2016 SHOW & CONFERENCE

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2ND EDITION

Optimizing Epoxy Toughness with Greater Formulation Latitude Using Reactive Liquid Polymers

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Contents

- Epoxy Toughening
- Epoxy Adduct Synthesis
- Glycidyl Ester Synthesis
- Adhesive Result Comparisons
- Conclusions

Epoxy Applications

- Coatings

- Composites

- Adhesives

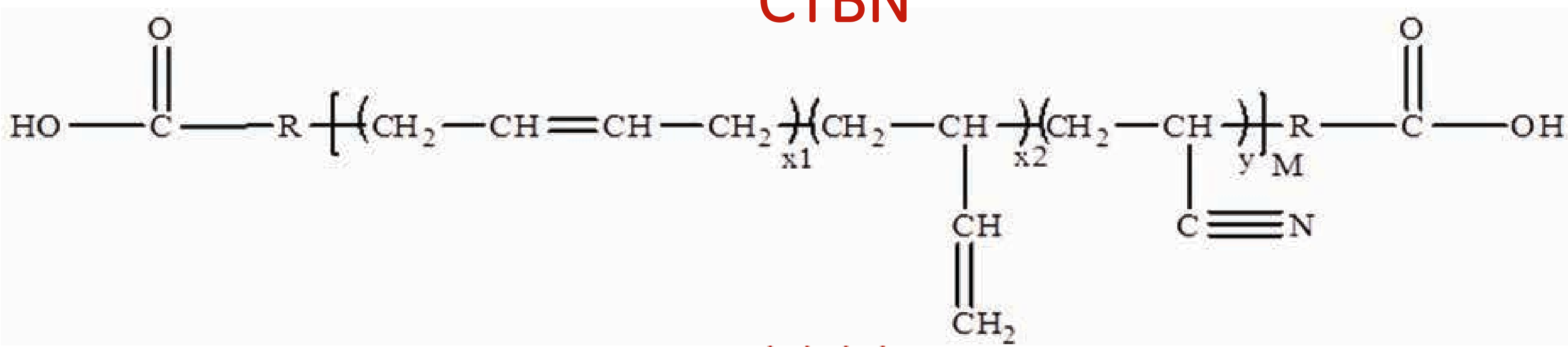
- Electrical Encapsulation

Epoxy Properties

- High modulus
- High dimensional stability
- Good elevated temperature performance
- Chemical resistance
- Low creep

What are Reactive Liquid Polymers?

CTBN



ATBN

AMINE TERMINATION

Reaction w/ diamine
AEP or Dytek A

VTBN

VINYL TERMINATION

Reaction w/ glycidyl
methacrylate

ETBN

EPOXY TERMINATED ADDUCT

Reaction w/ diepoxide
Contains free epoxy

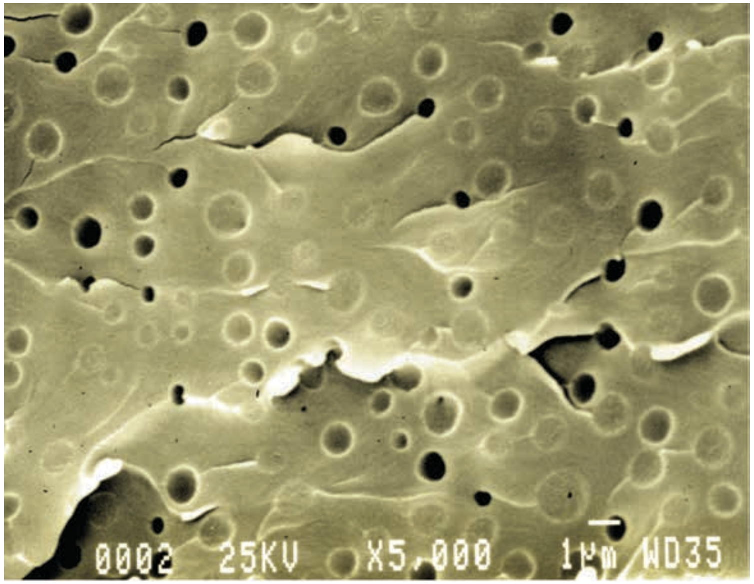
ETBN

EPOXY TERMINATION

Reaction w/ epichlorohydrin
100% rubber, no free epoxy

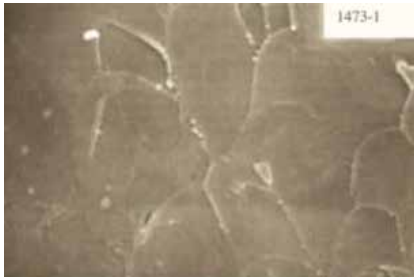
How Reactive Liquid Polymers Work

- Copolymer is initially soluble in epoxy resin
- End group chemistry is chosen to react into matrix
- MW grows, RLP phase separates into micron sized domains

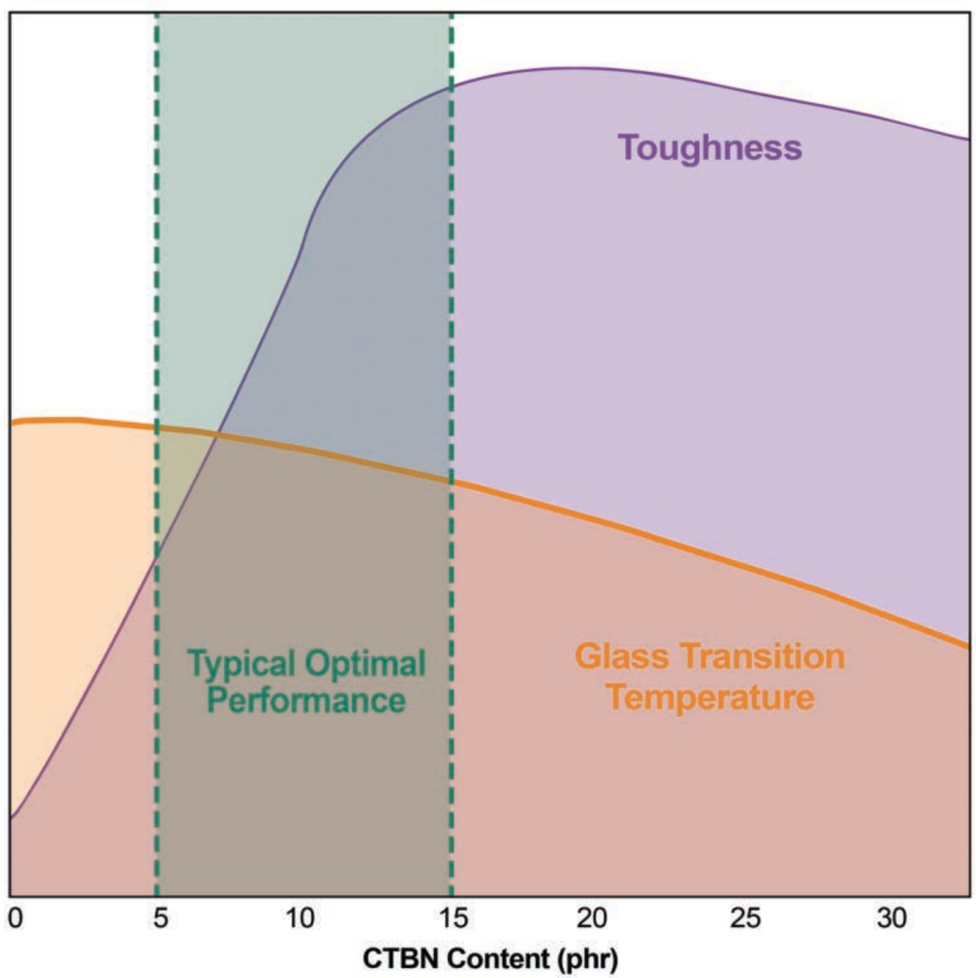


▲ RLP MODIFIED

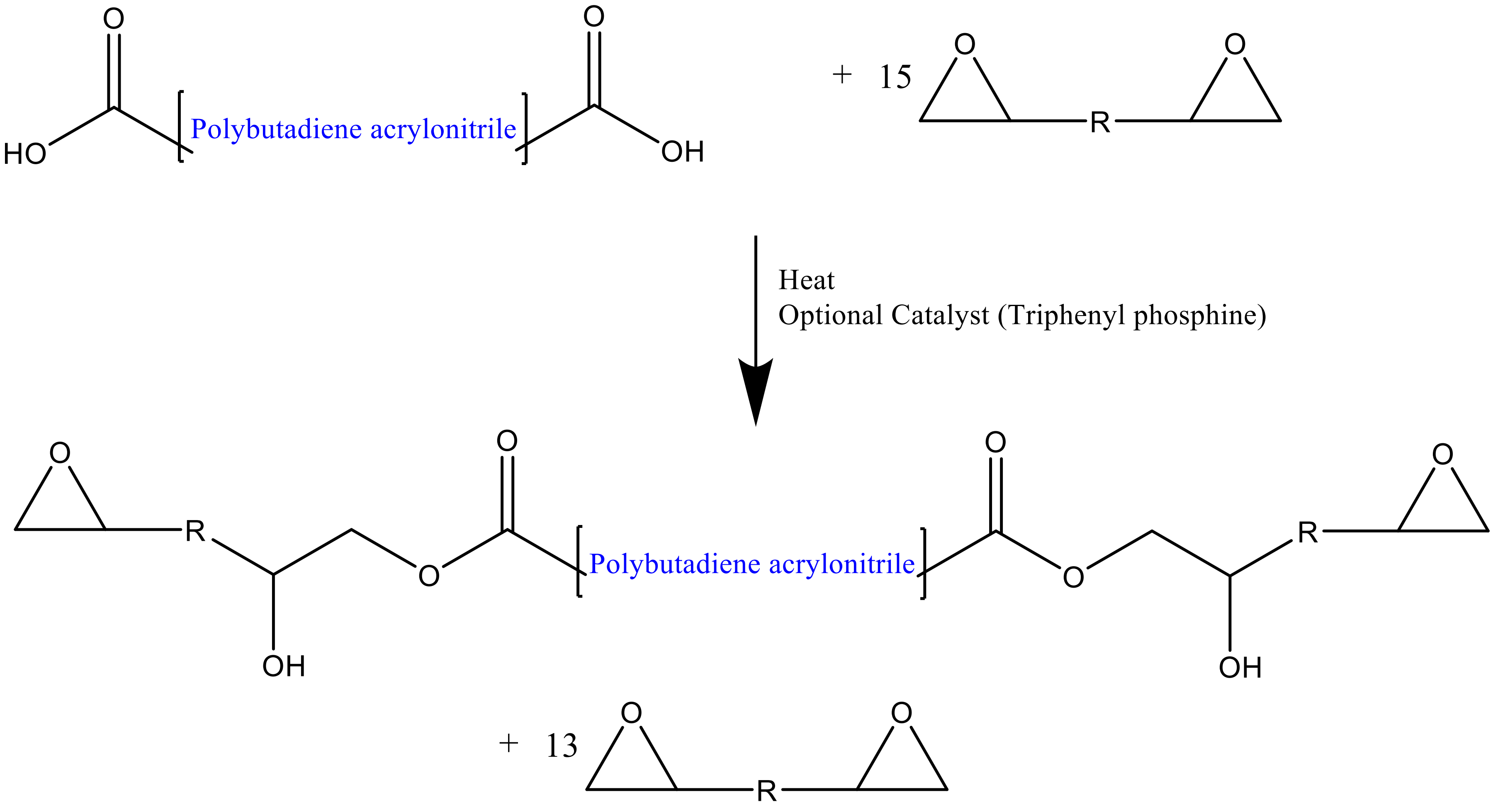
UNMODIFIED ▶



Optimizing Toughness Using Reactive Liquid Polymers

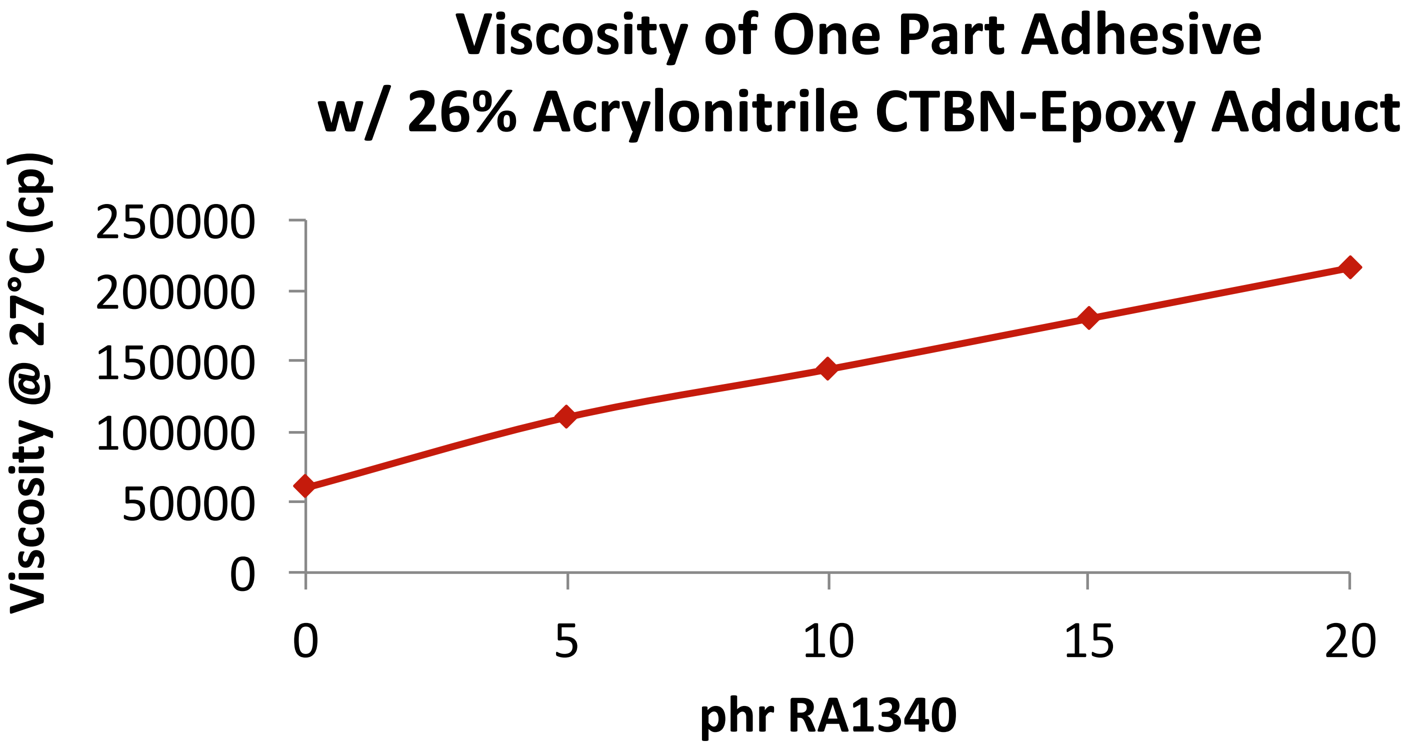


Epoxy Adduct Synthesis



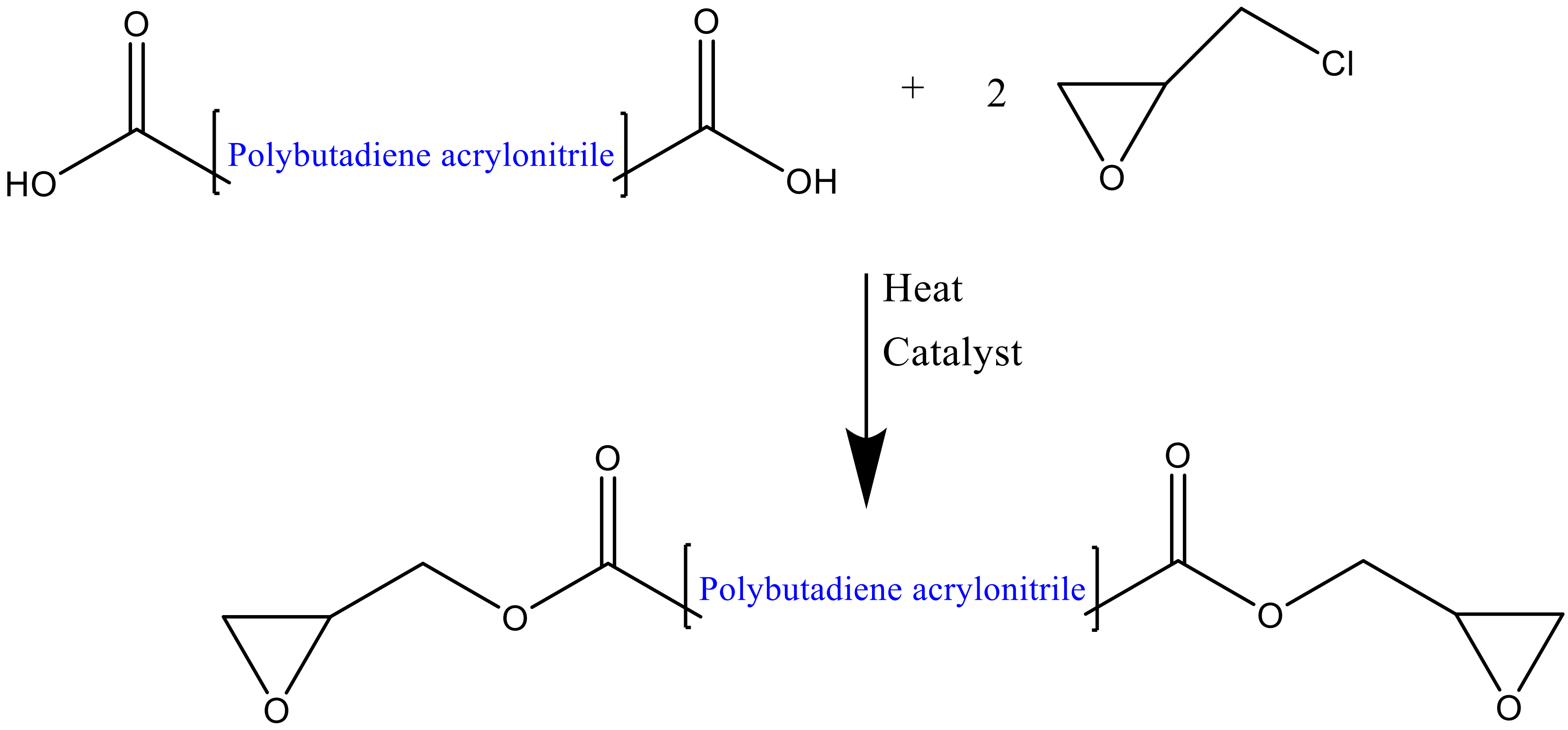
Disadvantages of Epoxy Adducts

- Increase in viscosity



- Unreacted epoxy

Glycidyl Ester Synthesis



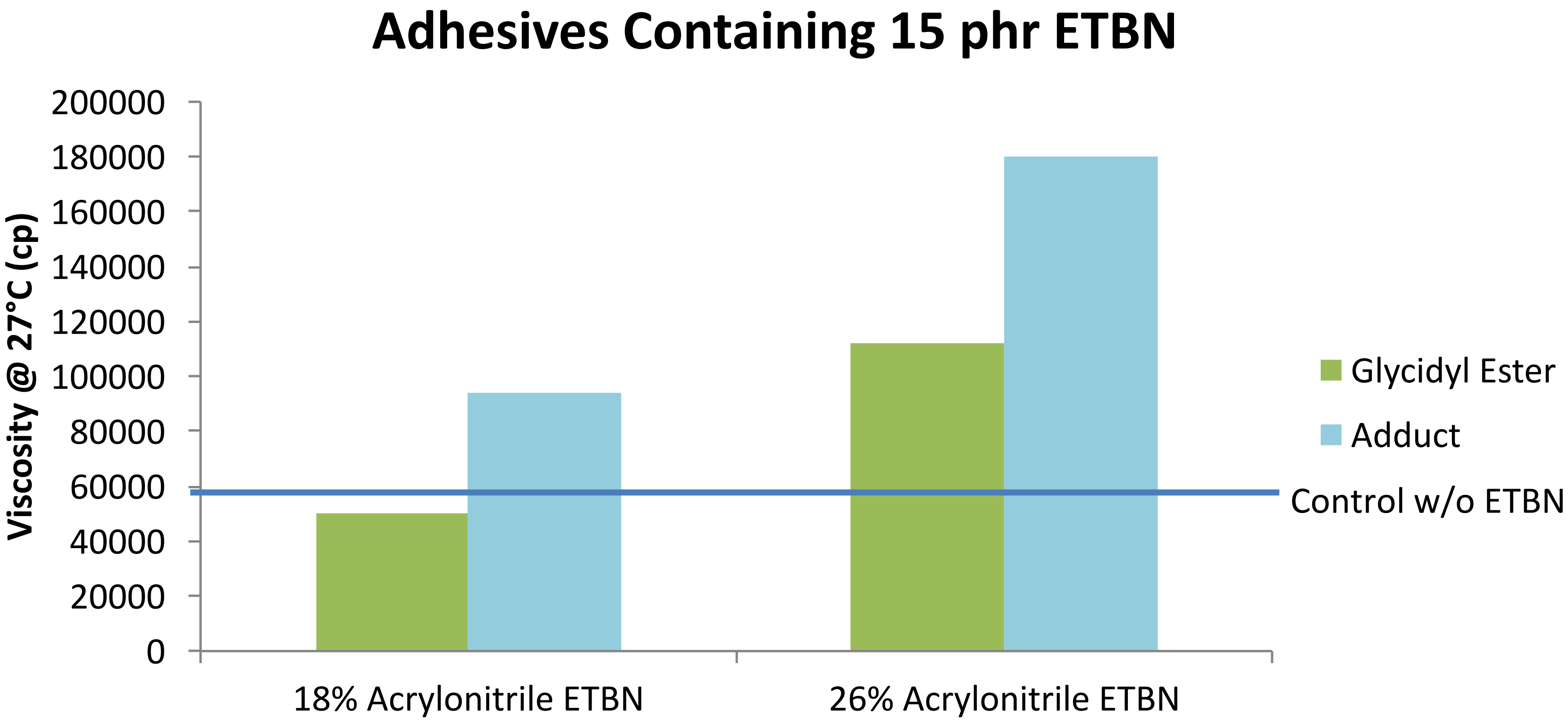
Epoxy Adhesive Formulations

- 100 parts epoxy (diglycidyl ether of bisphenol A – DGEBA)
- 5 parts dicyandiamide curative
- 2 parts urea accelerator
- 3 parts fumed silica

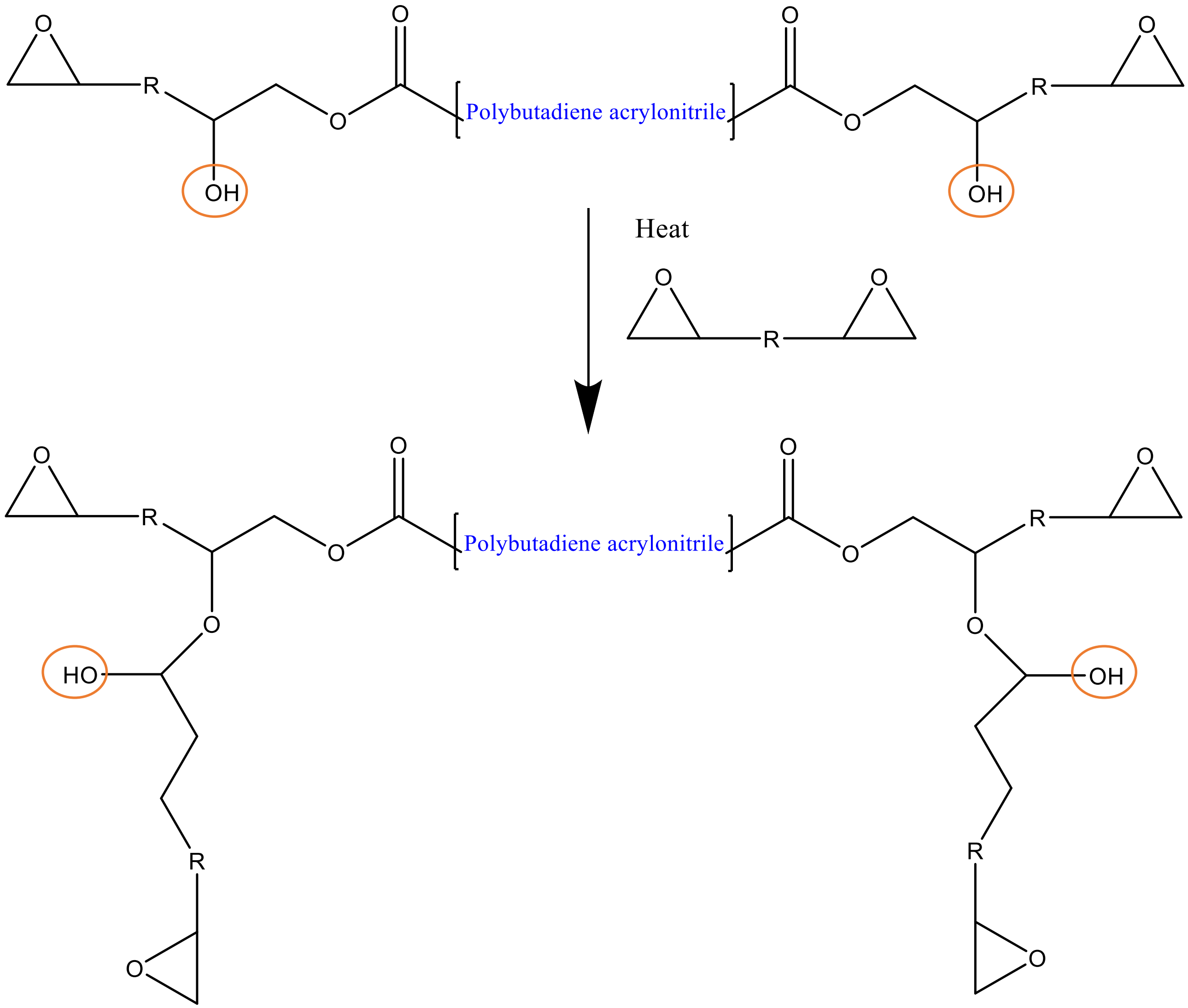
- Cured for 30 minutes at 177°C
- T-Peel and lap shear tested on electrogalvanized steel
- DSC tested at 10°C/min heated rate, Tg taken as midpoint

Advantages of Glycidyl Esters

- Minimal viscosity increase:



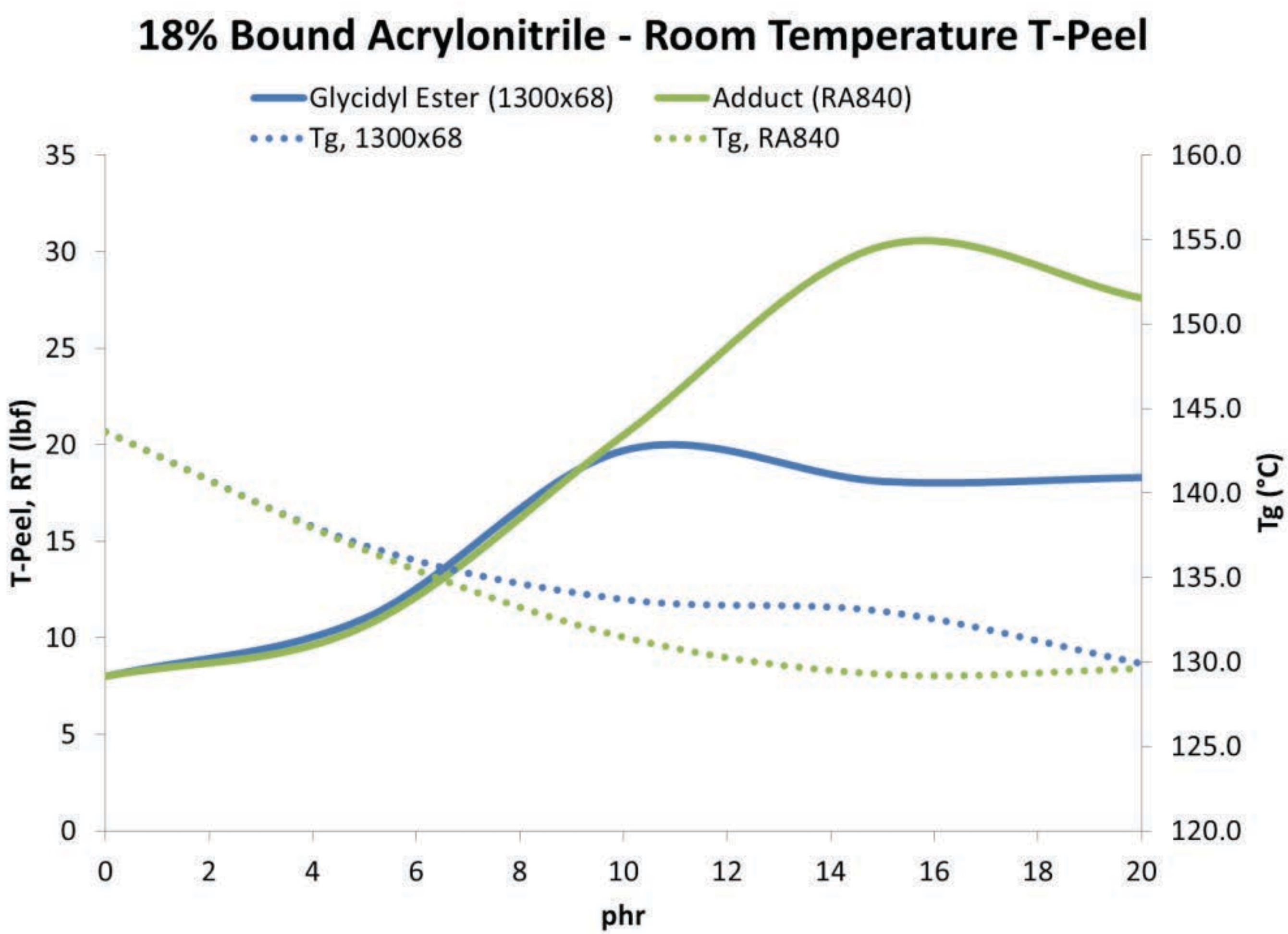
Adduct Chain Extension



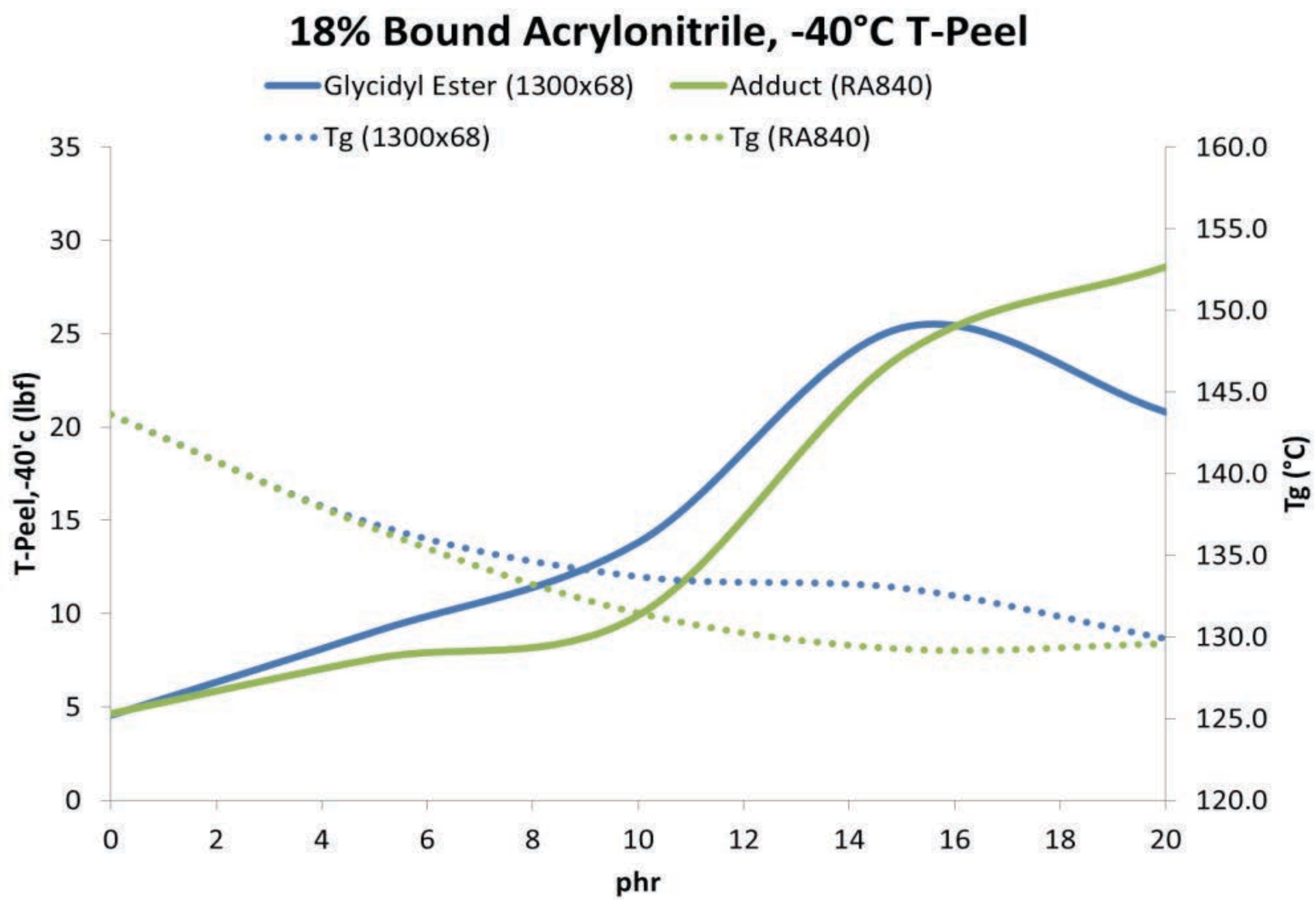
Molecular Weight Comparison

	% Bound Acrylonitrile	Polymer Type	Mn	Mw	PDI
1300x8	18	CTBN	4230	7510	1.78
1300x68	18	ETBN glycidyl ester	4650	7800	1.68
RA840	18	ETBN adduct	5370	8680	1.62
1300x13	26	CTBN	3690	6340	1.72
1300x63	26	ETBN glycidyl ester	4360	7780	1.79
RA1340	26	ETBN adduct	5390	9390	1.74

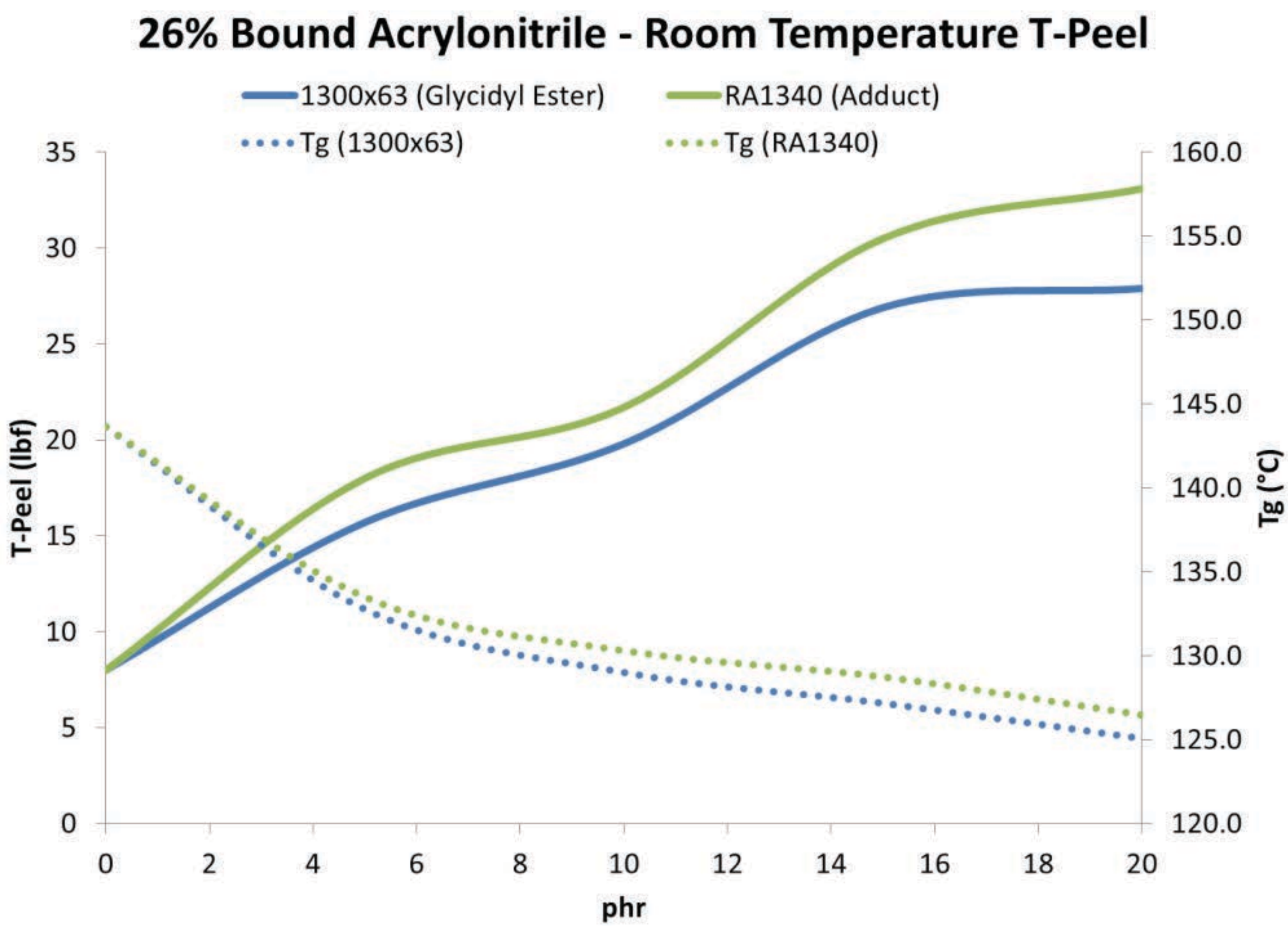
18% Acrylonitrile
Room Temperature T-Peel



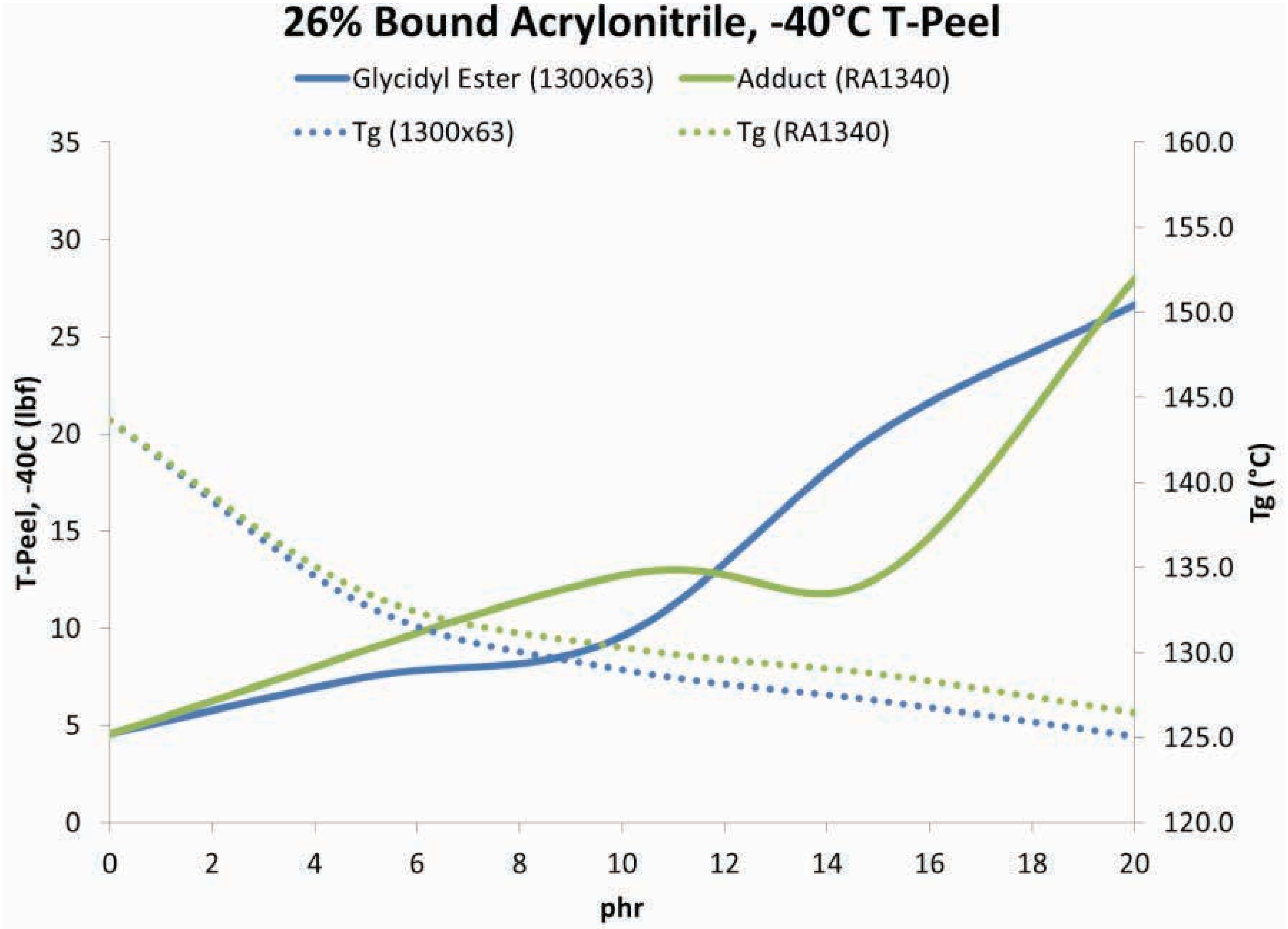
18% Acrylonitrile -40°C T-Peel



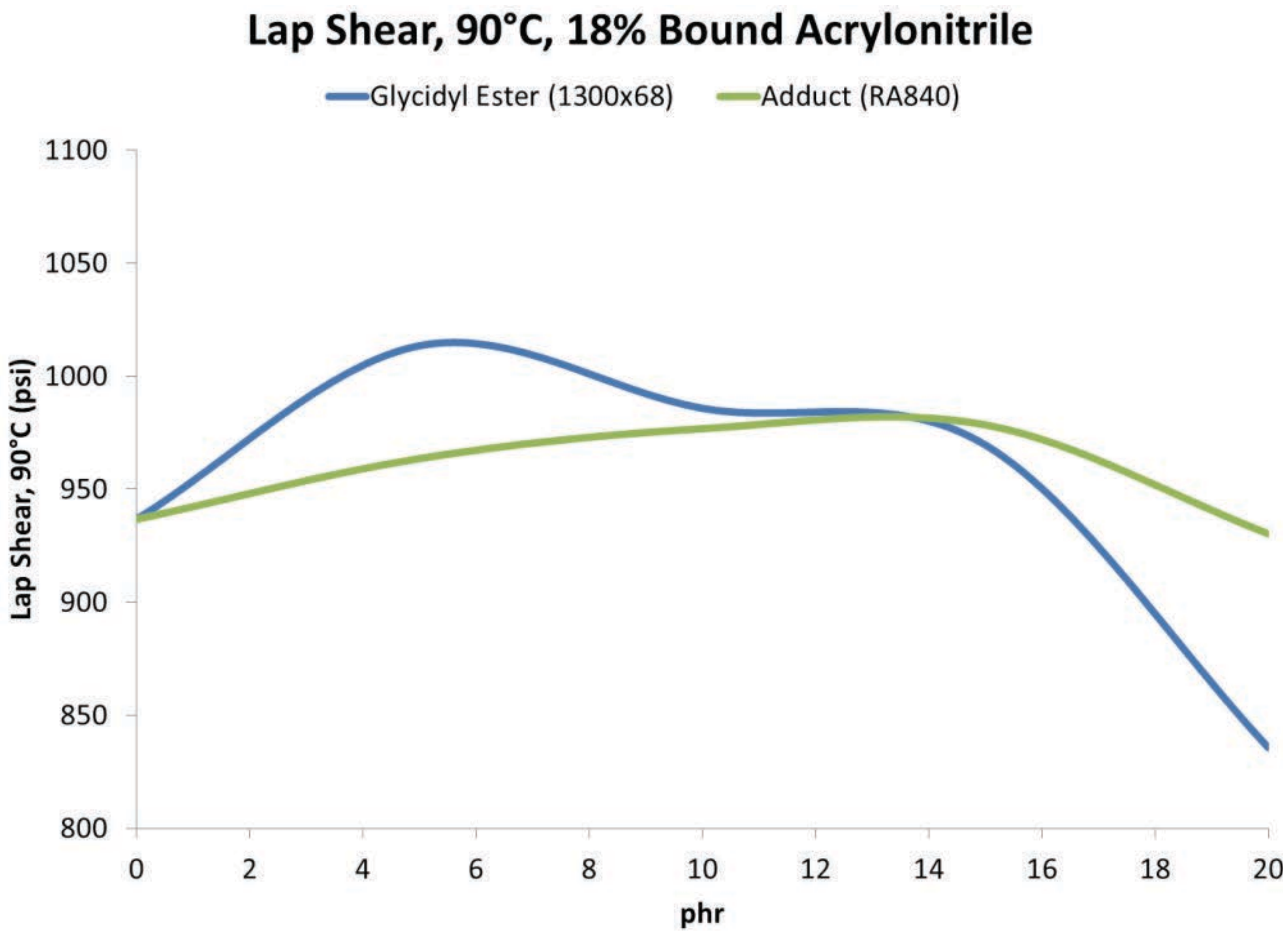
26% Acrylonitrile
Room Temperature T-Peel



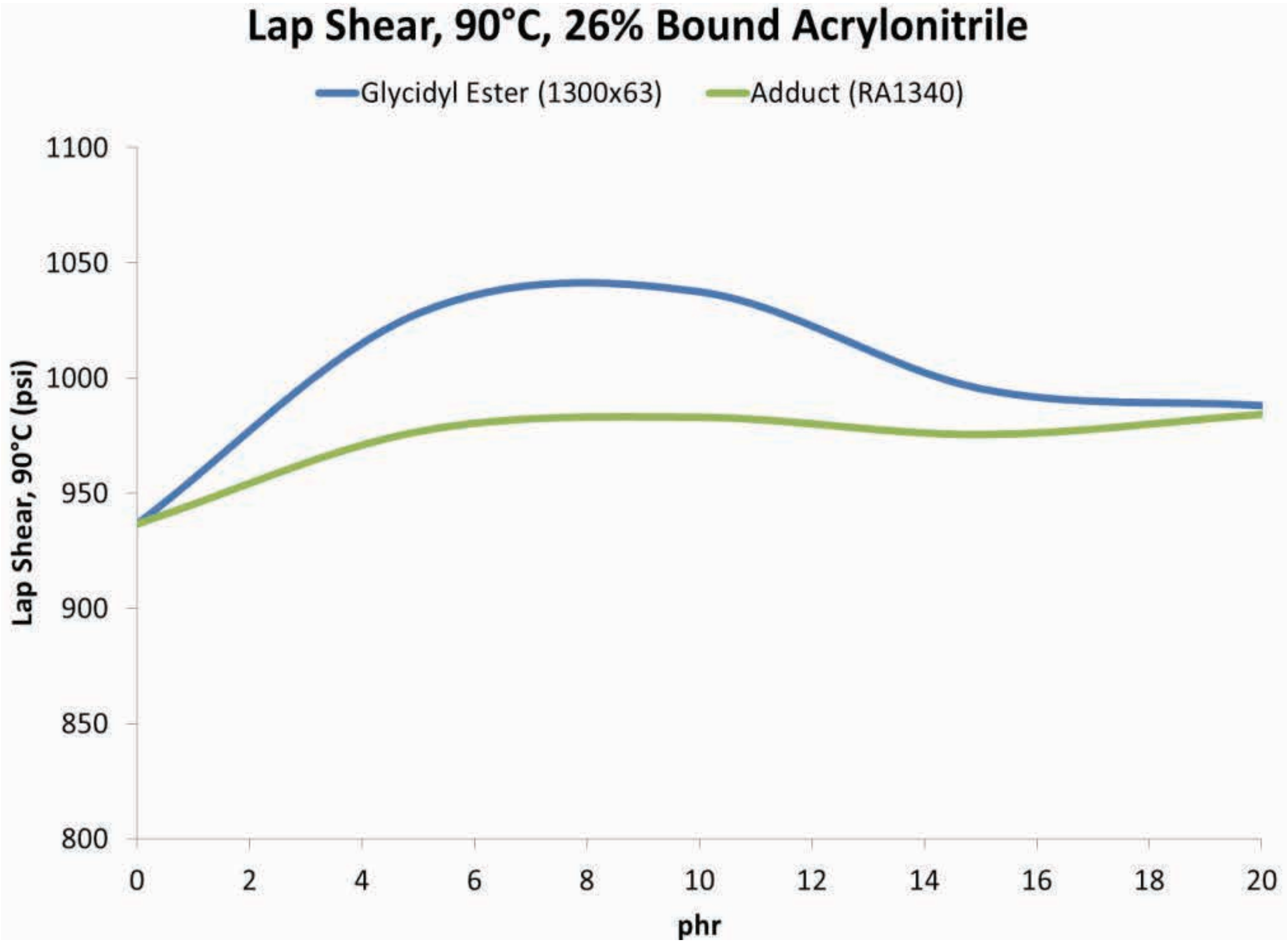
26% Acrylonitrile
-40°C T-Peel



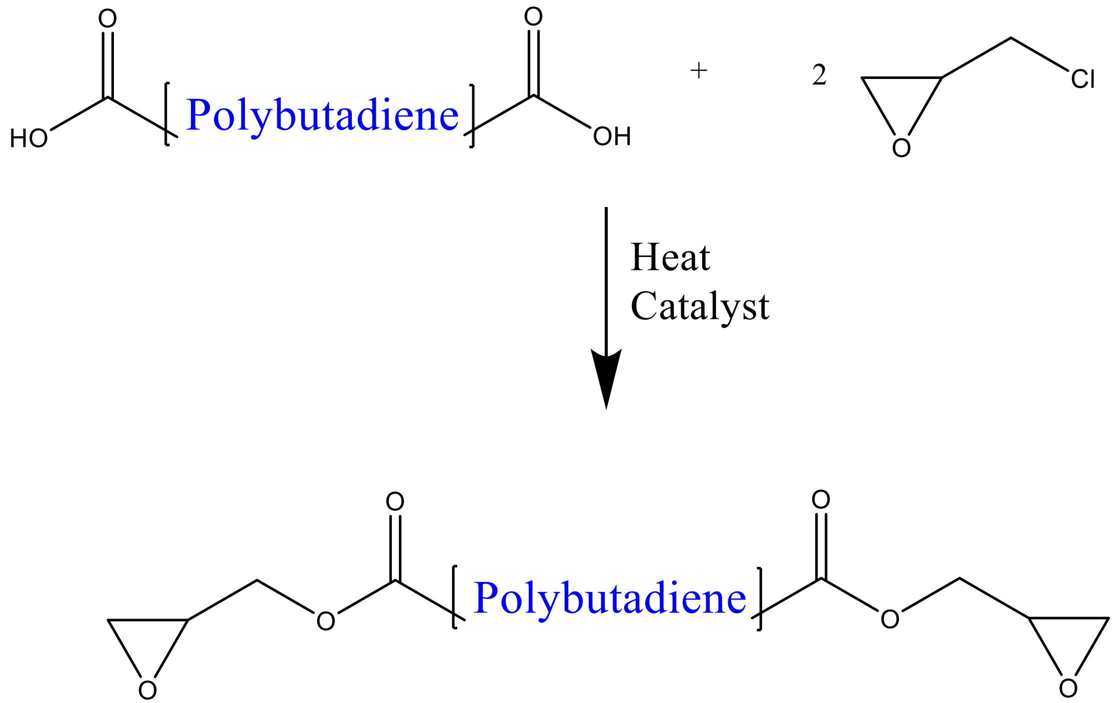
18% Acrylonitrile
90°C Lap Shear



26% Acrylonitrile
90°C Lap Shear



Glycidyl Ester of CTB



- Produces epoxy terminated polybutadiene without free epoxy, previously unachievable with traditional adduct synthesis

Conclusions

- Glycidyl Esters of CTBNs are epoxy terminated RLP
  - With no free epoxy
  - With minimal viscosity impact to the formulation

- 18% Acrylonitrile Glycidyl ester performance
  - T-Peel equivalent to adduct at < 10 phr
  - Improved lap shear at < 15 phr
  - Less T_g decrease at 10-20 phr

Conclusions Continued

- 26% Acrylonitrile Glycidyl ester performance
  - T-Peel slightly less than adduct, but still excellent toughening
  - Improved lap shear at all concentrations
  - Near equivalent T_g to adduct at all concentrations

- Polybutadiene glycidyl ester
  - Produces epoxy terminated polybutadiene directly
  - Application in systems compatible with polybutadiene

Questions?