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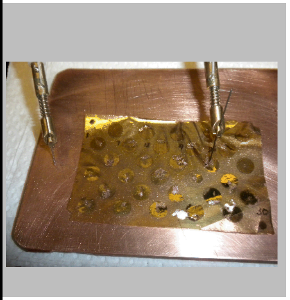

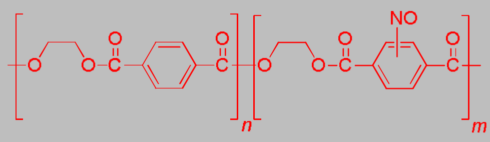

Mechanical Strengthening of Poly(ethylene terephthalate) By Nitration

Brent E. Dial, Victor Pinon III, Shawn M. Dirk, and Benjamin J. Anderson

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Application of PET

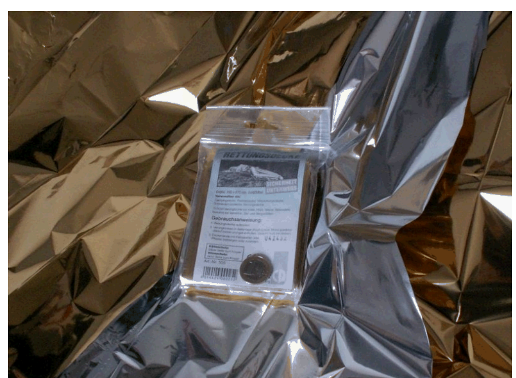
plastic and packaging

Sailcloth

Felt cloth and Clothing

dielectric

thermal insulation



magnetic tape

Image from http://en.wikipedia.org

Why Nitrate PET?

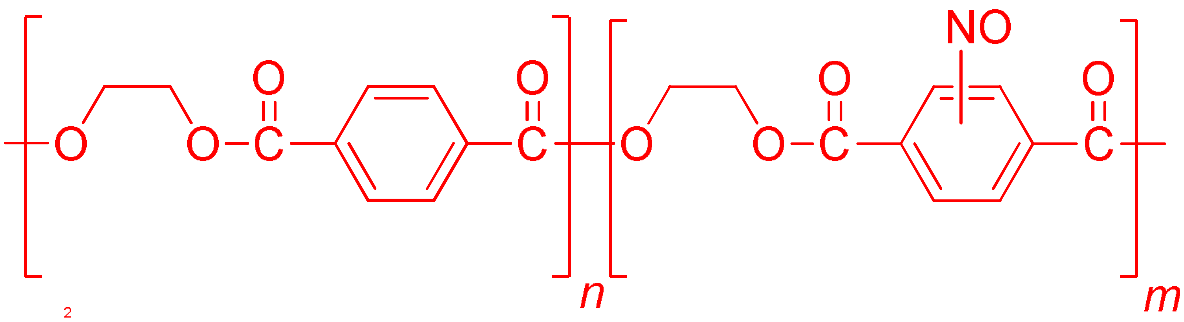
- Nitration of aryl groups shown to depress melting point (T_g unaltered)
  - Thermal failsafe
  - Processing advantages
  - T_m tunable
- Nitro groups serve as radical-traps
  - Radicals often the source of degradation in PET
  - Stability in extreme environments (i.e. radiation in outer space)

Polyester	T_g (°C)[a]	T_m (°C)[b]
PET	80	258
$PET_{95}NT_5$	82	248
$PET_{90}NT_{10}$	82	235
$PET_{85}NT_{15}$	84	223
$PET_{80}NT_{20}$	84	214
$PET_{70}NT_{30}$	83	180
$PET_{50}NT_{50}$	81	—
$PET_{25}NT_{75}$	85	—
PENT	88	—

- Nitro pendant groups can disrupt crystallinity
  - Processing advantages
  - Improve on certain material properties (solubility, pilling, brittleness, etc.)

D. P. R. Kint, et al. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3761- 3770.

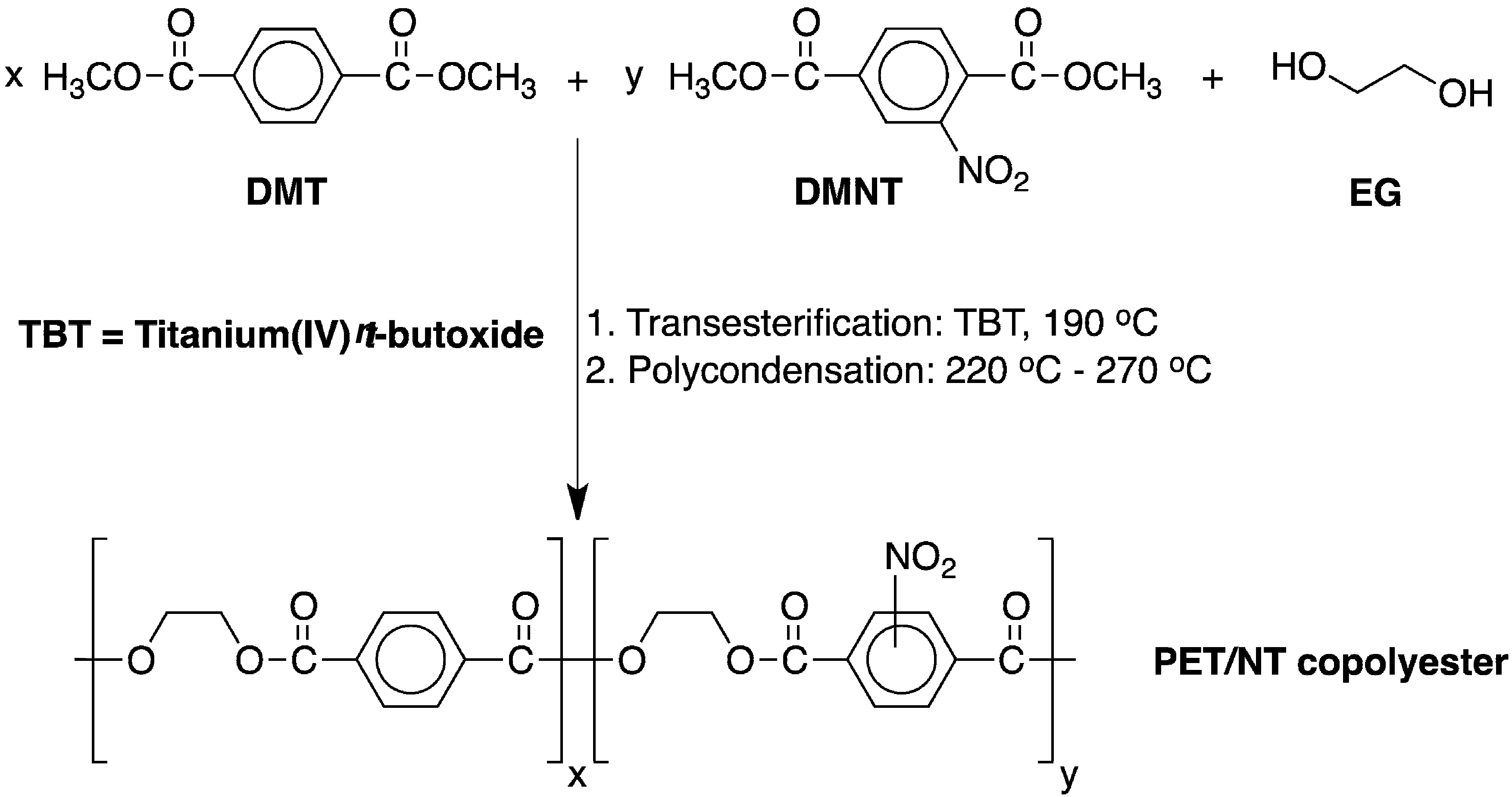
Nitrated PET



Project Goals

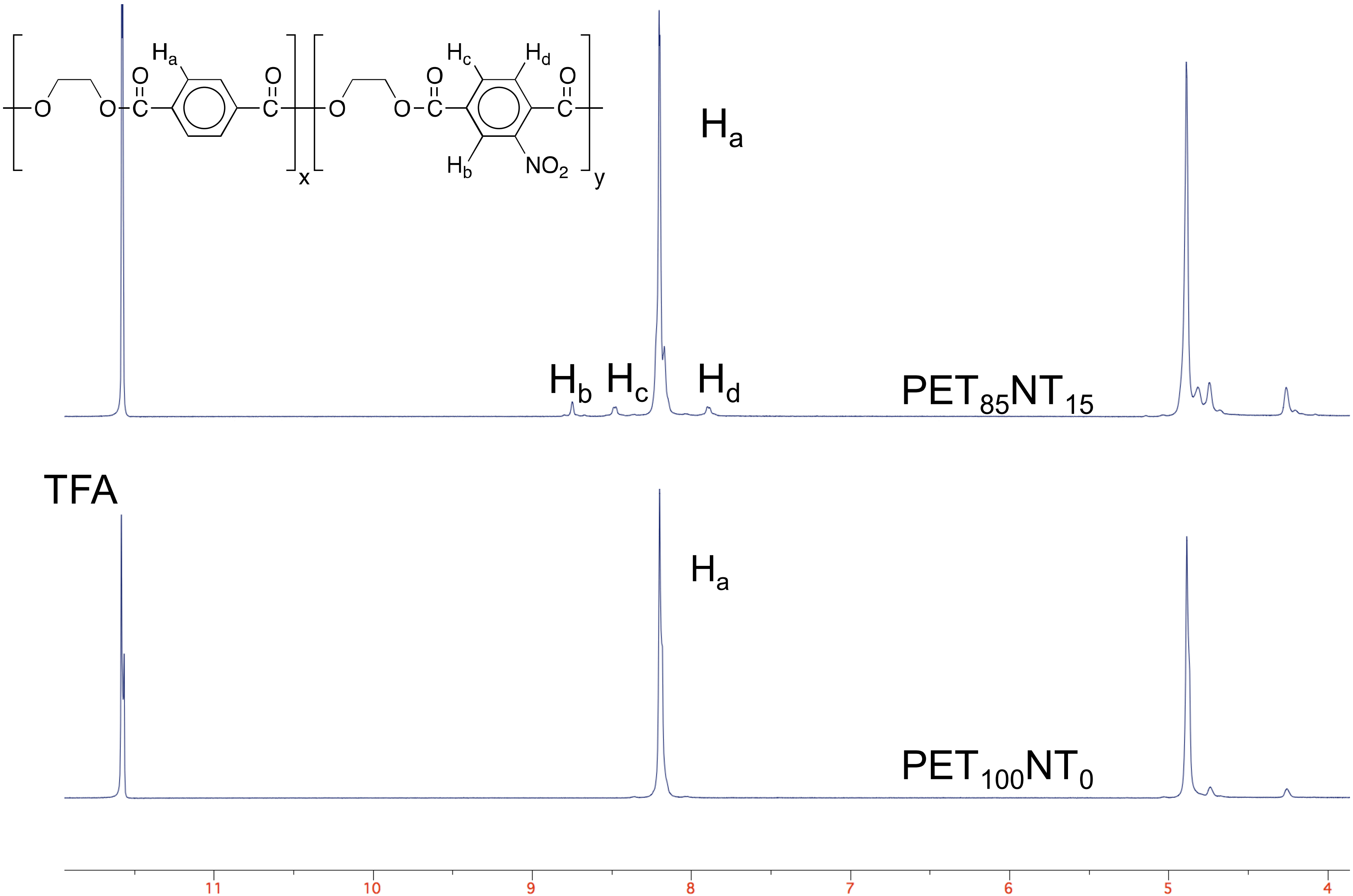
- Characterize the mechanical properties of nitrated-PET
- Identify copolymer that has best mechanical properties for processing (extrusion and capacitor winding)

Synthesis



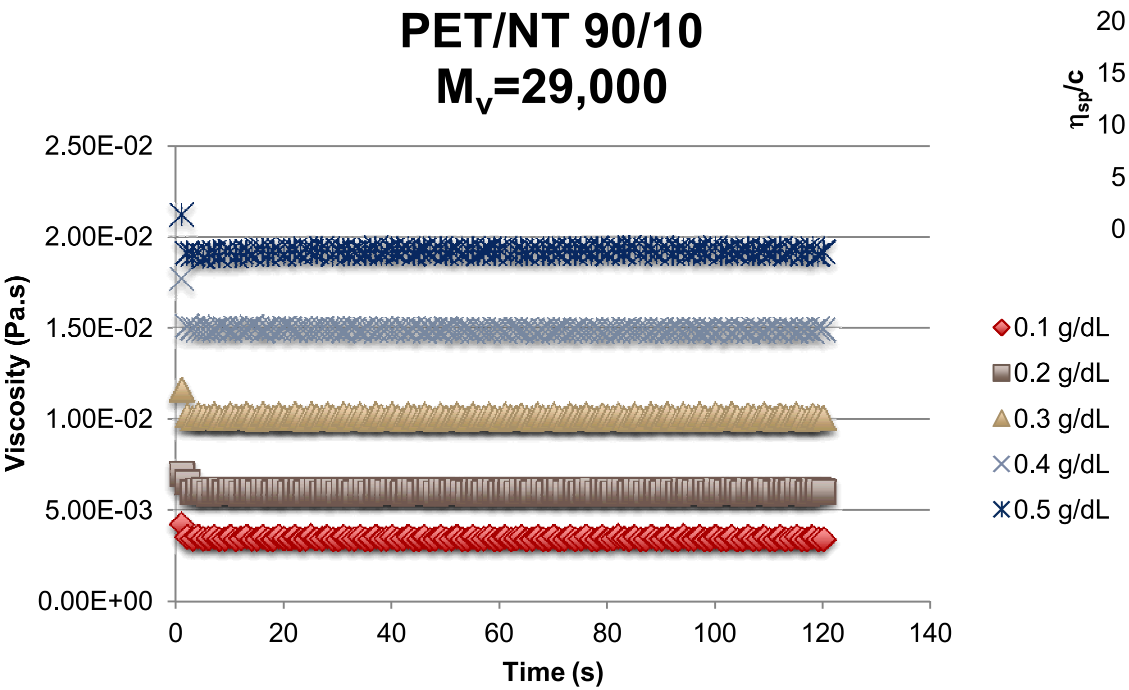
Kint, *et al. J. Polym. Sci., Part A: Polym. Chem.* **2000**, 3761-3770.

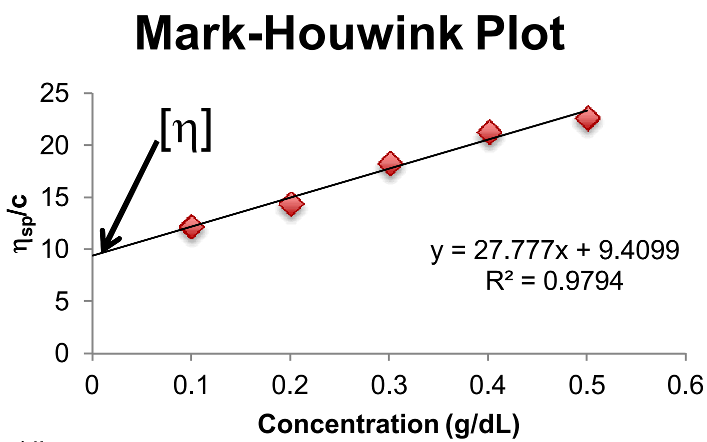
^{1}H NMR Verification of Nitration



Molecular Weight Determination

- Dilute solution viscosity employed





$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$$\eta_{sp} = \eta_{rel} - 1$$

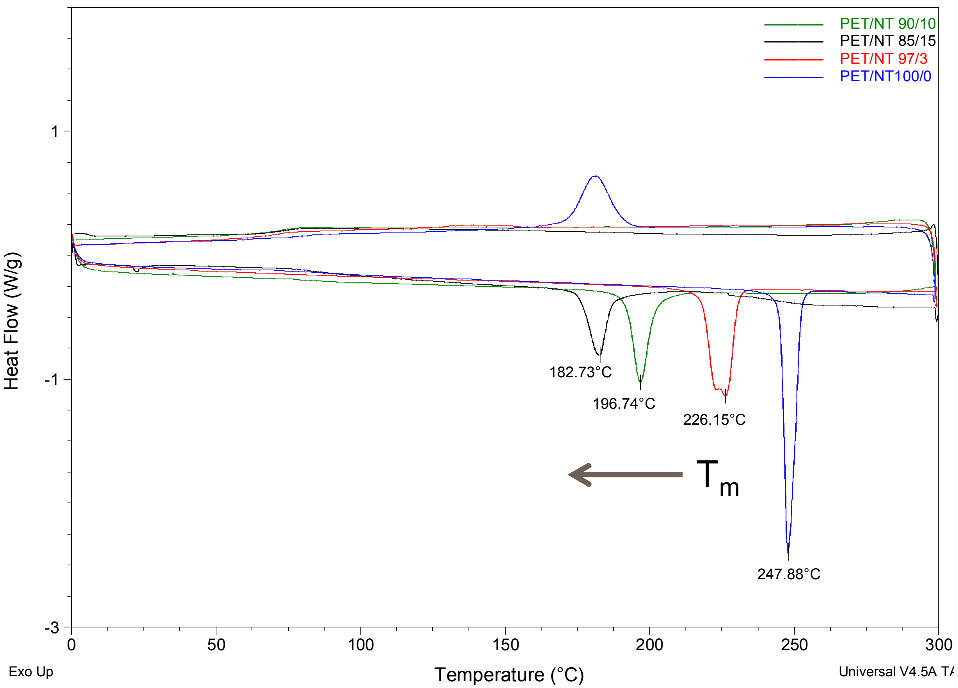
$$[\eta] = KM^{a}$$

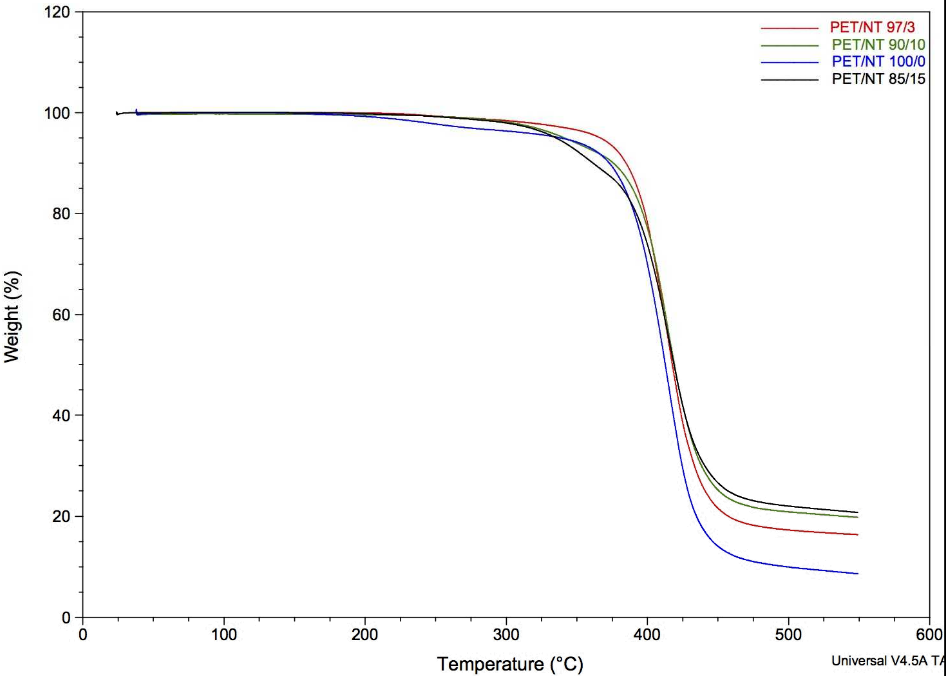
$$\eta_{red} = \frac{\eta_{sp}}{c}$$

Film Preparation

- Polymer is dissolved in 1,1,1,3,3,3-hexafluoroisopropanol
- Casted into film using a drawdown machine
- Dried and then annealed 20 °C below T_m for 12 hours.

Thermal Characterization

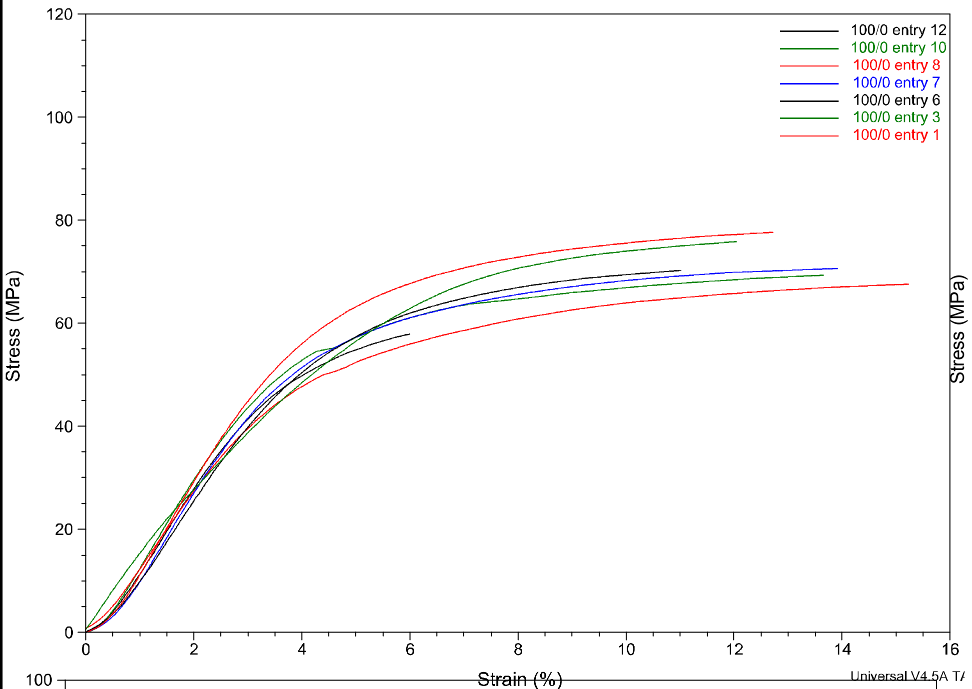


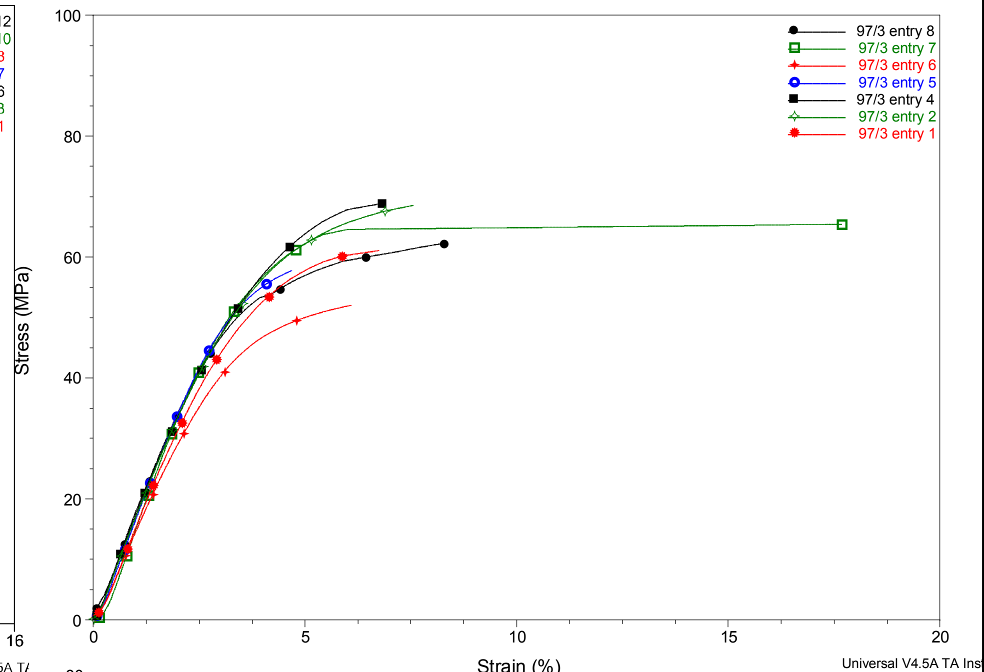


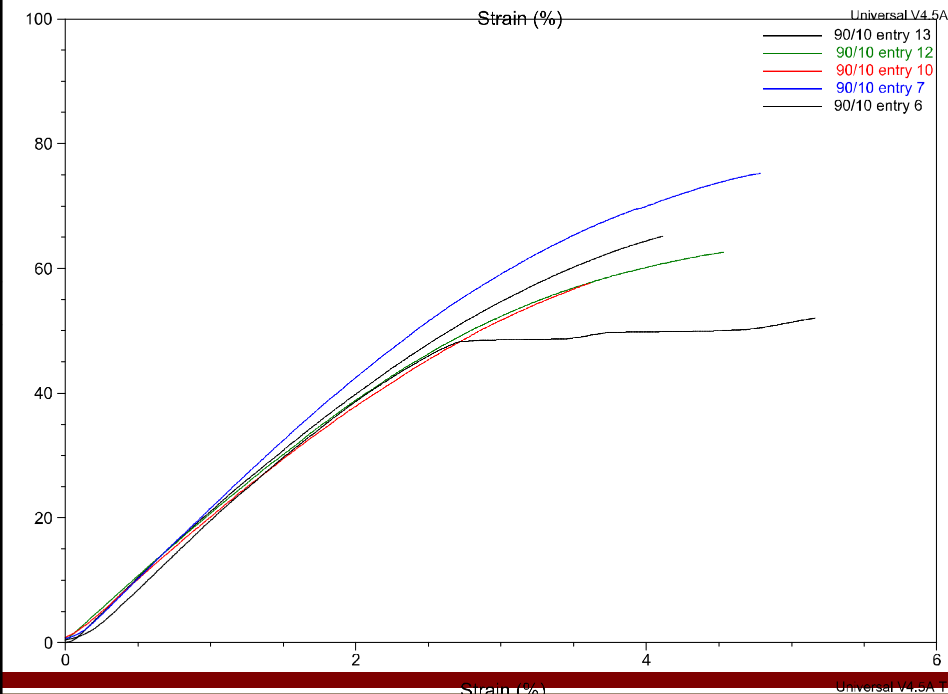
%NT	T_g (°C)	T_m (°C)	ΔH (J/g)
0	76	247	59
3	77	226	47
10	76	197	32
15	80	183	28

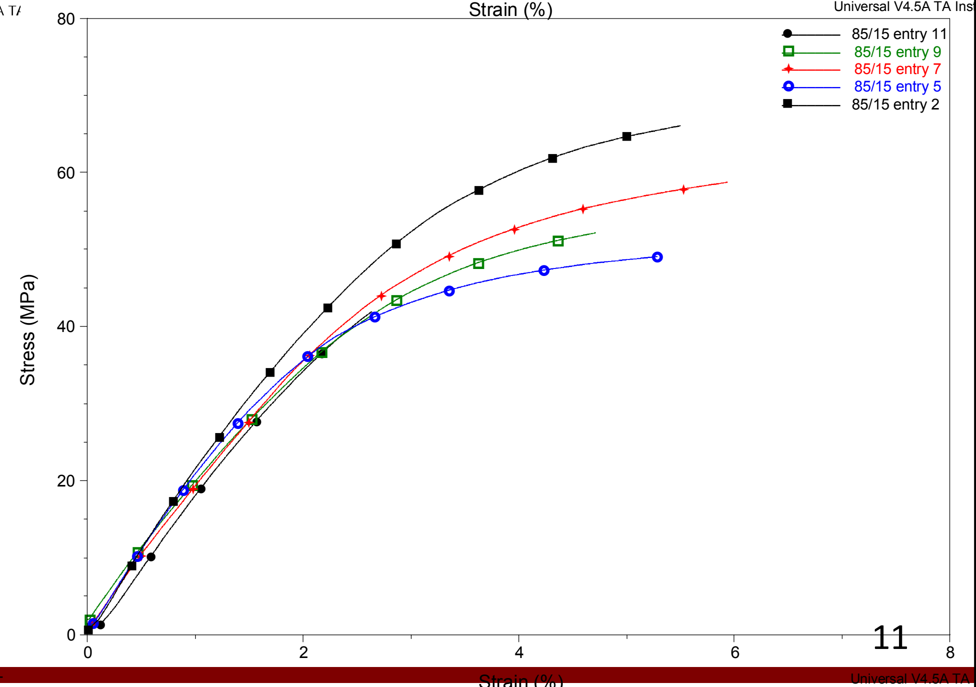
Study of Viscoelastic Properties: Below Melt Transition

MECHANICAL CHARACTERIZATION


100/0 entry 12
100/0 entry 10
100/0 entry 8
100/0 entry 7
100/0 entry 6
100/0 entry 3
100/0 entry 1
Stress (MPa)
Strain (%)
Universal V4.5A TA

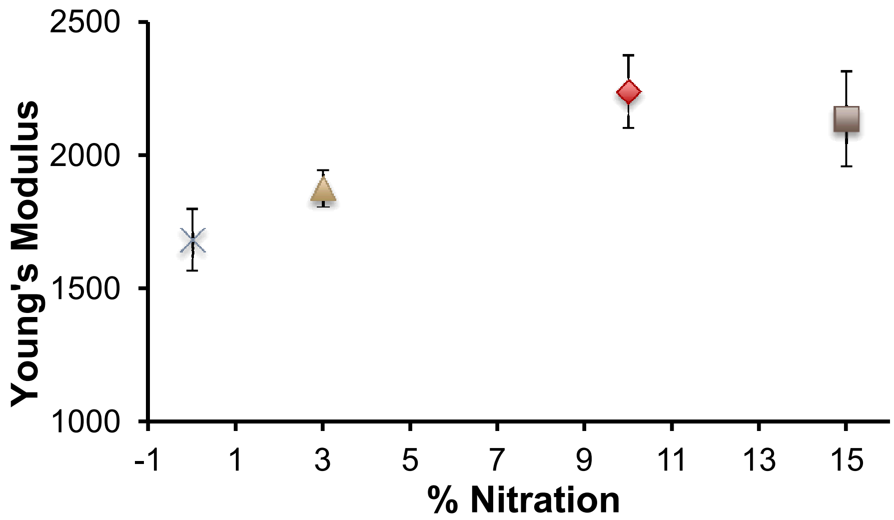

97/3 entry 8
97/3 entry 7
97/3 entry 6
97/3 entry 5
97/3 entry 4
97/3 entry 2
97/3 entry 1
Stress (MPa)
Strain (%)
Universal V4.5A TA Ins


90/10 entry 13
90/10 entry 12
90/10 entry 10
90/10 entry 7
90/10 entry 6
Strain (%)
Universal V4.5A T

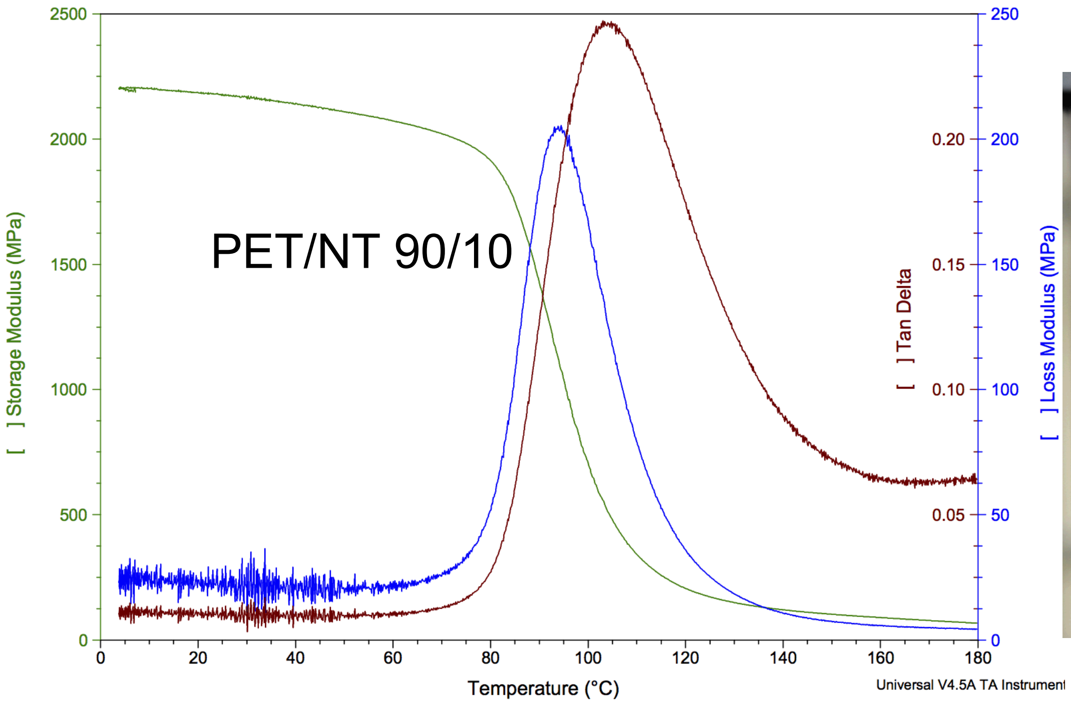

85/15 entry 11
85/15 entry 9
85/15 entry 7
85/15 entry 5
85/15 entry 2
Stress (MPa)
Strain (%)
Universal V4.5A TA

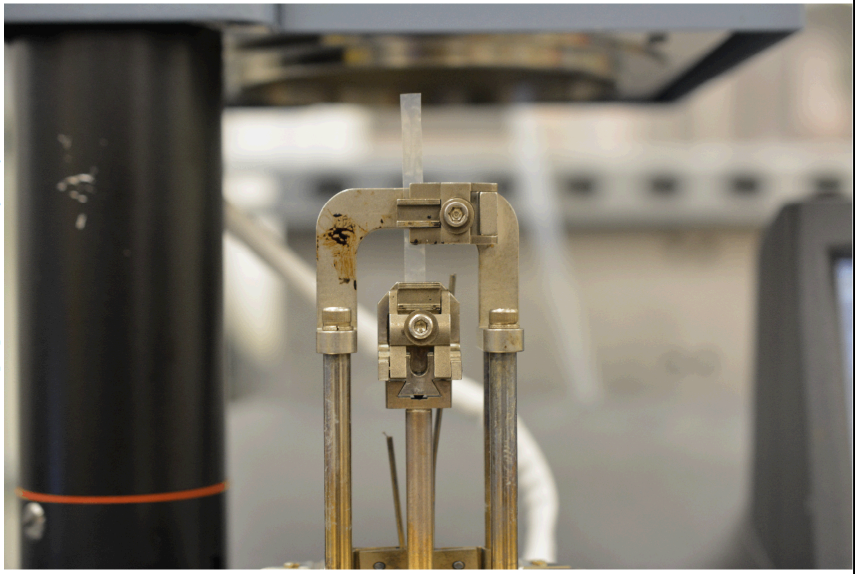
Stress-Strain Curve

Nitration (%)	M_v	*Modulus (MPa)*
0	49000	1891
3	23000	1893
10	29000	2245
15	57000	2120

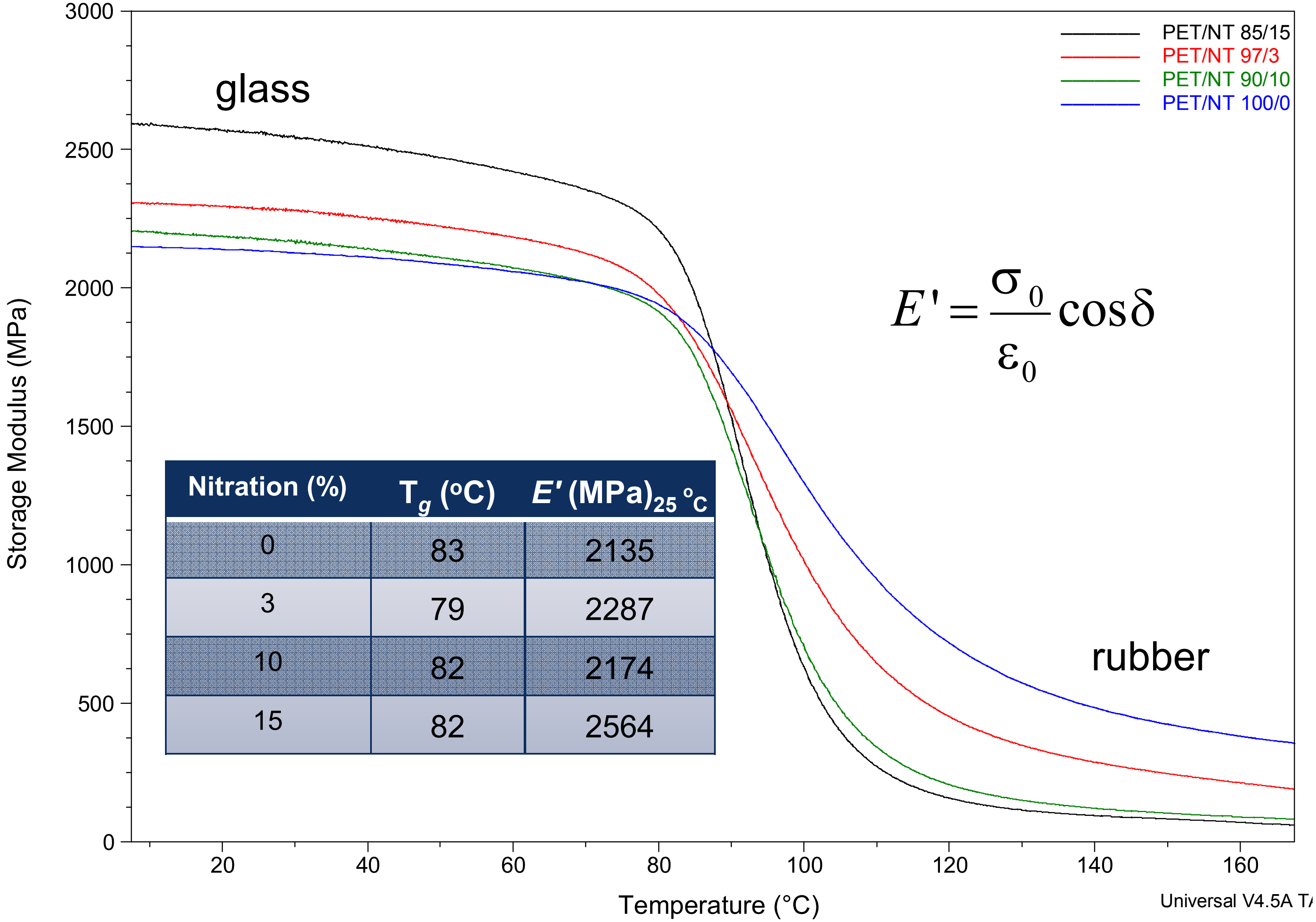


Viscoelastic Properties: Glass and Rubber Transition





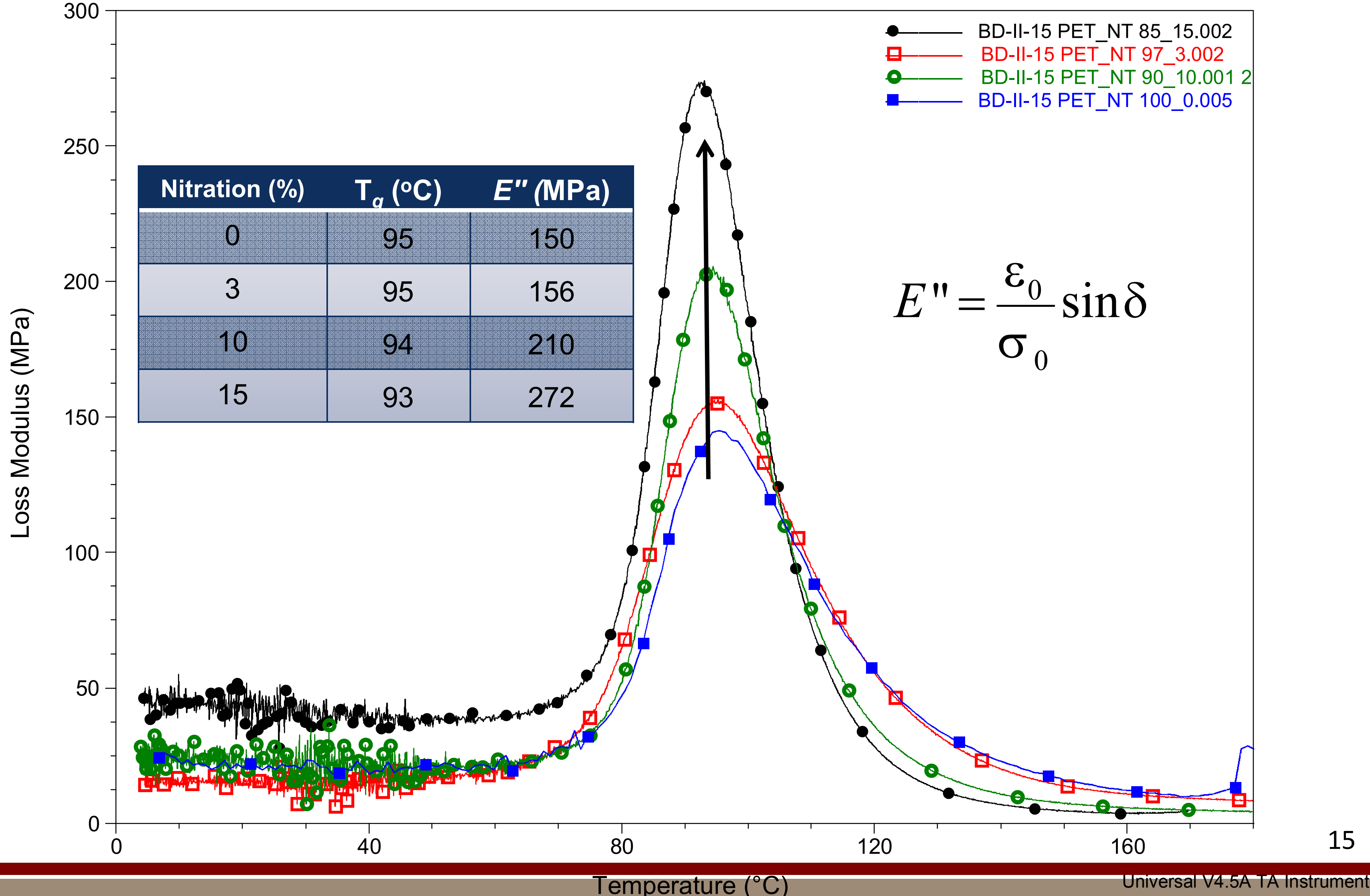
Storage Modulus of PET Copolymers



$$E' = \frac{\sigma_0}{\varepsilon_0}\cos\delta$$

Nitration (%)	T_g (°C)	E' (MPa)$_{25\,°C}$
0	83	2135
3	79	2287
10	82	2174
15	82	2564

Loss Modulus of PET Copolymers



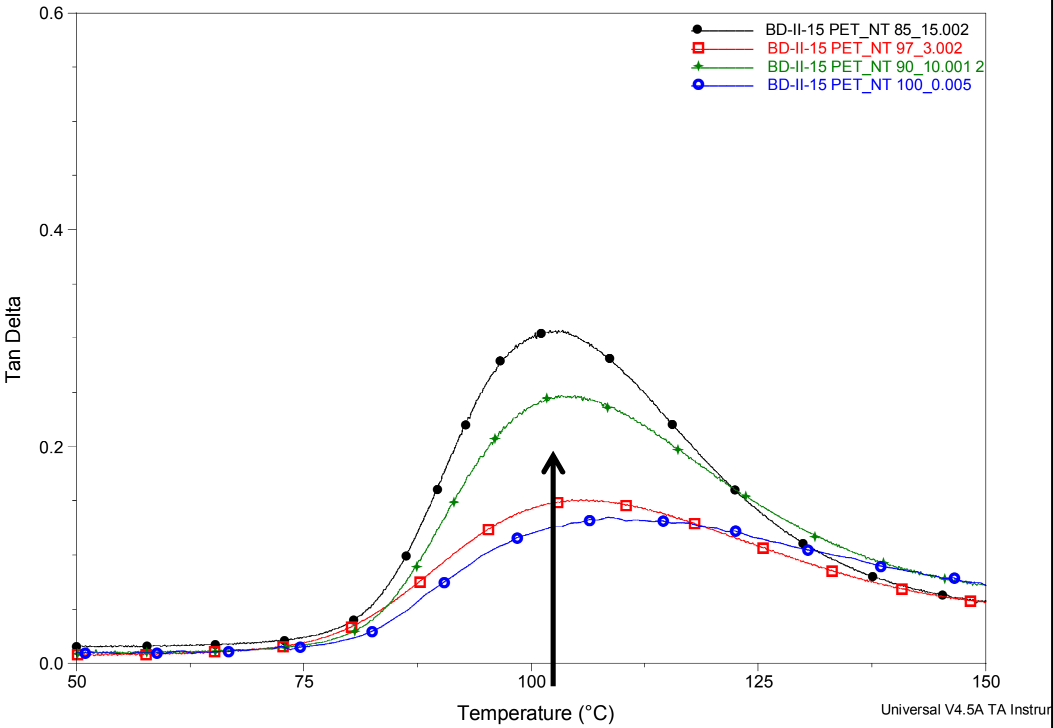
Nitration (%)	T_g (°C)	*E''* (MPa)
0	95	150
3	95	156
10	94	210
15	93	272

$$E'' = \frac{\varepsilon_0}{\sigma_0} \sin\delta$$

Tan Delta of PET Copolymers

Nitration (%)	T_g (°C)	*Tan Delta*
0	109	0.13
3	106	0.15
10	104	0.25
15	103	0.31

$$\tan\delta = \frac{E''}{E'}$$



- nitro group is assisting with collective motion
- nitro group break up packing

Conclusion

- A series of nitrated PET copolymers have been synthesized
- Incorporation of nitro-groups into the backbone have depressed the melting point of the polymers
- Nitrated-PET shows mechanical strengthening occurs upon nitration
- As nitration increases the tan delta increase
- Nitration allow processing to occur at lower temperature

Acknowledgements

- Shawn Dirk
- Michele Denton
- Kirsten Cicotte
- Lindsey Hughes
- Patti Sawyer
- Mark Stavig
- John Schroeder
- Greg White
- Robert Bernstein
- Mat Celina