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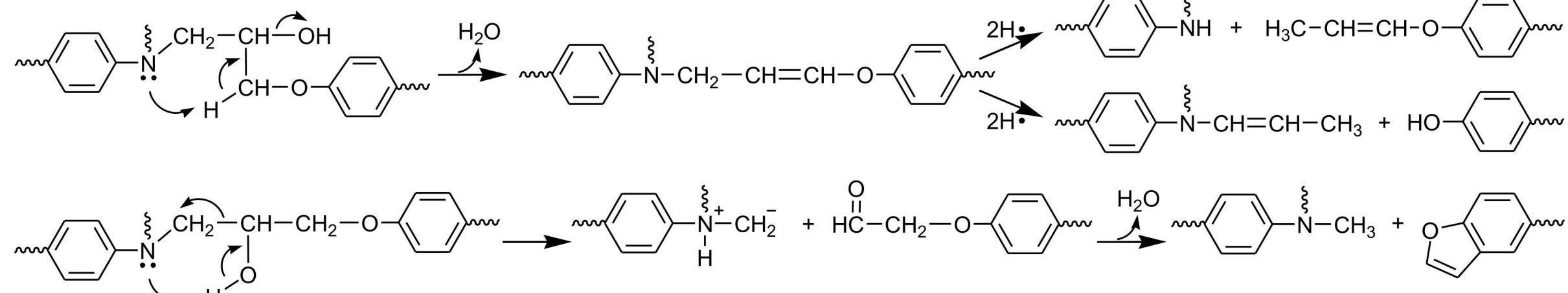


Alternative Materials for High Temperature Encapsulation and Adhesive Applications

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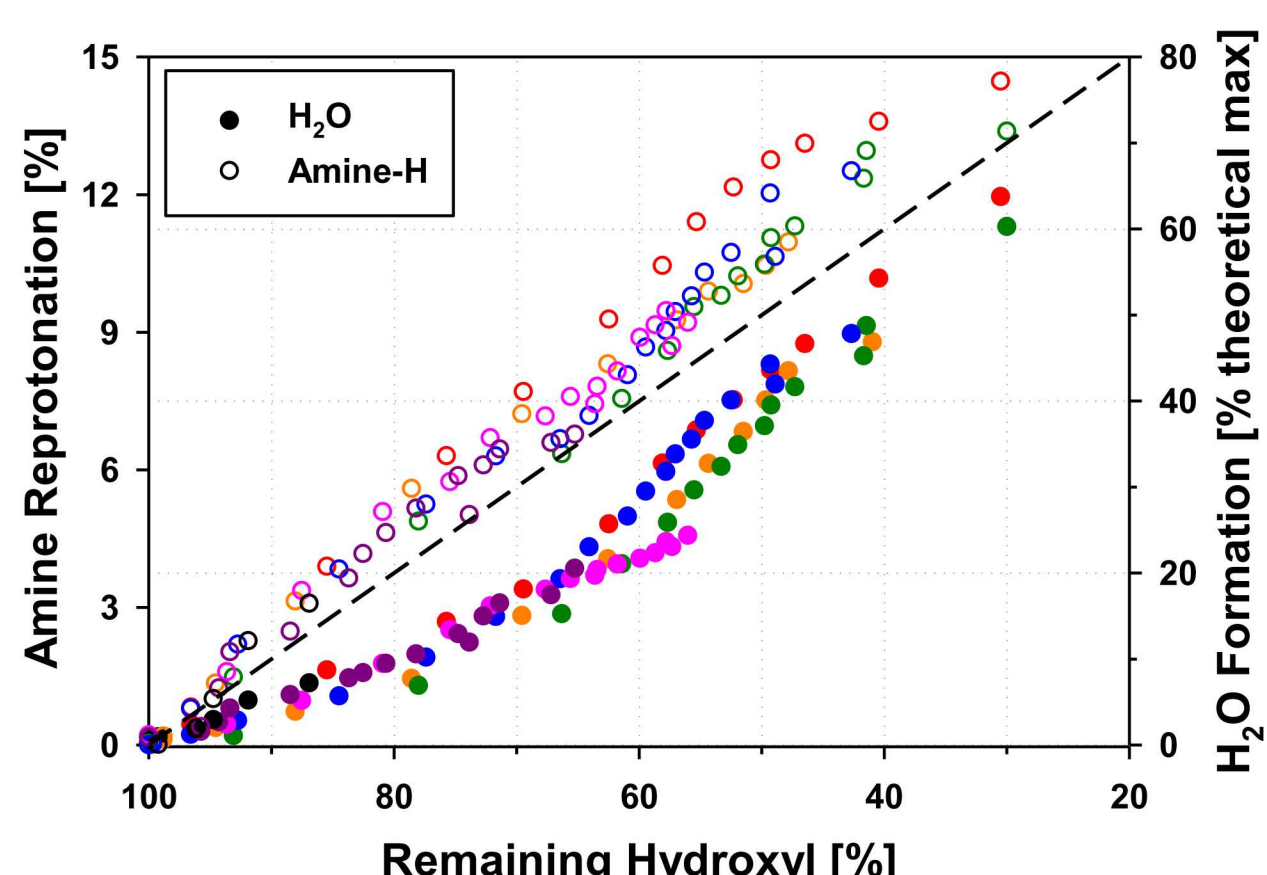
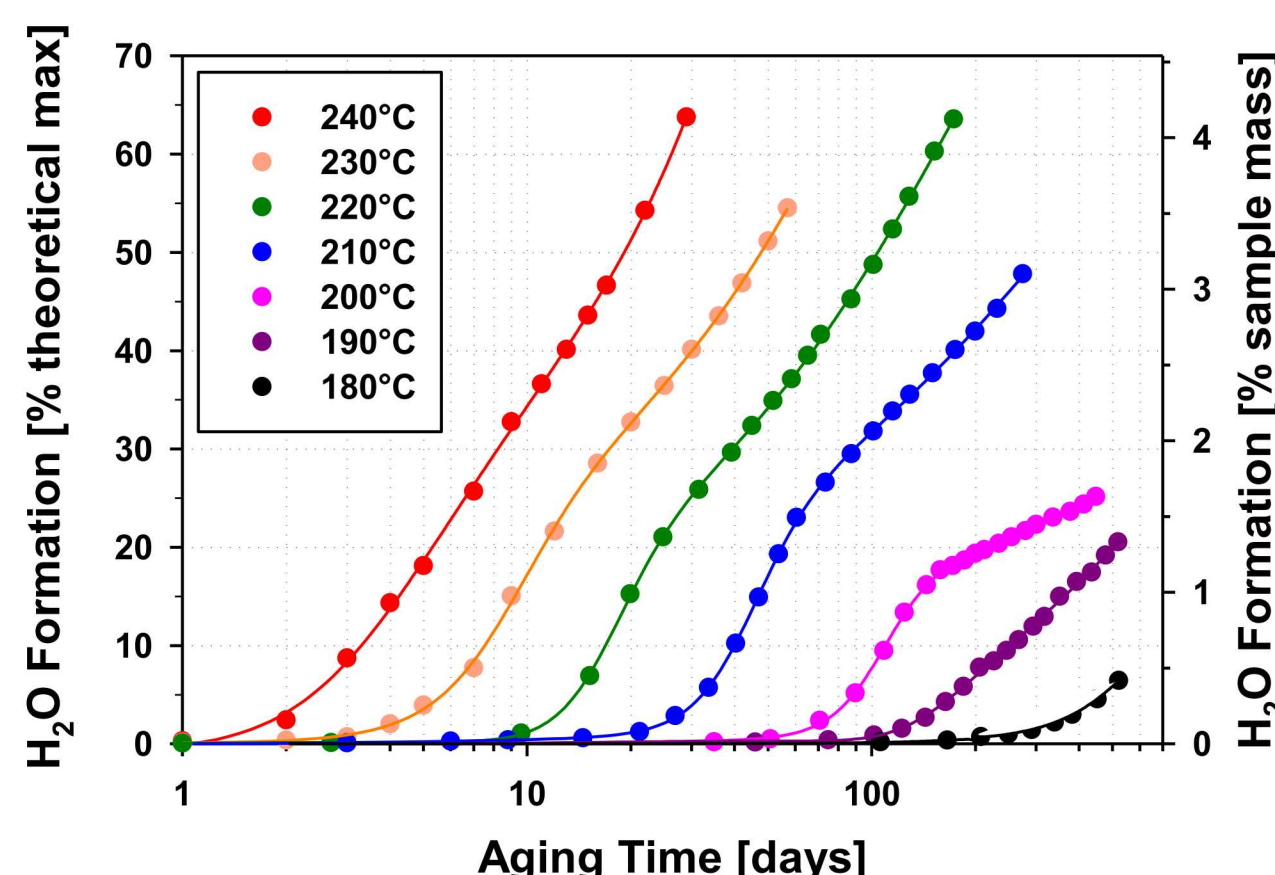
Limited Thermal Stability of Epoxy Materials

- Amine-cured epoxy materials have traditionally been used in high-performance adhesive, encapsulation, coating, and fiber-reinforced structural composite applications for moderate temperature service environments owing to their relatively low cost, excellent mechanical properties, and favorable processing characteristics.
- These materials have limited high temperature (>180°C) application however, due in large part to their susceptibility towards nucleophilic-initiated pyrolytic degradation as a result of the relatively strong nucleophilicity of tertiary amine groups generated during cure.



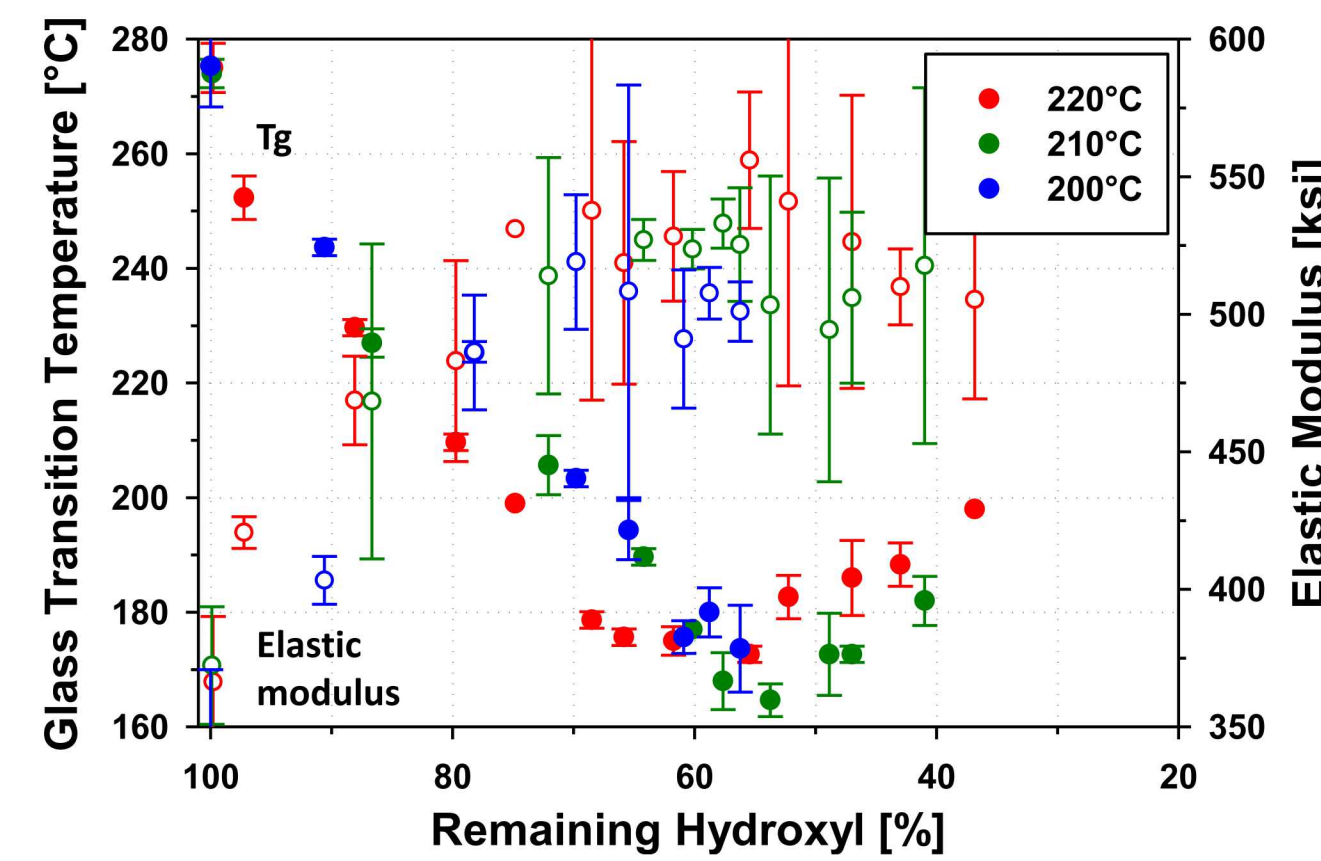
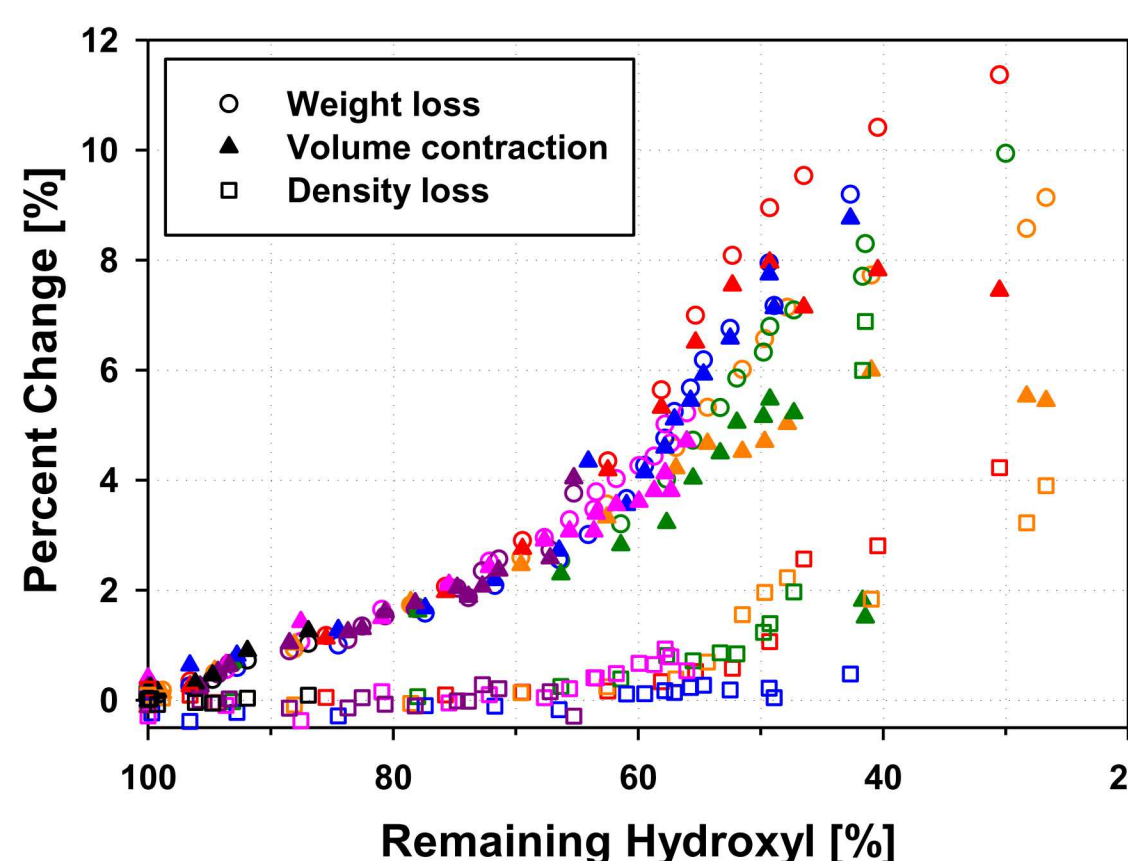
Pyrolytic degradation scheme proposed by Patterson-Jones et al. for aromatic amine cured epoxy materials. Nucleophilic chain breaking (bottom) appears to predominate at T's below ~350°C

- Primary degradation kinetics were evaluated for an epoxy material (1:1 Epon828/1031/4,4'-DDS) using an FTIR volatile analysis technique to monitor water evolution as function of time and temperature.
- Water is the main degradation product, accounting for 30-50% of observed weight loss at 240-210°C.
- Dehydration of OH groups gives a theoretical water yield of 6.9 %.
- Near-IR measurements were conducted in parallel to quantify decreases in hydroxyl and increases in 2° and 1° amine groups in the solid material. As expected, OH loss is clearly correlated with H₂O formation.



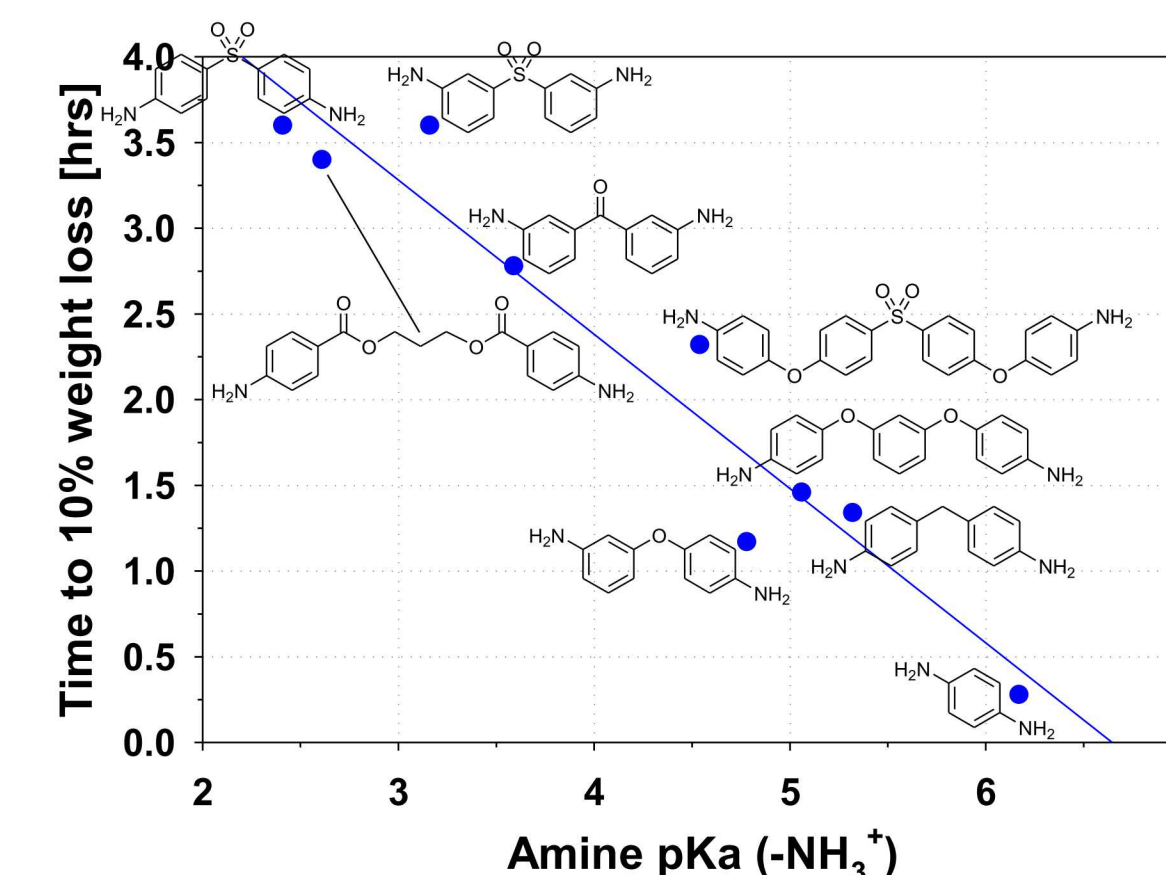
Chemical-Mechanical Property Correlations

- All major chemical and physical property changes studied (OH loss, H₂O formation, 2° amine formation, total weight loss and volume contraction) exhibited similar activation energies ranging from 167-173 kJ/mol.
- Physical and mechanical property changes are clearly correlated with primary degradation chemistry (OH loss)
- Weight loss and volume contraction occur at a similar rate resulting in very little change in density until relatively late in the degradation process (~60% OH remaining) when weight loss exceeds contraction.
- This appears to occur in parallel with a shift in mechanical property degradation trends, namely a levelling-off in T_g, compressive elastic modulus, flexural failure strain (not shown) and K_{1c} fracture toughness (not shown).

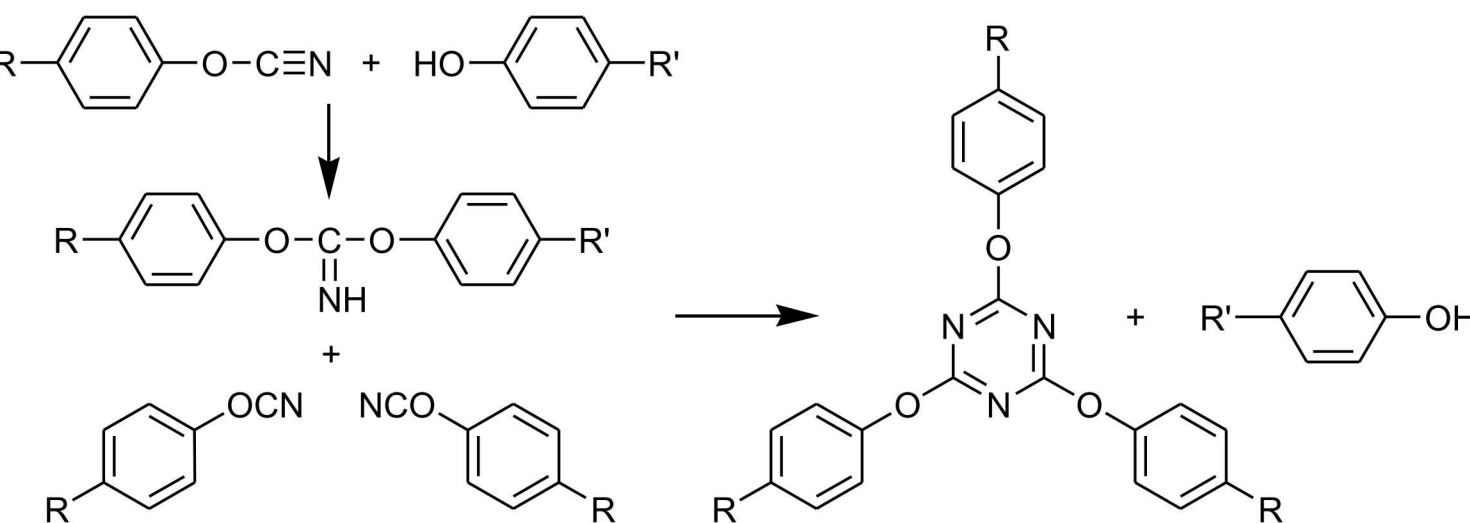


Formulation Optimization to Improve T Stability

- Several aromatic diamines were screened as alternative curatives, although the currently used 4,4'-DDS curative proved to be the most thermally stable which we attribute to its relatively low basicity and therefore decreased propensity towards nucleophilic initiated degradation
- Aromatic acid anhydrides such as pyromellitic dianhydride were also screened as alternative curatives, however, these materials proved to be less thermally stable and much more difficult to process due to their very high melting points
- A number of higher functionality epoxy resins showed improved thermal stability when substituted for Epon828, although their higher viscosities made processing difficult

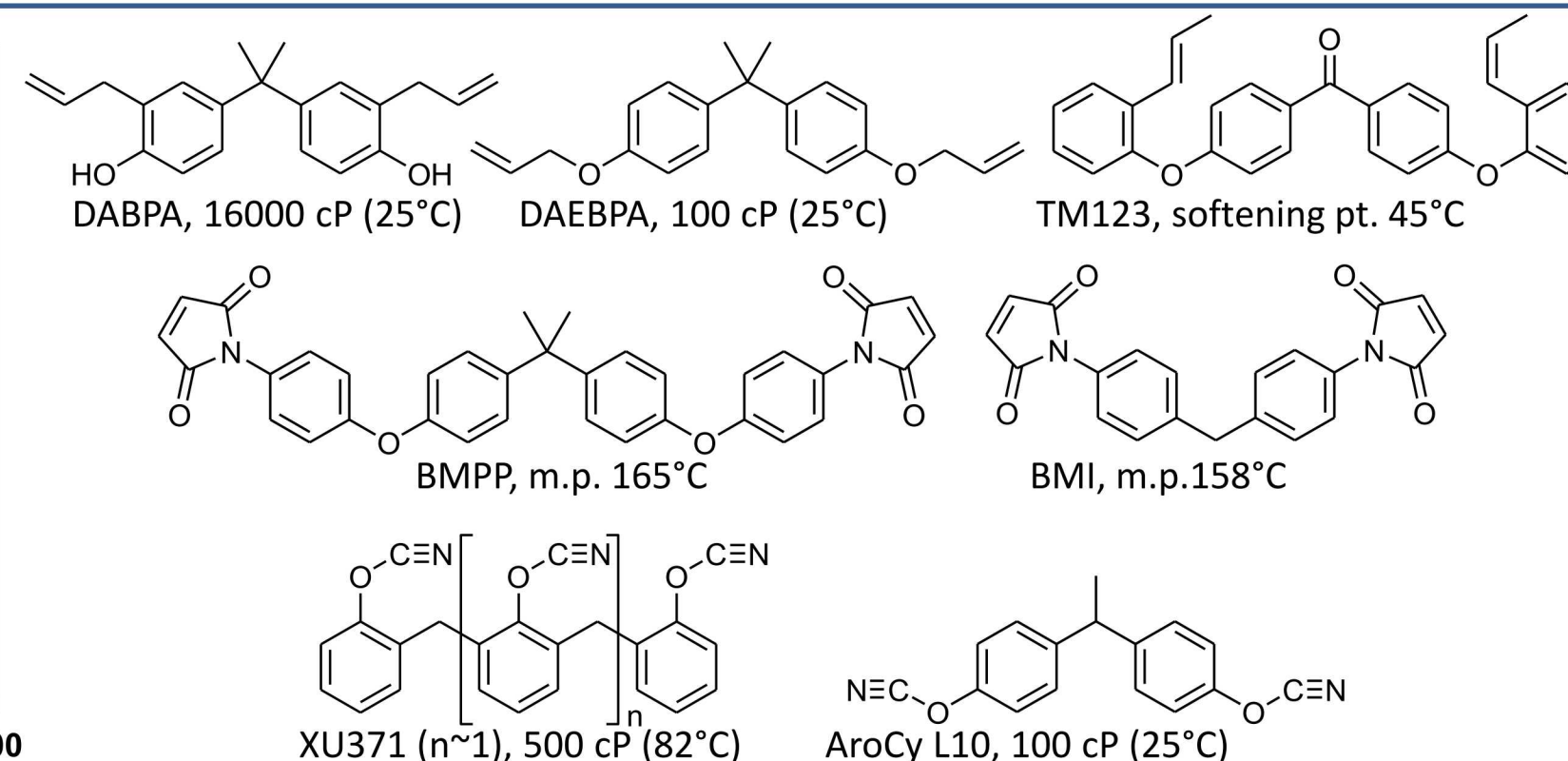
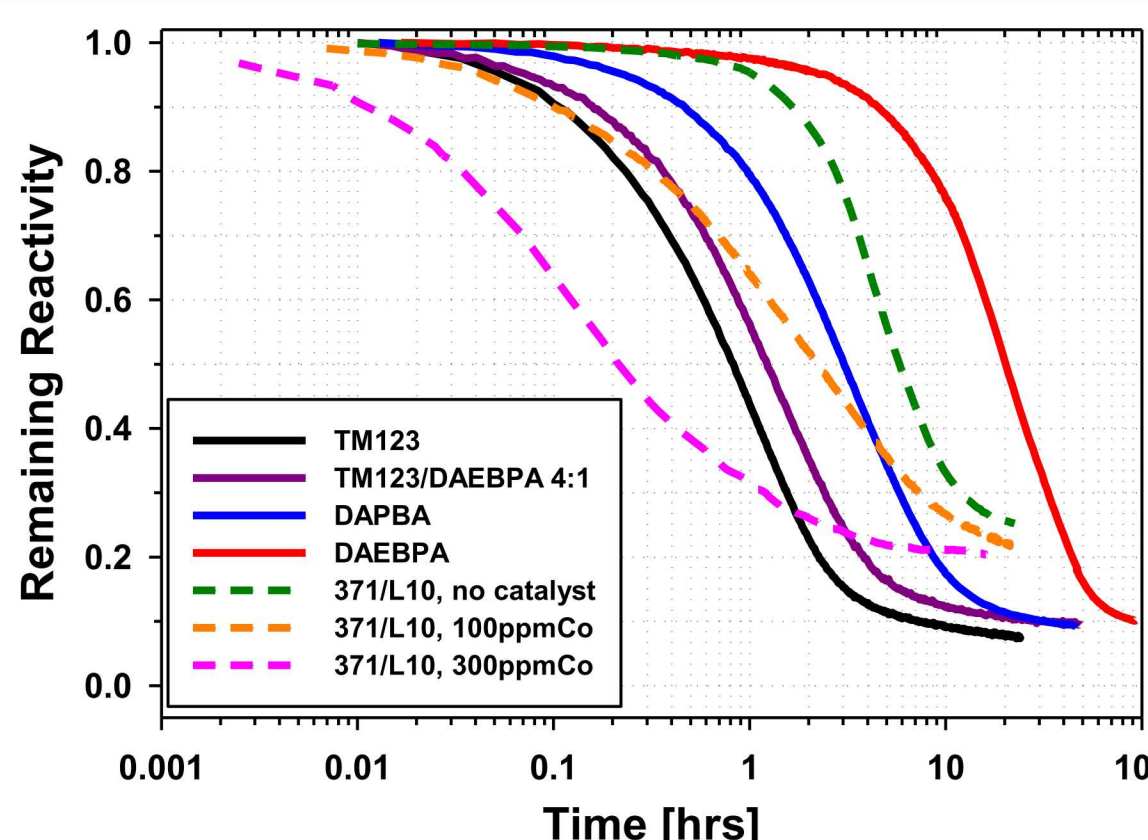
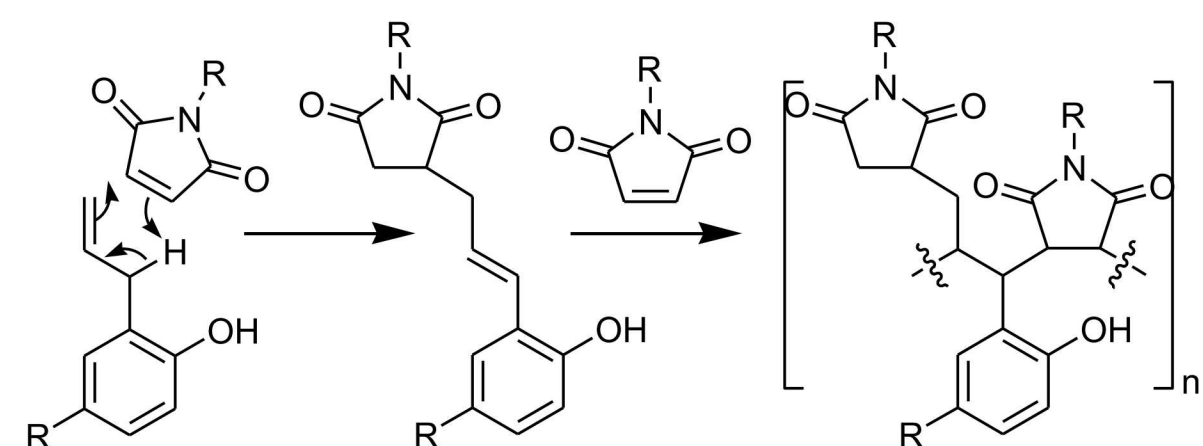


Bismaleimide (BMI) and cyanate ester (CE) materials have intrinsically better thermal stability than epoxies. Homopolymerized BMI is very brittle and therefore BMI's are typically toughened with a variety of co-curatives including diallyl, dipropenyl, and diamine compounds. CE's can be co-cured with epoxies or BMI's (BT resins), although homopolymerized di-functional CE's have comparable toughness to epoxies without needing a co-curative.

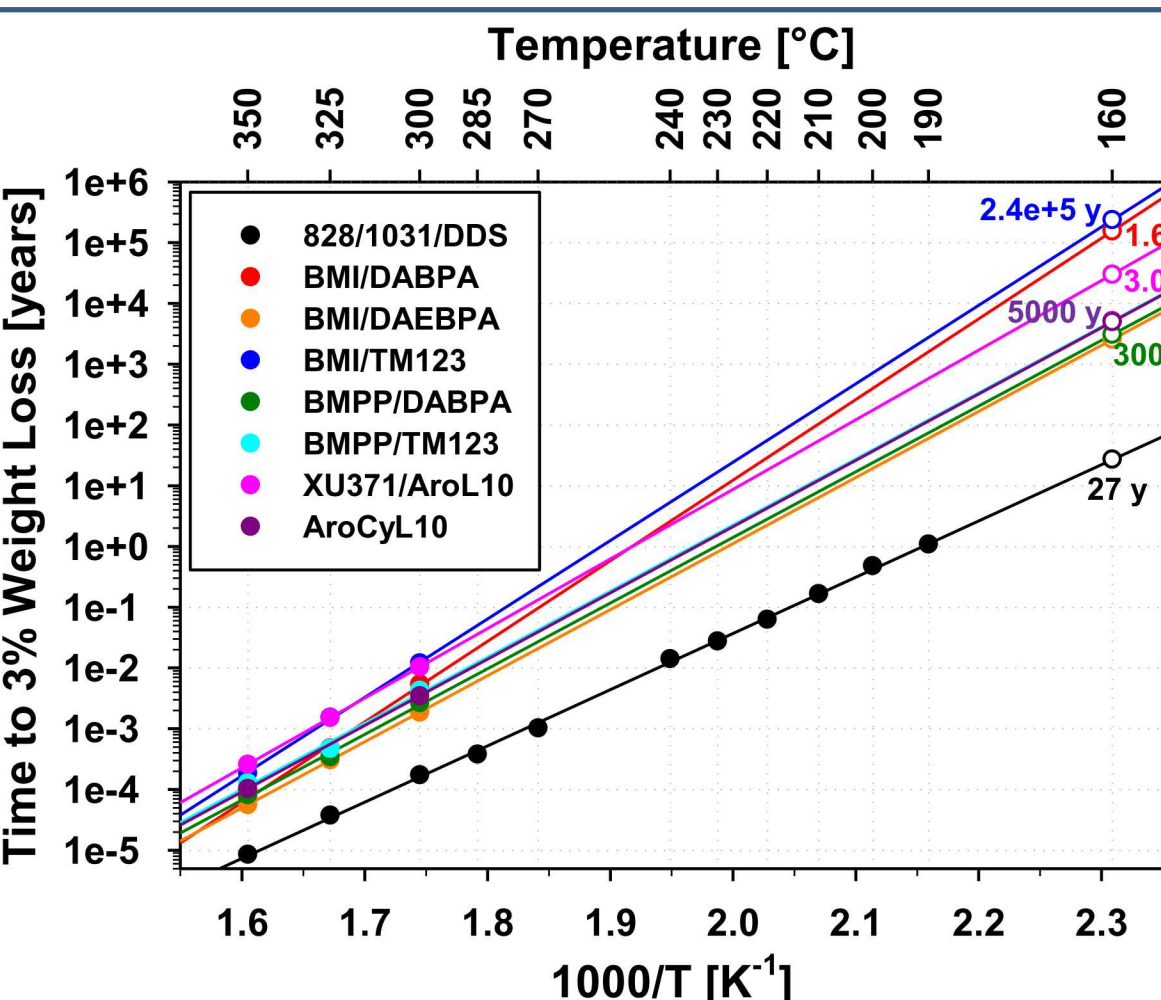


Cyanate ester polymerization is initiated by the reaction of a phenolic hydroxyl with a cyanate ester group to form an iminocarbonate intermediate which then undergoes a cyclotrimerization reaction with two more cyanate ester groups to form a triazine ring in a reaction that regenerates the initiator.

BMI's are typically co-cured with diallyls which react via a step-wise "ene" addition of the allyl to the maleimide double bond, forming a propenyl group which then reacts with another maleimide group in a radical chain-growth mechanism. Homo- polymerization of maleimide groups also occurs to some extent although is quite limited below 200°C.



- Cure kinetics** were evaluated isothermally at 200, 175 and 150°C (plot shown) using near-IR transmission spectroscopy for BMI's and mid-IR-ATR spectroscopy for CE's.
- BMI mixes were formulated in a 1.2:1 molar ratio of BMI/curative. The slowest BMI co-curative, DAEBPA, was found to be an effective reactive diluent for faster systems such as TM123.
- A transition metal chelate (Co(II)AcAc) dissolved in nonylphenol was used to catalyze the cure of 1:1 (mass) XU371/AroCyL10. CE resins were stored in a drybox to minimize the potential for hydrolysis of CE groups.



- Thermal stability** was assessed with isothermal TGA at 300, 325, and 350°C under nitrogen.
- All BMI and CE materials displayed significantly better thermal performance compared to the reference epoxy.
- Extrapolations of weight retention behavior to the intended use-temperature indicates performance predictions that are several orders of magnitude better than the reference material.
- However, it must be noted that extrapolations from very high to much lower T's should be used as initial guidance only since mechanistic changes in aging behavior are known to exist for many materials, causing significant deviations from Arrhenius behavior at lower T's.



- Anomalous aging behavior:** As an example of the inherent limitations of simple extrapolations from high to low T's, a CE matl. (AroCy L10) was found to have highly variable weight retention and dimensional stability at 240°C which deviated significantly from the predicted behavior based on extrapolations of TGA data.
- Samples 1 and 2 were aged in nearly identical clean ampoules for IR gas analysis while sample 3 was aged in an ampoule containing three other materials (two BMI's and one XU371 bar).
- The aging behavior of sample 3 was clearly accelerated by the presence of the 3 other materials as evidenced by its substantial volume expansion, char formation, and weight loss. By comparison, the 3 other materials did not exhibit any unexpected aging behavior.

Material	Mechanical Properties							Cure Kinetics		Thermal Stability	
	T _g (°C)	Shear modulus (GPa) at 150°C	Flexural Strength (ksi)	Failure Strain (%)	Elastic Modulus (ksi)	Yield stress (ksi)	Fracture Toughness K _{1c} (Mpa*m ^{0.5})	Cure viscosity time to 1 Pa-s (min) at 155°C	Time (min) to 50% conversion at 150°C (FTIR)	Weight Loss (20 days) 240°C	Shrinkage (20 days) 240°C
828/1031/DDS	253	0.85	22	5	360	22.5	0.7	25	45	10.5%	- 2.3%
BMI/DABPA	285	1.01	25	4.2	444	29.5	1.2	36	180	0.1%	Stable
BMI/DAEtherBPA	245	1.10	-	-	-	-	-	> 60	1200	0.04%	Stable
BMI/TM-123	281	0.86	19	3	430	29	0.7	17	48	0.07%	- 0.08%
BMPP/DABPA	-	-	28	8.4	370	22.5	1.45	-	312	-	-
BMPP/TM-123/DAEBPA	242*	0.78*	29	7	390	22.5	1.55	23	-	0.06%	0.06%
XU371/AroCy L-10	323	0.92	23	3.6	360	26.5	0.7	15	132	0.31%	- 0.24%

Impact and Future Work

- An optimized amine-cured epoxy material (Epon828/1031/DDS) was thoroughly characterized in terms of degradation behavior by monitoring changes in chemical, physical, and mechanical properties as a function of t & T
- Given the inherent thermal stability limitations of the reference material, several BMI and CE alternative materials were screened as replacements
- All BMI and CE materials that were screened showed substantially better thermal stability and similar mechanical performance and processing characteristics compared to the reference. material
- The 3 best performing materials (BMI/DABPA, BMPP/TM123/DAEBPA, & XU371/AroCyL10) were selected for an accelerated aging study at 260-200°C to assess chemical and mechanical property stability