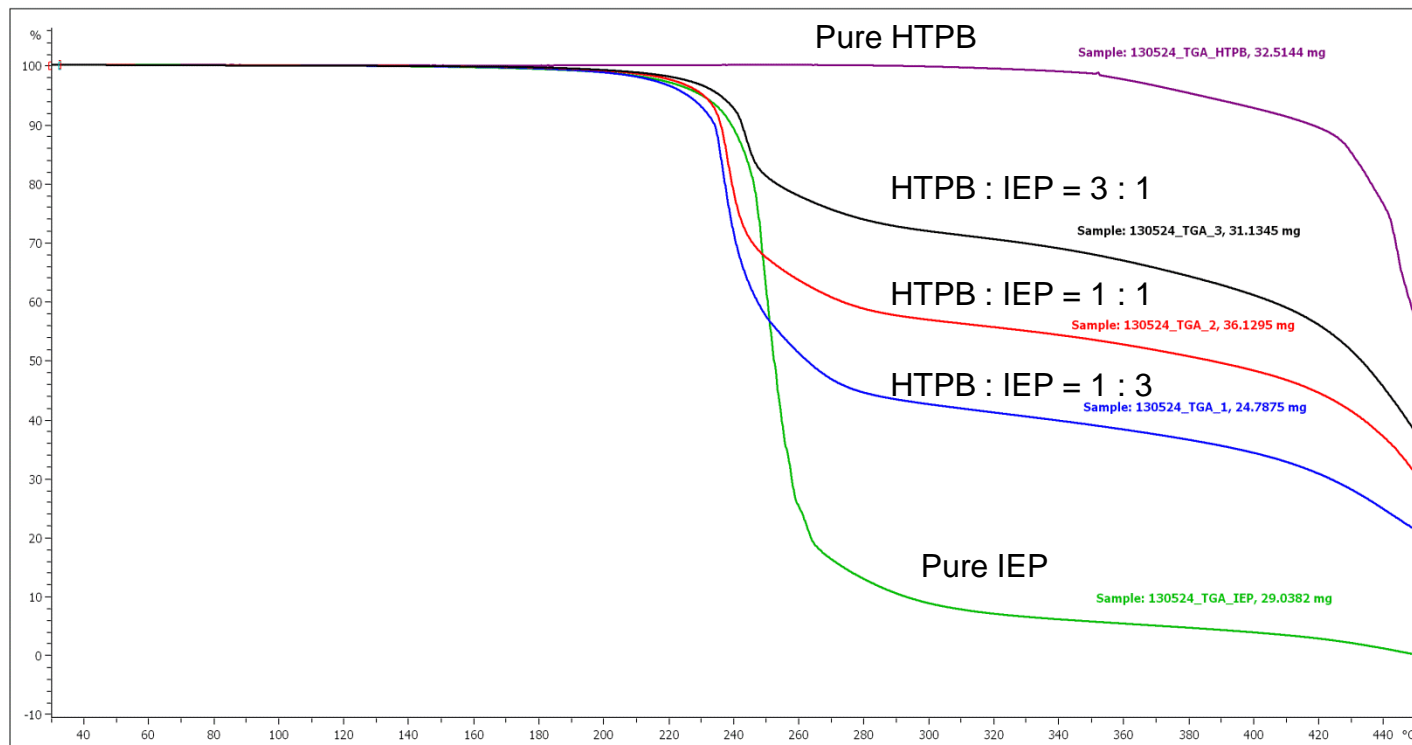


Sample	Stress at break (MPa)	Elongation (%)	Modulus (Mpa)
HTPB_PU	0.608±0.046	295±50	0.812±0.005
PU_33%DOA	0.218±0.026	535±59	0.193±0.006
PU_50%DOA	0.090±0.015	588±79	0.067±0.008
PU_33%IEP-1	0.285±0.008	749± 4	0.184±0.004
PU_50%IEP-1	0.126±0.001	714± 1	0.073±0.008

Thermal Properties(DSC)



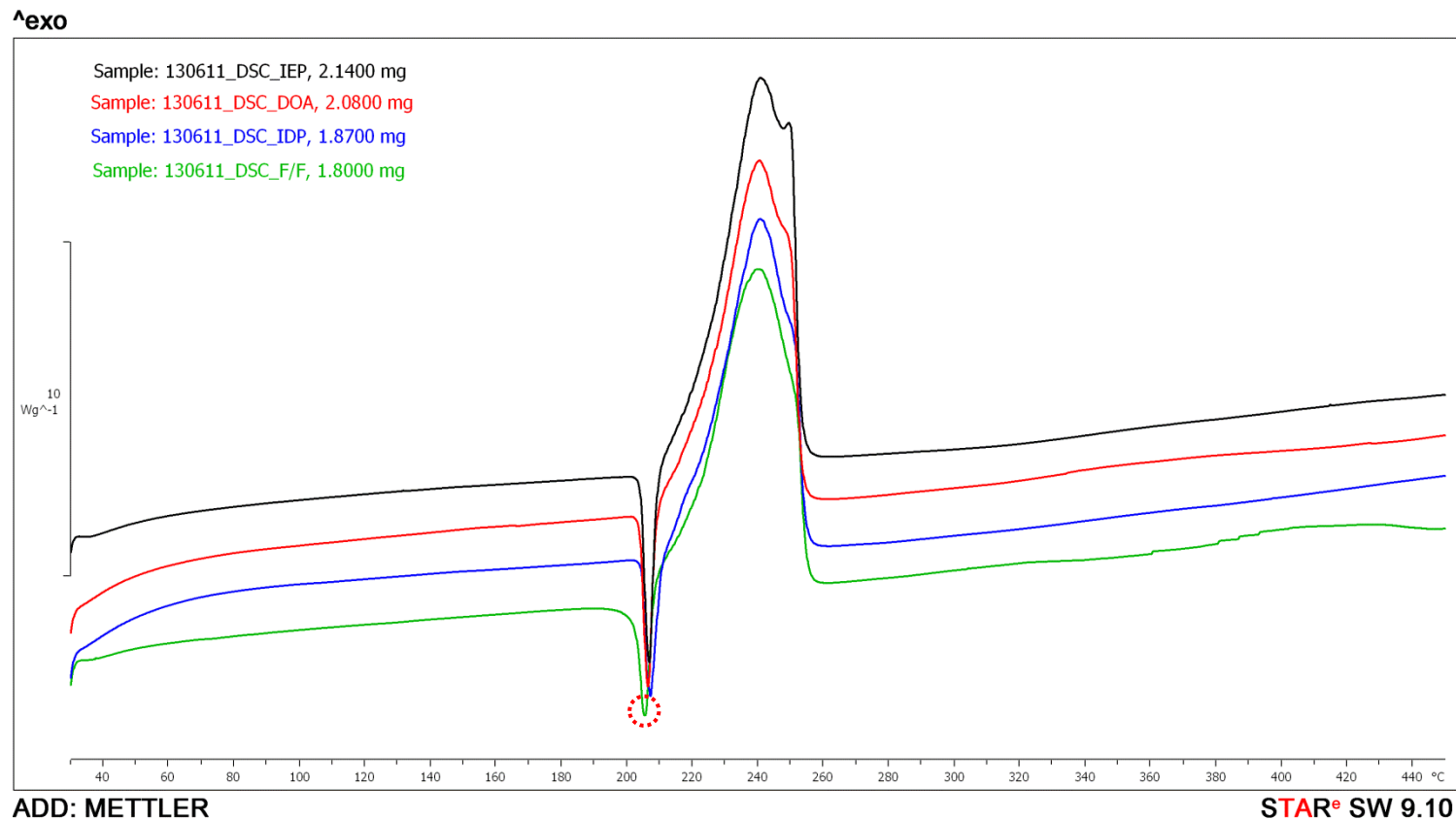
Thermal Properties(TGA)



ADD: METTLER

STAR^e SW 9.10

Thermal Properties of Coated RDX



* 5% plasticizer coated RDX

Impact Sensitivity & Vacuum Stability

➤ Impact Sensitivity

Sample name	Impact Sensitivity(J)
RDX	7.3
DOA	> 100
F/F	16.3
IEP	> 100
DOA Coated RDX(5%)	8.5
F/F Coated RDX(5%)	7.8
IEP Coated RDX(5%)	8.4

➤ Vacuum Thermal Stability

Sample name	Evolved gas(ml/g)
RDX	0.03
DOA	0.23
F/F	0.18
IEP	0.28
DOA Coated RDX(5%)	0.05
F/F Coated RDX(5%)	0.04
IEP Coated RDX(5%)	0.05



Need LSGT to confirm insensitivity

➤ New Insensitive Energetic Plasticizer

- ✓ Low Viscosity
- ✓ Low solubility for molecular explosive(RDX)
- ✓ Good Plasticizing Effect
- ✓ Promising for Insensitive formulation
- ✓ Miscible with HTPB
- ✓ Good thermal properties
- ✓ Simple & Cheap Process



Thank You
Very Much