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Nitrated Poly(ethylene terephthalate) from Synthesis to Extrusion

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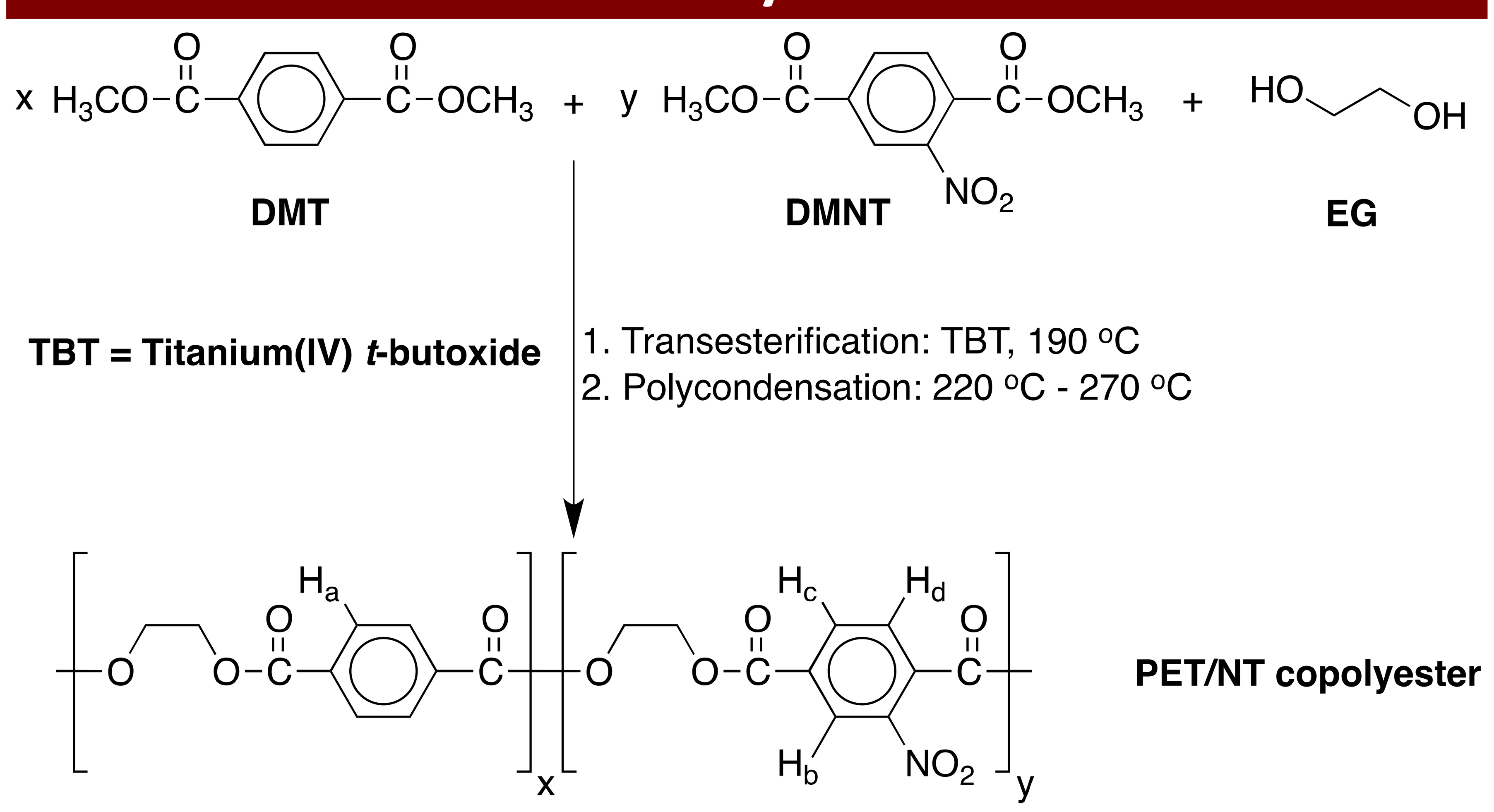
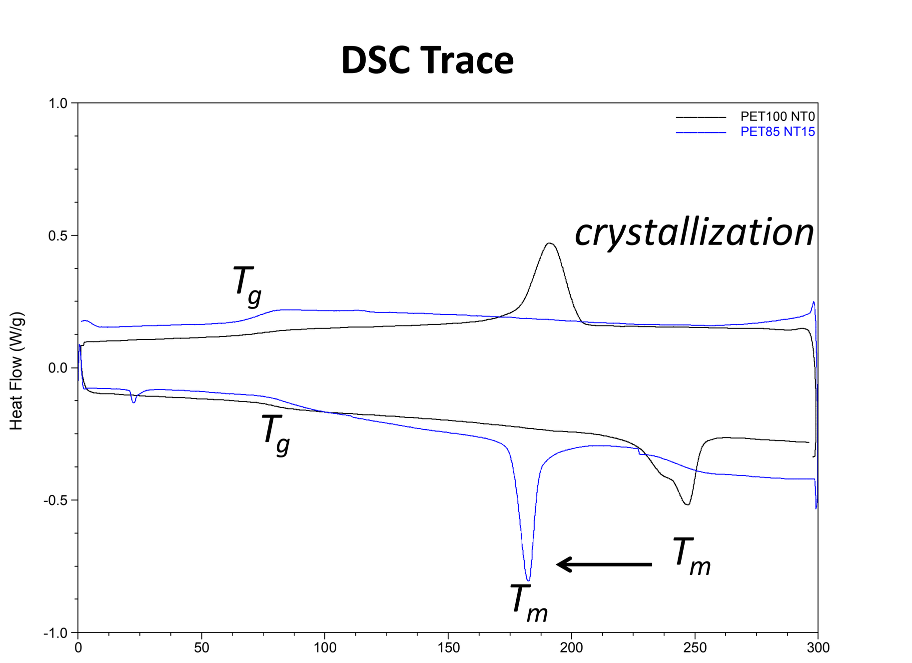
Overview

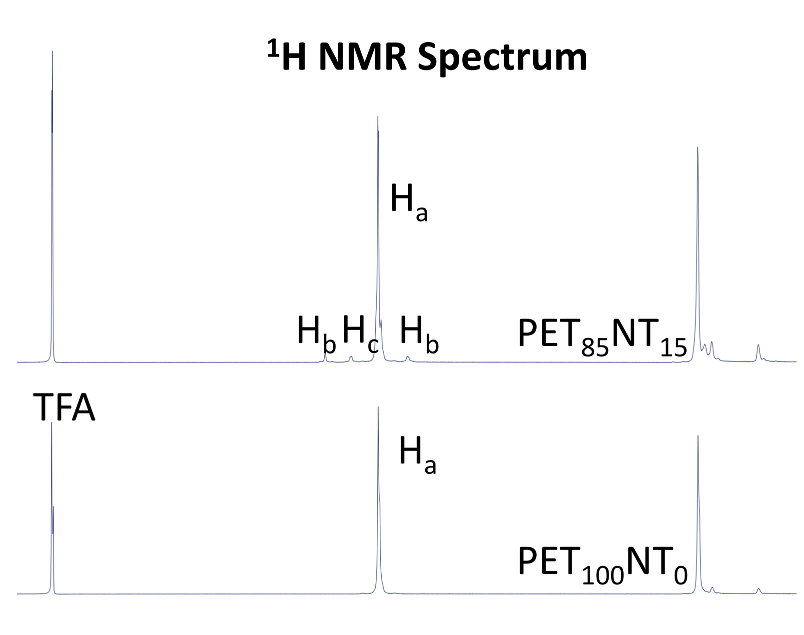
- Nitrated poly(ethylene terephthalate) (PET)-based copolymers were synthesized of varying nitration contents
- Increasing nitro-content affected various thermal and mechanical properties of the polymers:
  - Depressed melting temperature (T_m) while minimally affecting the glass transition temperature (T_g)
  - Increased Young's modulus
  - Decreased onset temperature for degradation
- By combining viscosity and degradation data, an extrusion plan for the synthesized copolymers can be developed
- Comparing the processing parameters of virgin PET to the nitrated analogues will highlight the advantages of the copolymer system (energy and cost savings)

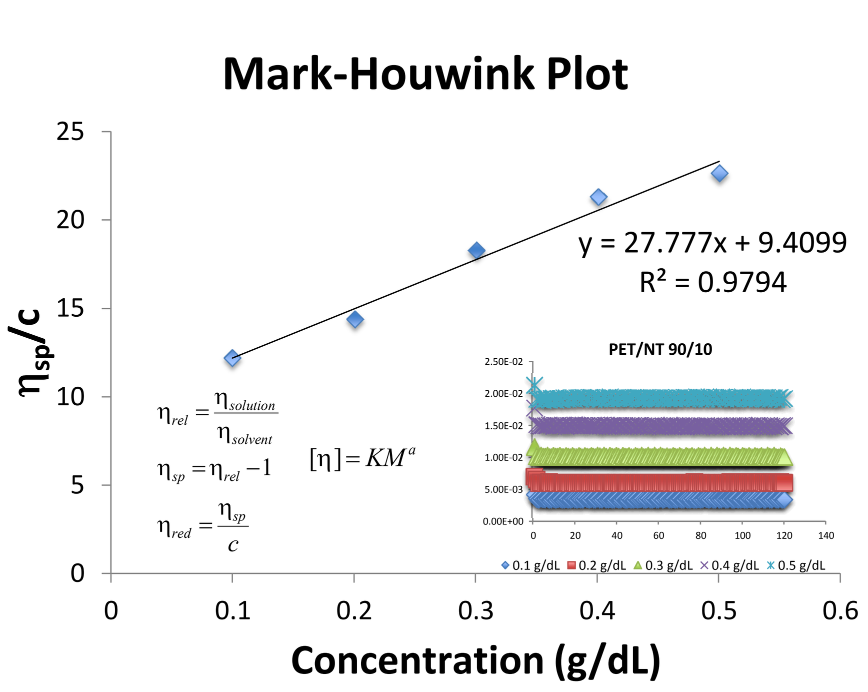
NT-PET Synthesis



NT-PET Characterization

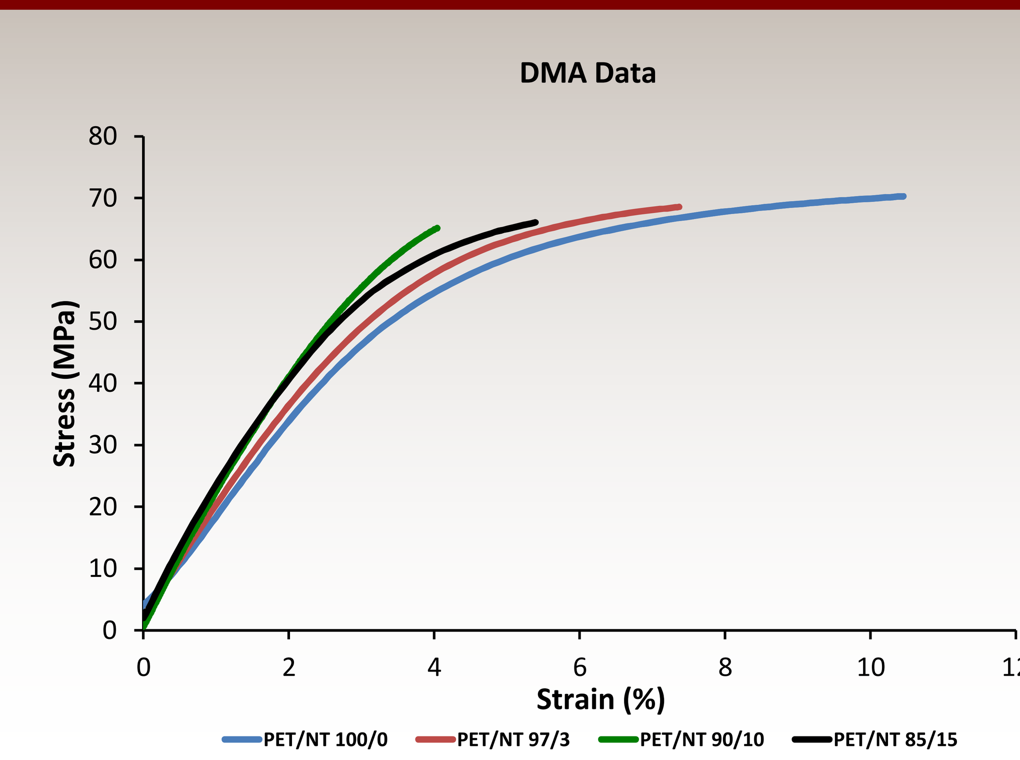






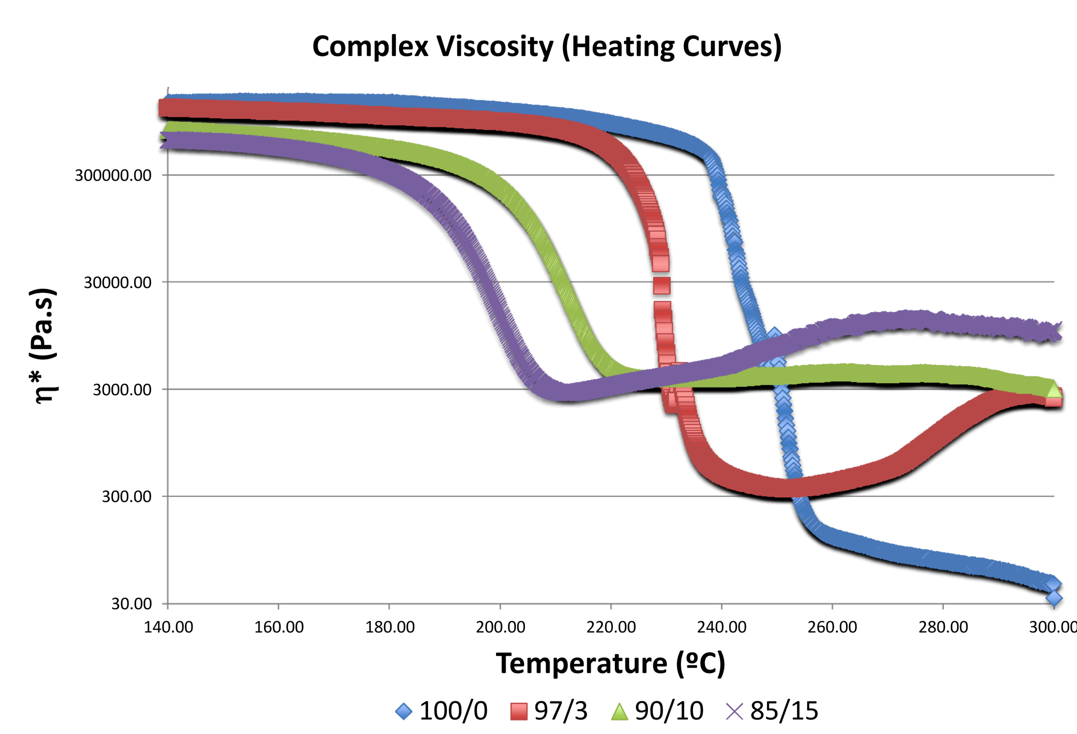
Composition	M_v	T_g (°C)	T_m (°C)	ΔH (J/g)	% Crystallinity
100/0	49,000	76	250	37	26.6
99.9/0.1	42,000	78	235	26	18.4
99.5/0.5	31,000	73	231	31	21.9
99.25/0.75	38,000	73	222	31	22.2
99/1	52,000	79	231	27	19.2
97/3	23,000	77	214	17	12.2
90/10	29,000	76	194	16	11.7
85/15	57,000	80	183	28	19.8

Mechanical Properties



Composition (PET/NT)	Young's Modulus (GPa)
100/0	1.9
97/3	2.3
90/10	2.5
85/15	2.6

Increase in Young's Modulus caused by secondary interactions of nitro-groups



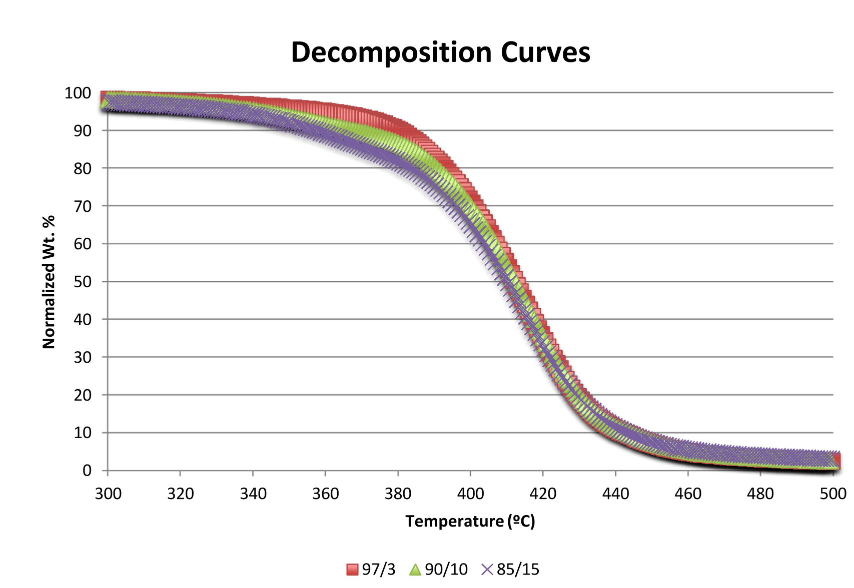
- Increase in viscosity at high temperatures indicative of decomposition/crosslinking
- Phenomenon only seen in nitrated-PET
- Can this decomposition be avoided during extrusion?

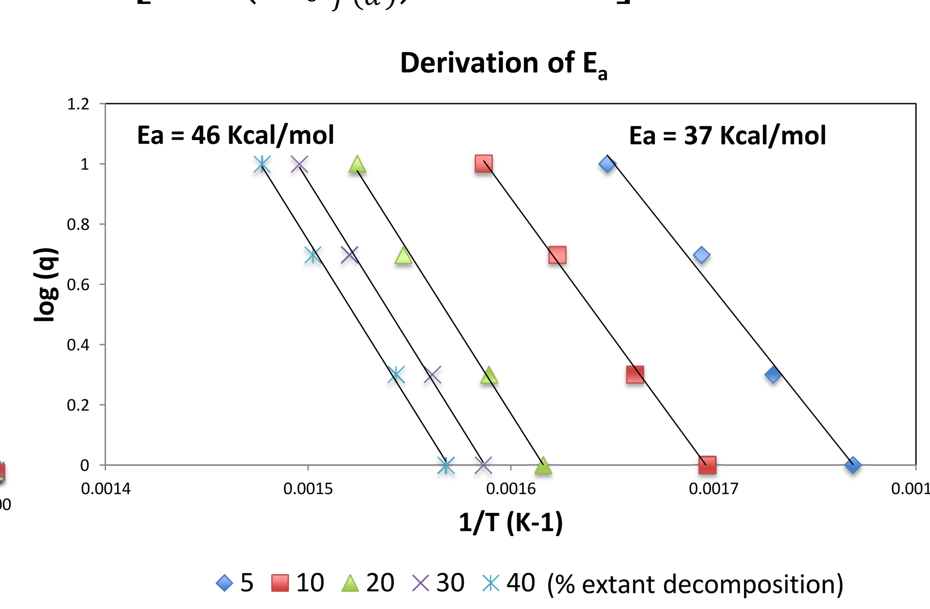
Thermal Decomposition

Dynamic heating TGA experiments were conducted to calculate the E_a of decomposition for the polymers

Degradation kinetics
$$\frac{d\alpha}{dt} = k(T)f(\alpha) = k_0 e^{\frac{-E_a}{RT}} f(\alpha)$$

Kinetics Analysis
$$\log q = \left[\log\left(\frac{k_o E_a}{R\int_0^\alpha \frac{d\alpha}{f(\alpha)}}\right) - 2.315\right] + \frac{0.475 E_a}{RT}$$





Composition (PET/NT)	E_a (kcal/mol)
100/0	58
97/3	47 (LT) 49 (HT)
90/10	43 (LT) 48 (HT)
85/15	36 (LT) 46 (HT)

- Decomposition curves show two possible decomposition regimes in polymers with 10% and 15% nitration
- Low temp decomposition has lower Ea
- Using these data, time tables can be calculated to determine allowable residence times for polymers in extruder

Future Work

Moving towards extrusion, further decomposition studies will be conducted to provide a better picture of the allowable processing parameters for our polymers. In addition, the melt-flow properties will be further investigated to explore the possibility of injection-molding these materials.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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