SAND20XX-XXXXR
LDRD PROJECT NUMBER: 220604
LDRD PROJECT TITLE: Increasing the Lifetime of Epoxy Components with Antioxidant Stabilizers
PROJECT TEAM MEMBERS: Hannah Narcross, Erica Redline, Mat Celina, Ashley Bowman

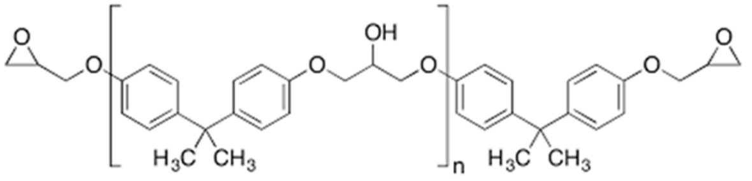
ABSTRACT:

Epoxy thermoset resins are ubiquitous materials with extensive applications where they are used as encapsulants, composites, and adhesives/staking compounds used to secure sensitive components. Epoxy resins are inherently sensitive to thermo-oxidative aging, especially at elevated temperatures, which changes the bulk properties of the material and can lead to component failure for example by cracking due to embrittlement or by adhesion failure between the epoxy and filler material in a composite. This project investigated the effects of three commercial antioxidants (Irganox® 1010 (I-102), butylated hydroxytoluene (BHT), or Chisorb® 770 (HALS)) at two different loadings (2.5 and 5 wt%) on the mechanical and chemical aging of a model epoxy system (EPON™ 828 / Jeffamine® T-403) under ambient conditions, 65, 95, and 110 °C. Additionally, synthetic routes towards an antioxidant capable of being covalently bound to the resin so as to prevent leaching were explored with one such molecule being successfully synthesized and purified. One commercial antioxidant (Irganox® 1010) was found to reduce the degree of thermo-oxidatively induced damage in the system.

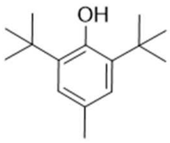
INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

As previously stated, epoxy resins are widely used materials found in a variety of critical systems. Epoxies are inherently sensitive to thermo-oxidative degradation, where unstable peroxy radicals form in the polymer network which continue to react, leading to changes in the network structure and the loss of mechanical properties of the material.[1-3] Additives which reduce the oxidation rate of epoxies would provide a generalized solution to increase the lifetime and reliability of a number of mission critical components. One approach currently used to prevent to thermo-oxidative degradation in thermoplastic materials such as polyolefins and polyurethanes is to include small amounts of an additive referred to as an antioxidant. These antioxidants preferentially react with unstable peroxy radical intermediates to form stabilized radicals that do not undergo any further reactions with the polymer network, preventing any further degradation.[4] Despite the common usage of antioxidants in thermoplastics, there is a lack of work investigating the effects of antioxidants on thermoset epoxies in the literature. Since the ability of an antioxidant to quench reactive free radicals is limited by its mobility and ability to diffuse to the reactive site, there is a risk that commercial antioxidants will be ineffective at inhibiting thermo-oxidative aging in glassy cross-linked epoxy resins and/or that at loadings high enough to effectively reduce aging, the changes in mechanical properties (due to a reduction in cross-link density) or amount of additive leaching are unacceptable. These effects from high additive loading are expected since commercial antioxidants are not graftable with epoxies. Therefore, we explored the effects of three commercial non-graftable antioxidants (Irganox® 1010 (I-102), butylated hydroxytoluene (BHT), or Chisorb® 770 (HALS)) on the thermo-oxidative aging behavior of EPON™ 828 cured with Jeffamine® T-403 and also synthesized a novel stabilizer that is graftable to epoxies (SAGE) with the intention of achieving a high loading of antioxidant without disrupting network structure or leaching.

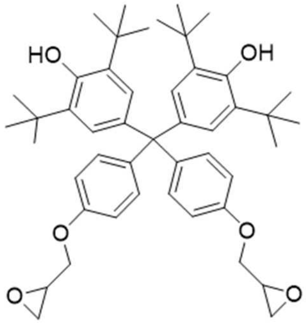
EPON™ 828



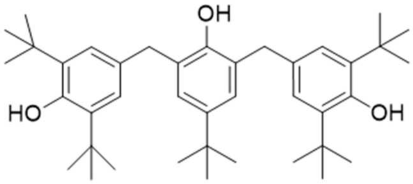
BHT



Target SAGE



Alternative SAGE



The target SAGE was selected due to its similarity (both structurally and degree of functionality) to the monomer of EPON™ 828 and the anticipated minimization in impact on the bulk mechanical properties of the cured resin, while being functionalized with BHT functional groups expected to act as antioxidants. An alternative SAGE was also identified due to it's established antioxidant properties while possessing a hydroxy group capable of covalently binding with EPON™ 828. The hydroxy groups on the BHT are not expected to participate in crosslinking due to steric hindrance, thus maintaining their antioxidant capability.[5]

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

Coupon Preparation:
EPON™ 828 was purchased from Miller-Stephenson and used as received. All other chemicals were purchased from Sigma-Aldrich and used as received without further purification.

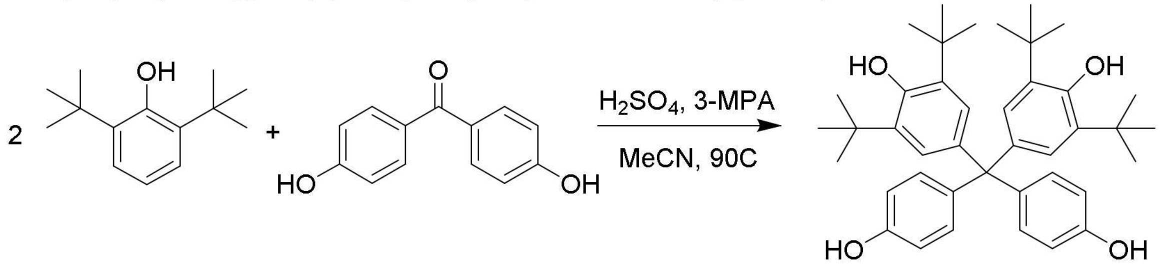
Coupons of EPON™ 828 cured with Jeffamine® T-403 (29 x 29 x 1 mm thick) were prepared with 0 wt%, 2.5 wt% (0.4 g), or 5 wt% (0.83 g) of either Irganox® 1010 (I-102), butylated hydroxytoluene (BHT), or Chisorb® 770 (HALS). The indicated antioxidant amounts were mixed into 11 g of 828 EPON in a Thinky mixer for 1 minute at 2000 rpm and 10.1 kPa. Samples were heated to just above melting temperature of the antioxidant (70, 120, and 90 °C for BHT, I-102, and HALS respectively) and swirled until no visible particles remained. Jeffamine T403 (4.73 g) and 5-10 drops of the degassing agent, Shin-Etsu KF105, were then added. Samples were again mixed in a Thinky mixer for 1 minute at 2000 rpm and 10.1 kPa, then degassed in a vacuum oven at 65 °C for ~5 minutes. Finally, samples were poured into silicone molds and cured at 80 °C for 10 hours. Coupons were then aged under ambient conditions or in forced air circulating ovens at 65, 95, and 100°C.

Analysis:
Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR). ATR-FTIR was carried out at room temperature on a Bruker Tensor II. The Tensor II uses a KBr beamsplitter and a deuterated triglycine sulfate detector (DTGS). The instrument was fitted with a Pike GladiATR ATR accessory with a diamond crystal. Thirty-two spectra were taken for each sample in the range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. DSC was performed on a TA Instrument Q200 series differential scanning calorimeter and calibrated with an internal standard of indium. Approximately 5-10 mg of material were placed into Al pans and equilibrated at 25 °C. Samples were then heated at 10 °C/min from 25 °C to 140 °C or 180 °C, equilibrated for 1 minute, then cooled at 10 °C/min back to 25 °C with 1 min equilibration at 25 °C. This sequence was repeated a second time. T_g was determined via the middle of the inflection point on the second cooling cycle. Images were taken with a Zeis Axioscope 5 digital microscope. Nuclear magnetic resonance spectra were recorded on a Spinsolve 80 spectrometer. Leaching studies were preformed by soaking coupons in 20 mL of distilled water in sealed containers and stored under ambient conditions.

Synthesis

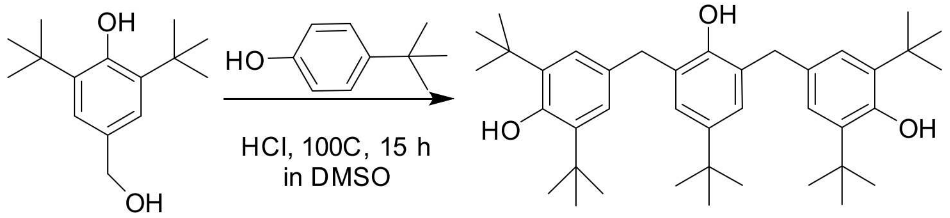
4,4′-Dihydroxybenzophenone was purchased from TCI America and used as received. All other reagents were purchased from Sigma-Aldrich and used without further purification.

4,4'-(bis(4-hydroxyphenyl)methylene)bis(2,6-di-tert-butylphenol)



2,6-di-tert-butylphenol (14.44 g, 6.0 eq.), 4,4′-Dihydroxybenzophenone (2.50 g, 1.0 eq.), and a catalytic amount of 3-mercaptopropanoic acid were dissolved in 40 mL acetonitrile. Sulfuric acid (1.60 g, 1.4 eq.) was then added dropwise, turning the solution from clear to orange. The reaction mixture was then refluxed at 90 °C for either 24 hours, 48 hours, or 7 days. After cooling to room temperature, the product was extracted with DCM twice and the combined organic layers were washed three times with DI H_2O. The organic layer was dried over magnesium sulfate and filtered. Excess solvent was removed under vacuum using a rotary evaporator, and the resulting product was further dried under vacuum at 40 °C overnight followed by recrystallization from methanol to remove contaminants. The desired product was not obtained in any appreciable yield, with only small amounts of the monofunctionalized intermediate produced despite increases in reaction time (maximum yield after 7 days was 0.64 g (13%)). This was attributed to a lack of reactivity of the diarylketone precursor, therefore an alternative molecule was pursued.

4,4'-((5-(tert-butyl)-2-hydroxy-1,3-phenylene)bis(methylene))bis(2,6-di-tert-butylphenol)[6]



4-(tert-butyl)phenol (1.9 g, 12.6 mmol) and 2,6-di-tert-butyl-4-(hydroxymethyl)phenol (6.0 g, 25.4 mmol), and hydrochloric acid (33.3 mL) were added to 150 mL of DMSO. The reaction mixture was stirred at 100 °C for 15 hours in a pressure bottle. After cooling to room temperature, DI H2O (200 mL) was added to quench the reaction. The crude product was extracted twice with ethyl acetate, and the combined organic layers were washed three times with brine. The organic layer was dried over magnesium sulfate and filtered. Excess solvent was removed under vacuum using a rotary evaporator, and the resulting product was further dried under vacuum at 40 °C overnight. Silica gel column chromatography with hexanes and toluene yielded 10 mg of the desired product (1.9%). ^{1}H NMR (100 MHz $CDCl_3$) δ (ppm) 1.43 (m, 45H), 3.98 (s, 3H), 7.06 (m, 6H).

RESULTS AND DISCUSSION: 400

SAGE Synthesis:
Synthesis of the target SAGE was unsuccessful due to poor reactivity; even after 7 days there was no appreciable yield of the di-functionalized product and only a poor yield (13%) of the mono-functionalized intermediate according to thin layer chromatography and ^{1}H NMR. This was in agreement with literature synthesis of the same target molecule produced via a photochemical route, where hydroxy functionalized di-aryl ketone precursors suffered from low reactivity and poor yields. While the literature showed an alternative route towards the same target molecule[7], the multi-step process coupled with poor reported yields made it an unattractive candidate; therefore an alternative target molecule was pursued and synthesized albeit in poor yield of the purified product which was attributed to insufficient separation on the column and can likely be optimized in the future.

Aging Studies:

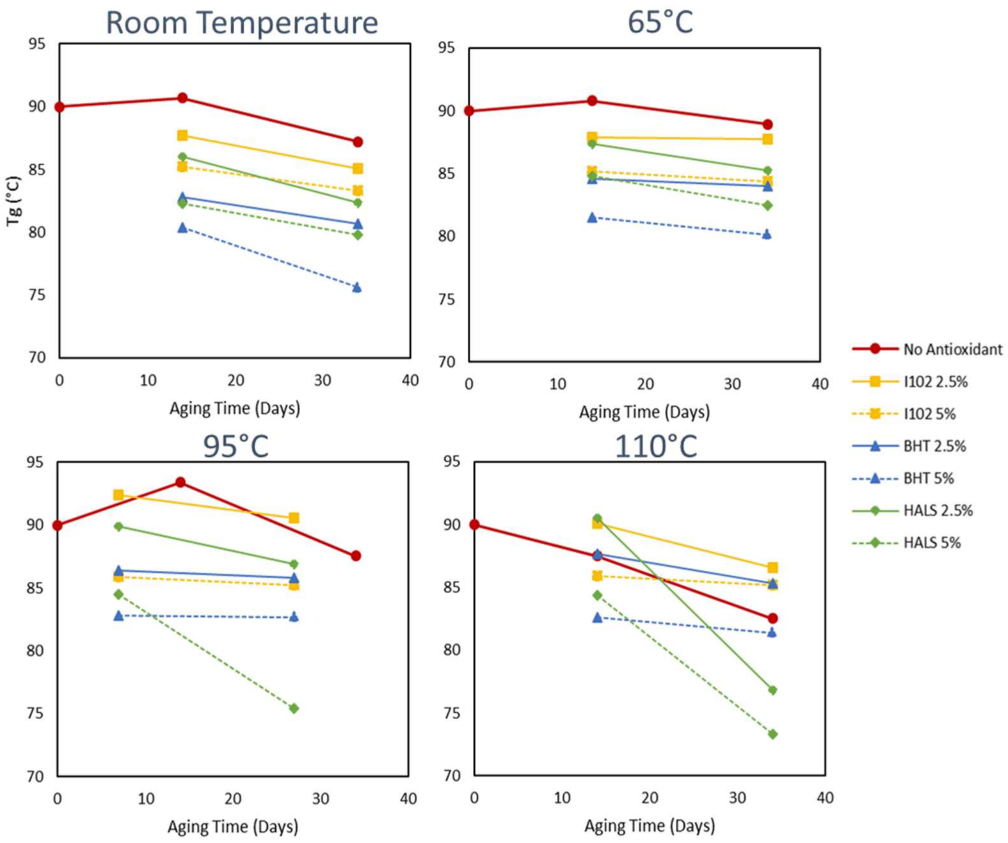


Figure 1. Changes in T_g (determined by DSC) over time of a DGBEA epoxy with and without antioxidant aged at different temperatures

The addition of antioxidant resulted in a decrease in glass transition temperature (T_g) in all samples, which were further lowered at higher loadings. This can be attributed to plasticization of the polymer network by the addition of a small molecule additive, and potentially reduced cross-link density. While the limited amount of data makes it difficult to establish trends, it can be noted that T_g values either stayed the same or lowered over time, with the greatest degree in change in samples aged at higher temperatures. This is likely due to thermo-oxidatively induced chain scission (damage) in the polymer network.[8] Samples prepared with I-102 showed less reduction in T_g than control or other antioxidant samples, suggesting it is the best preforming antioxidant.

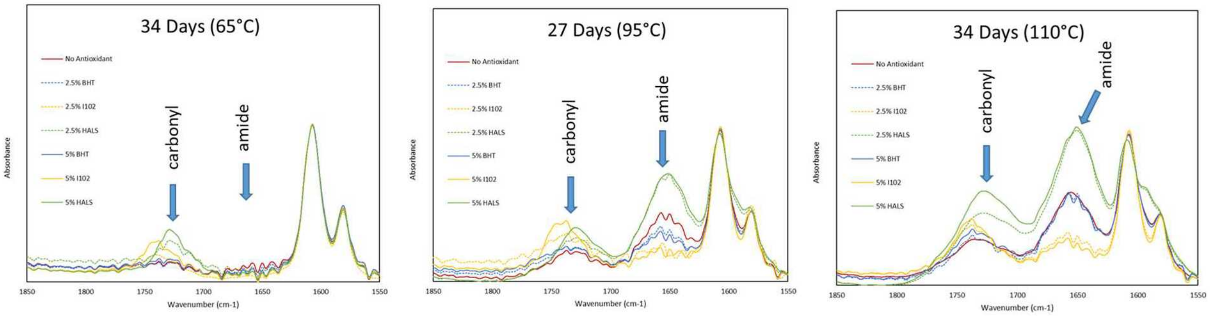


Figure 2. FT-IR spectra normalized at 1606 cm^{-1} of a DGBEA epoxy resin with and without antioxidant aged at different temperatures

Oxidation of amine cross-linked epoxy resins is expected to lead to the formation of carbonyl (1710-1770 cm^{-1}) and amide (1660 cm^{-1}) species whose growth can be tracked using FT-IR and normalizing the spectra using the peak at 1606 cm^{-1} as an internal standard.[8] After 34 days at 65°C, no amide species were observed in any of the samples, with some carbonyls observed in samples using BHT or I-102 as the antioxidant. These were attributed to the carbonyl-containing structure of both antioxidants and not from aging. After 27 days at 95°C, carbonyl and amide species were observed in all samples. Samples containing BHT and I-102 showed less amide formation than the control prepared with no antioxidant (with I-102 showing the least), with little difference between samples prepared with 2.5 or 5wt% loadings. Surprisingly the addition of HALS appears to have accelerated aging, as these samples show greater formation of both the carbonyl and the amide species. This was also true for samples aged at 110°C for 34 days. Under these conditions, no major differences between samples with BHT and the control were observed. However, samples with I-102 had lower amide formation indicating that of all the additives investigated I-102 has the greatest antioxidant activity in this epoxy system.

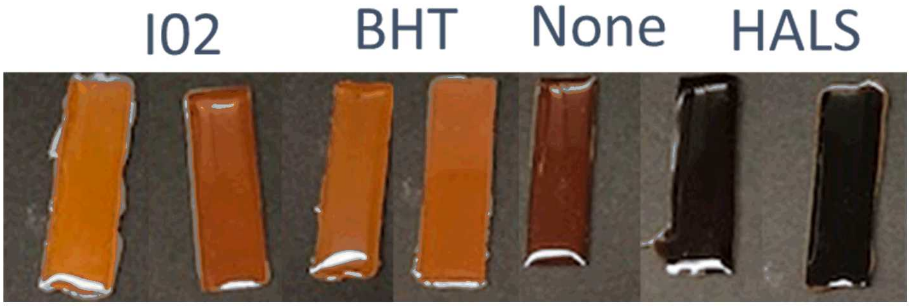


Figure 3. Samples aged at 110°C for 34 days

Samples aged at elevated temperatures all discolored (yellowed) after 34 days, with the greatest amount of discoloration observed in samples containing HALS. Samples prepared with BHT or I-102 discolored less than control samples prepared without antioxidant. This is consistent with previous results that showed beneficial antioxidant activity from BHT and I-102, and accelerated aging in HALS containing samples.

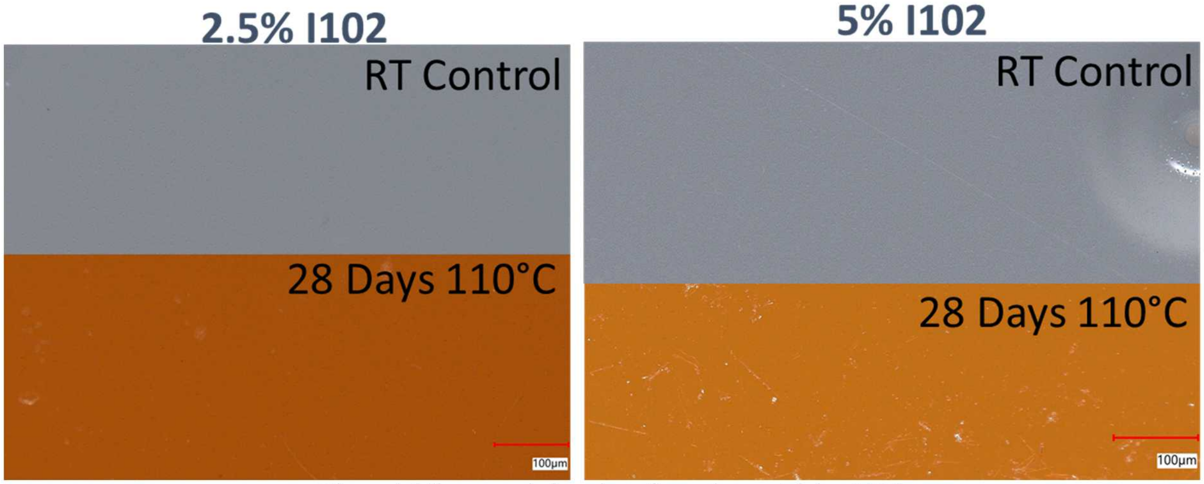


Figure 4. Miscroscopic imaging of samples containing I-102

Microscopic imaging of all aged samples did not show any changes in the surface (i.e. cracking or pitting). It did, however, reveal solubility issues of I-102 at higher loadings (5 wt%) where crystals of undissolved antioxidant could be observed. Water leaching studies (1 month in distilled water at ambient temperature) also showed no differences in changes in weight between samples with or without antioxidant at both loading.

ANTICIPATED OUTCOMES AND IMPACTS: 300

- Bought down risk on future programs by finding synthetic route to target molecule and identifying best preforming antioxidant for 828/T403 system.
- Currently in discussions for follow on work to complete aging studies

CONCLUSION: (400 word limit)

Two commercial sterically hindered phenol antioxidants (Irganox® 1010 (I-102) and butylated hydroxytoluene (BHT)) were found to reduce thermo-oxidative aging in a model epoxy system. A synthetic route towards a graftable antioxidant was realized.

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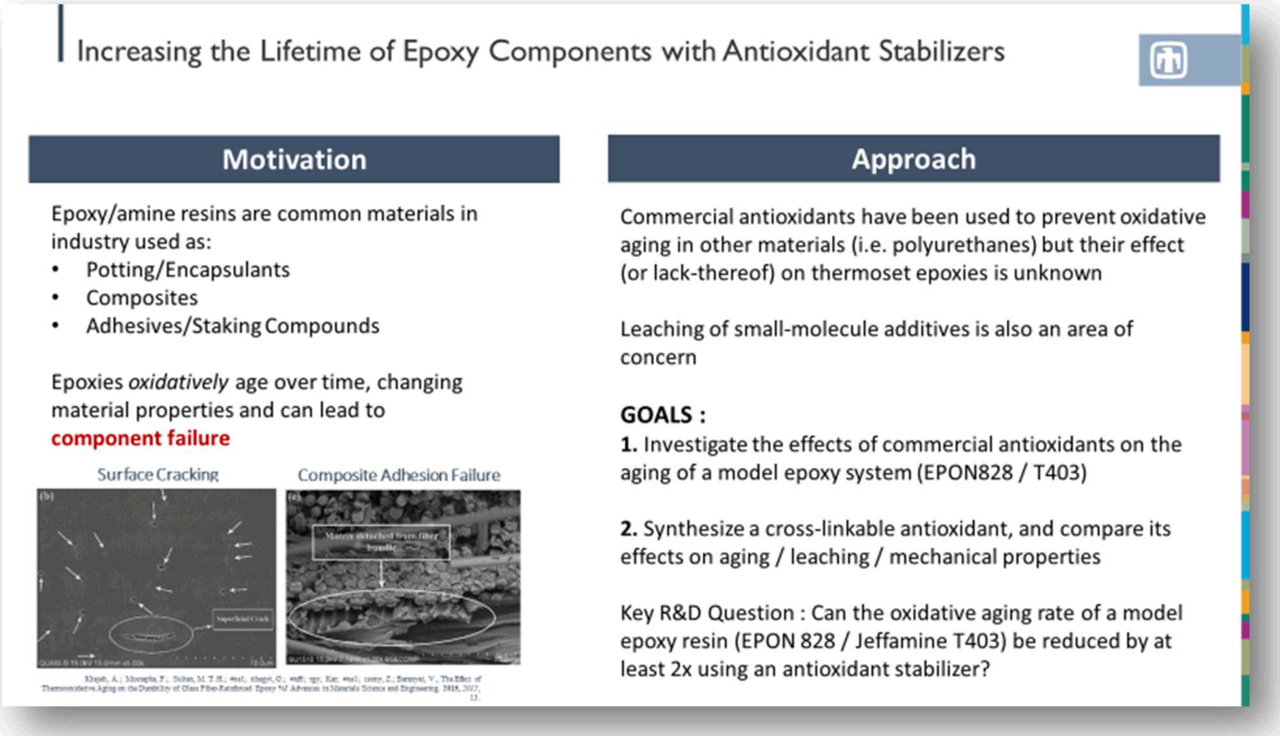
4. Pospíšil, J., Mechanistic action of phenolic antioxidants in polymers—A review. *Polymer Degradation and Stability* **1988,** *20* (3), 181-202.
5. Narcross, H.; Sharp, B. L.; Tolbert, L. M.; Henderson, C. L., Crosslinkable photoacid generators for ultrahigh loading in epoxide functionalized molecular resists. **2017,** *35* (6), 06GE02.
6. Yu, S.; Wang, Y.; Ma, Y.; Wang, L.; Zhu, J.; Liu, S., Structure, thermal stability, antioxidant activity and DFT studies of trisphenols and related phenols. *Inorganica Chimica Acta* **2017,** *468*, 159-170.
7. Becker, H.-D., Photochemical Reactions with Phenols. II. The Photochemical Reactions of Diaryl Ketones with Phenols. *The Journal of Organic Chemistry* **1967,** *32* (7), 2124-2130.
8. Djouani, F.; Zahra, Y.; Fayolle, B.; Kuntz, M.; Verdu, J., Degradation of epoxy coatings under gamma irradiation. *Radiation Physics and Chemistry* **2013,** *82*, 54-62.

ADDENDUM:



Increasing the Lifetime of Epoxy Components with Antioxidant Stabilizers

Motivation

Epoxy/amine resins are common materials in industry used as:

- Potting/Encapsulants
- Composites
- Adhesives/Staking Compounds

Epoxies *oxidatively* age over time, changing material properties and can lead to **component failure**

Surface Cracking

Composite Adhesion Failure

Khajeh, A.; Mustapha, F.; Sultan, M. T. H.; [illegible]; Baranyai, V., The Effect of Thermo-oxidative Aging on the Durability of Glass Fiber-Reinforced Epoxy [illegible] Advances in Materials Science and Engineering. 2015, 2015, 13.

Approach

Commercial antioxidants have been used to prevent oxidative aging in other materials (i.e. polyurethanes) but their effect (or lack-thereof) on thermoset epoxies is unknown

Leaching of small-molecule additives is also an area of concern

GOALS :

1. Investigate the effects of commercial antioxidants on the aging of a model epoxy system (EPON828 / T403)

2. Synthesize a cross-linkable antioxidant, and compare its effects on aging / leaching / mechanical properties

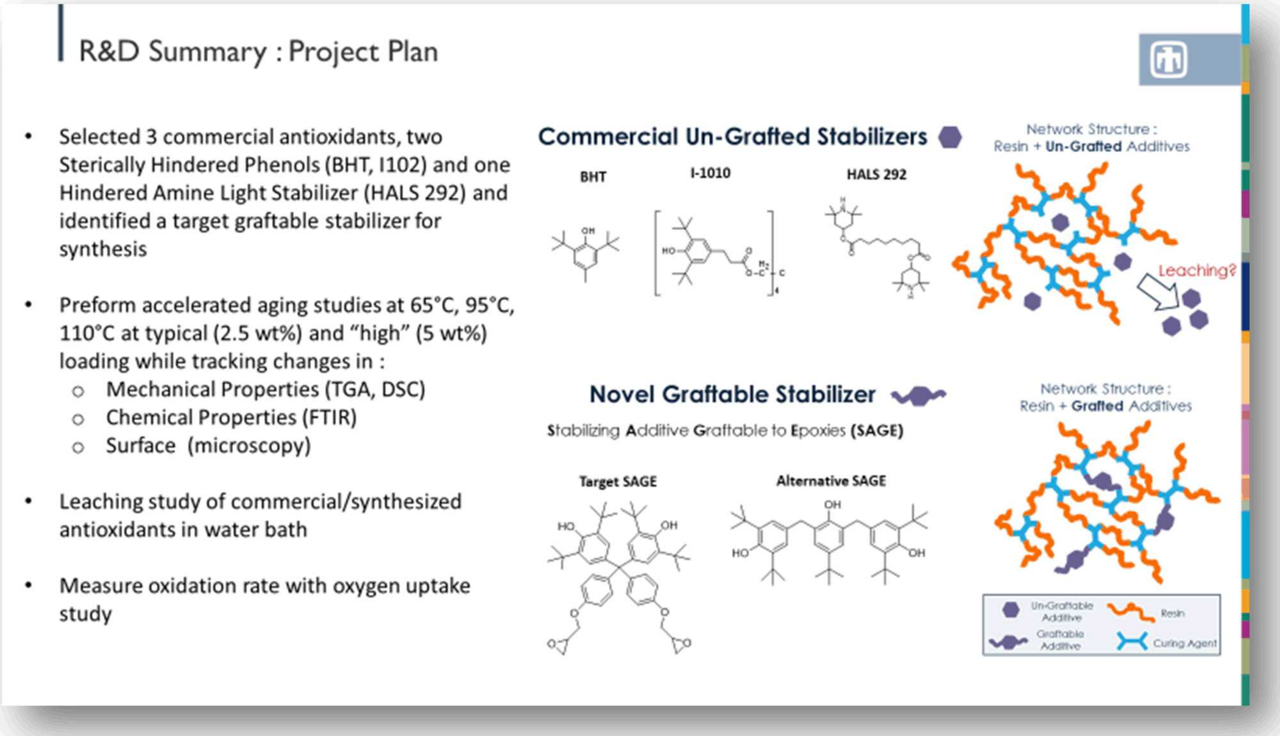
Key R&D Question : Can the oxidative aging rate of a model epoxy resin (EPON 828 / Jeffamine T403) be reduced by at least 2x using an antioxidant stabilizer?

LDRD

LABORATORY DIRECTED

RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS



R&D Summary : Project Plan

- Selected 3 commercial antioxidants, two Sterically Hindered Phenols (BHT, I102) and one Hindered Amine Light Stabilizer (HALS 292) and identified a target graftable stabilizer for synthesis
- Preform accelerated aging studies at 65°C, 95°C, 110°C at typical (2.5 wt%) and "high" (5 wt%) loading while tracking changes in :
  - Mechanical Properties (TGA, DSC)
  - Chemical Properties (FTIR)
  - Surface (microscopy)
- Leaching study of commercial/synthesized antioxidants in water bath
- Measure oxidation rate with oxygen uptake study

Commercial Un-Grafted Stabilizers

BHT

I-1010

HALS 292

Network Structure : Resin + **Un-Grafted** Additives

Leaching?

Novel Graftable Stabilizer

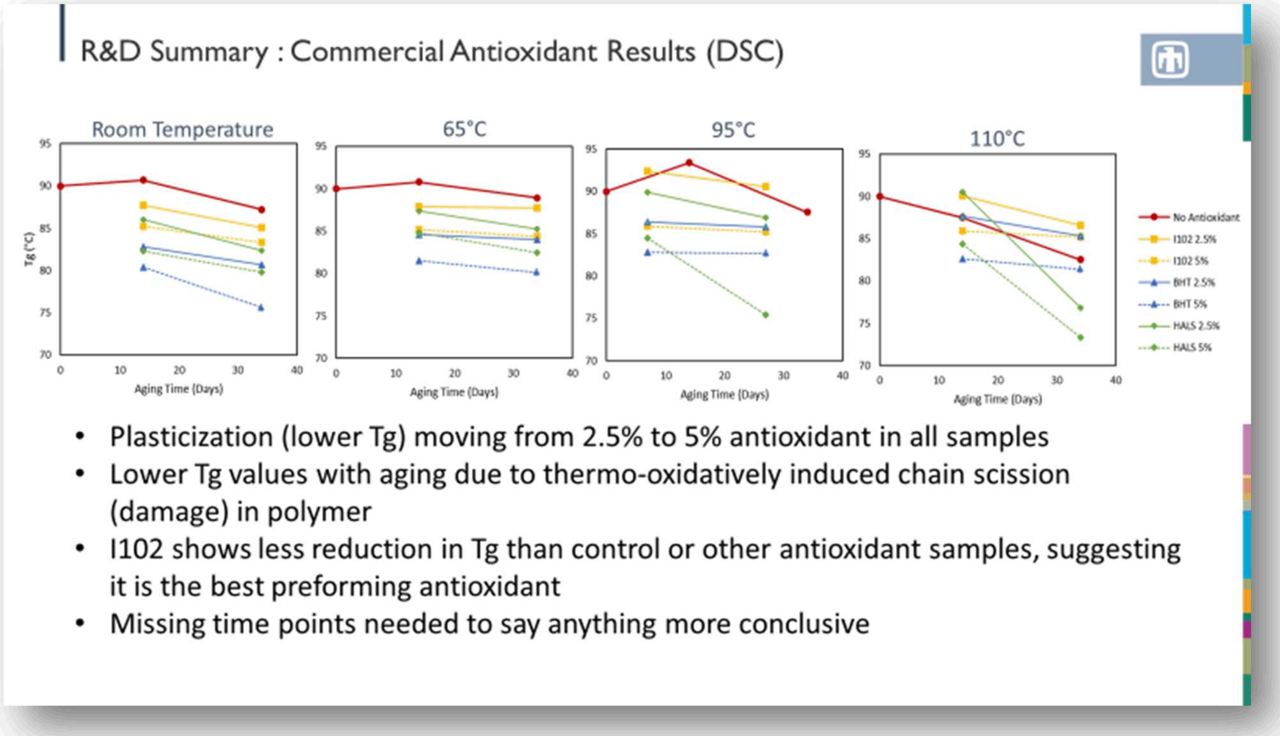
Stabilizing **A**dditive **G**raftable to **E**poxies **(SAGE)**

Target SAGE

Alternative SAGE

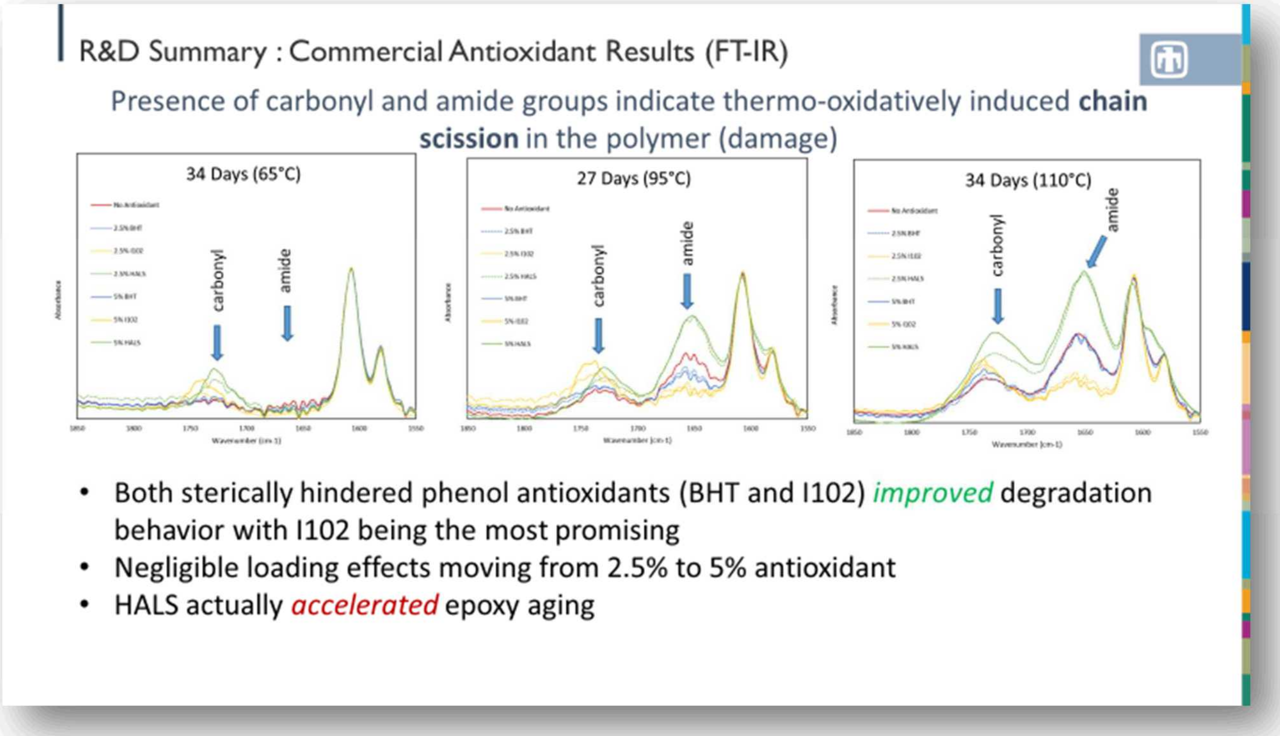
Network Structure : Resin + **Grafted** Additives

●	Un-Graftable Additive		Resin
	Graftable Additive		Curing Agent



R&D Summary : Commercial Antioxidant Results (DSC)

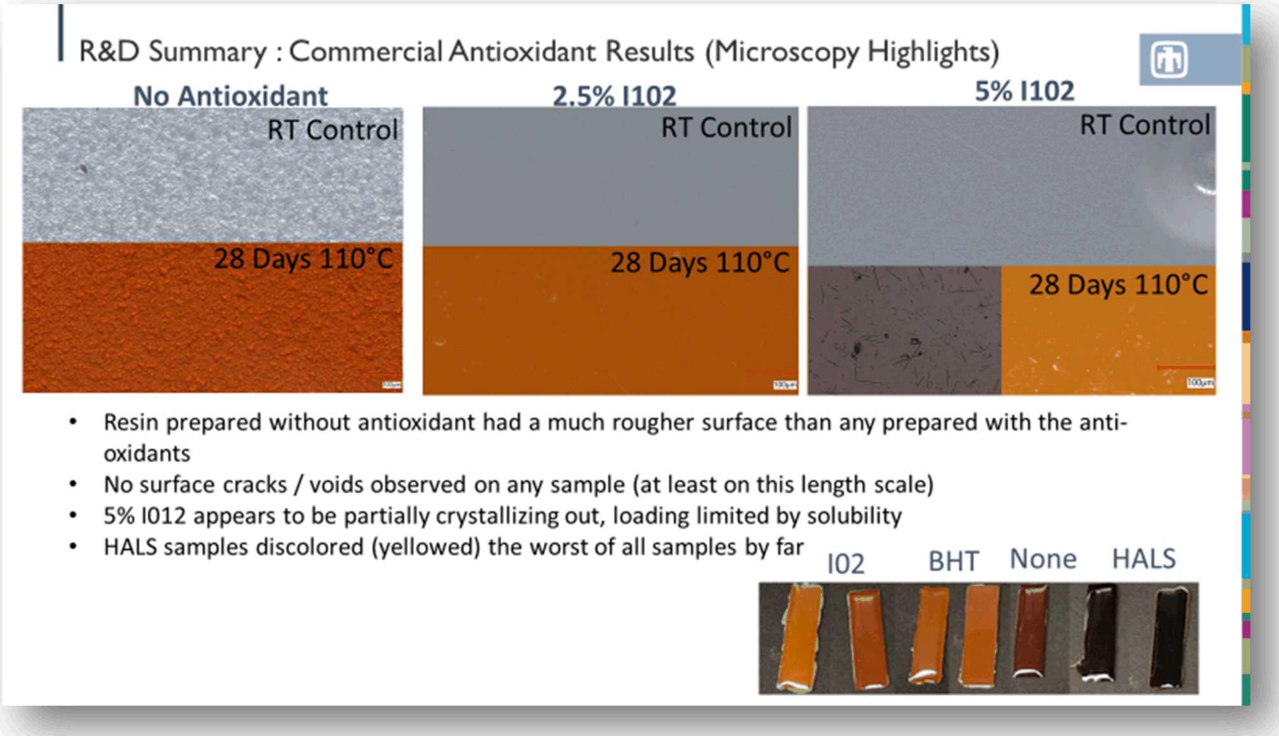
- Plasticization (lower Tg) moving from 2.5% to 5% antioxidant in all samples
- Lower Tg values with aging due to thermo-oxidatively induced chain scission (damage) in polymer
- I102 shows less reduction in Tg than control or other antioxidant samples, suggesting it is the best preforming antioxidant
- Missing time points needed to say anything more conclusive



R&D Summary : Commercial Antioxidant Results (FT-IR)

Presence of carbonyl and amide groups indicate thermo-oxidatively induced **chain scission** in the polymer (damage)

- Both sterically hindered phenol antioxidants (BHT and I102) *improved* degradation behavior with I102 being the most promising
- Negligible loading effects moving from 2.5% to 5% antioxidant
- HALS actually *accelerated* epoxy aging

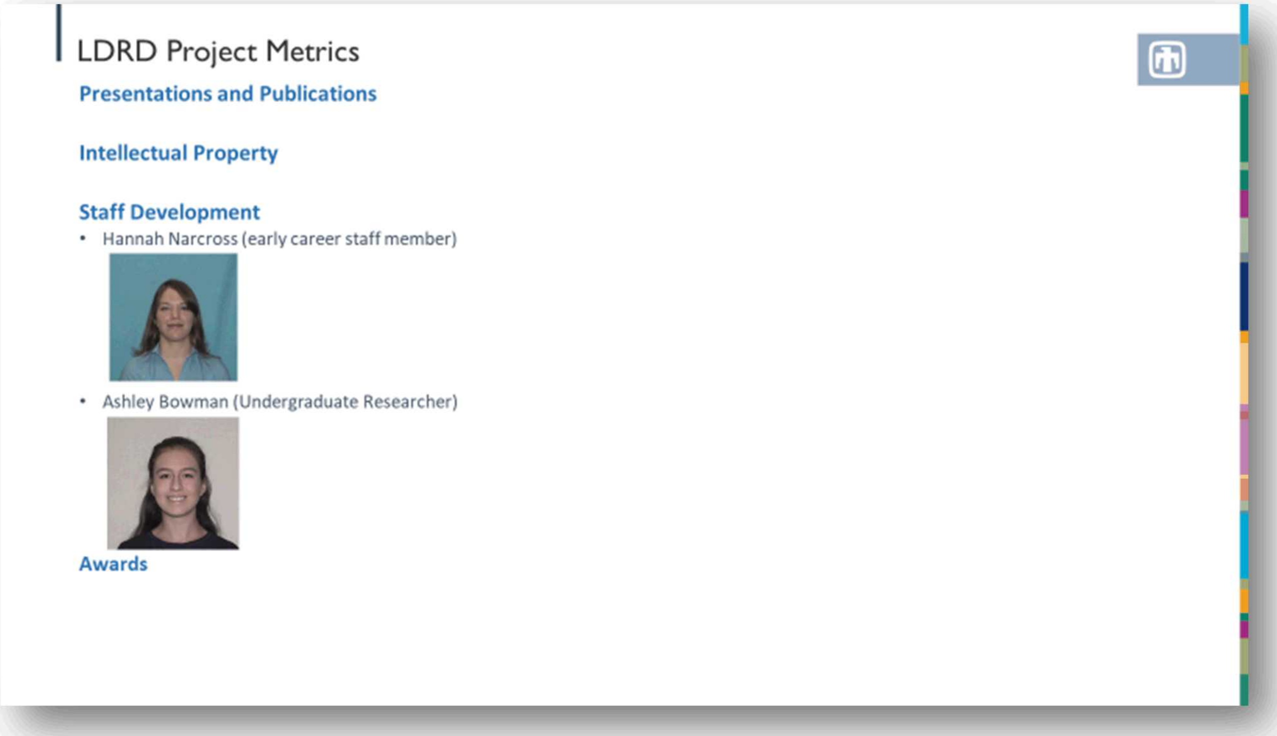


R&D Summary : Commercial Antioxidant Results (Microscopy Highlights)

- Resin prepared without antioxidant had a much rougher surface than any prepared with the anti-oxidants
- No surface cracks / voids observed on any sample (at least on this length scale)
- 5% I012 appears to be partially crystallizing out, loading limited by solubility
- HALS samples discolored (yellowed) the worst of all samples by far

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS



LDRD Project Metrics

Presentations and Publications

Intellectual Property

Staff Development

- Hannah Narcross (early career staff member)
- Ashley Bowman (Undergraduate Researcher)

Awards