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## Preparation and Detection of Degradation and Chain Scission Events In Epoxy-Amine Networks Using a Profluorescent Nitroxide Probe

Kylee F. Fazende  
*University of Southern Mississippi*

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THE UNIVERSITY OF SOUTHERN MISSISSIPPI

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**PREPARATION AND DETECTION OF DEGRADATION AND  
CHAIN SCISSION EVENTS IN  
EPOXY-AMINE NETWORKS USING A PROFLUORESCENT  
NITROXIDE PROBE**

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BY

KYLEE FAZENDE

A THESIS  
SUBMITTED TO THE HONORS COLLEGE OF  
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
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IN THE SCHOOL OF POLYMERS AND HIGH PERFORMANCE MATERIALS

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Approved by

---

James W. Rawlins  
Associate Professor  
School of Polymers and High Performance Materials

---

Robert Y. Lochhead, Director  
School of Polymers and High Performance Materials

---

David R. Davies, Dean  
Honors College

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**ABSTRACT**

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Thermosetting polymers comprise a significant part of polymer research that is in progress today because thermosets are especially critical in the field of aerospace composites. In this context the proposed research project is designed to develop a novel method to detect and quantify chain scission and thermal degradation of matrix materials using profluorescent nitroxide probes as well as, to study the interaction of the thermoset with its environment during utilization and property degradation. Acquisition of this knowledge will allow for a better understanding of early, i.e., premacroscopic, thermoset degradation and to establish whether these early events are predictive of material lifetimes during real applications.

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## CHAPTER I. INTRODUCTION

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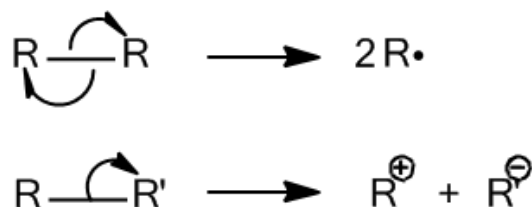
### *1.1 INTRODUCTION*

Polymers are classified in a variety of ways; one such classification divides polymers into thermoplastics and thermosets. The difference between thermosets and thermoplastics originates from the unique molecular structure of thermosets known as crosslinking. The degree of crosslinking, i.e., the extent to which polymer chains are connected with each other to create a network, governs the structure of a thermoset polymer, which in turn strongly influences the polymer properties. As crosslinking increases, the density of the connected polymer network increases, the mobility of the polymer chains decreases, and the polymer glass transition temperature ( $T_g$ ) increases.<sup>1</sup> The  $T_g$  is the temperature at which a polymer structure gains enough mobility to transition from a rigid glass to a soft, rubbery material.<sup>1</sup> The  $T_g$  is a property unique to polymers that, more so than any other property, determines whether a polymer is suitable for a given application. While thermosets lose their rigidity above  $T_g$ , they do not flow like thermoplastics because of their infinite molecular weight network, a characteristic unique to thermoset networks.<sup>1</sup>

Thermoset polymers are found in a variety of products such as coatings, adhesives, and composite resins.<sup>1</sup> Prior to complete crosslinking and cure, thermosetting systems can be set into a desired shape for a specific function. Once a thermoset network is cured however, it cannot be reshaped without destroying or degrading the network integrity.<sup>1</sup> In this study, we will employ one of the most commonly used thermoset resins, i.e., epoxy-amine resins.

## 1.2 DEGRADATION IN THERMOSET NETWORKS

By definition, polymer degradation includes both chemical and physical changes to the polymer network.<sup>2</sup> Degradation can be induced in several ways: physically (mechanically), thermally, or chemically, i.e. exposure to an organic solvent or corrosive material. Physical degradation can occur in a variety of ways, all of which involve the breakage of chemical bonds.<sup>2</sup> Motyakin *et al.* showed that thermal degradation causes relatively homogenous degradation within an entire polymer sample whereas other forms of degradation can be localized within a polymer sample.<sup>3</sup> Schlick *et al.* observed that an oxygen atmosphere increases the rate of sample degradation specific to the surface during elevated thermal temperatures.<sup>4</sup> Generically, shown in Scheme 1.1, chemical bonds can be produced and broken in two ways, i.e., homolytic bond cleavage (also called chain scission) that creates radical species in the polymer sample or heterolytic bond cleavage that creates ion species.<sup>1</sup>



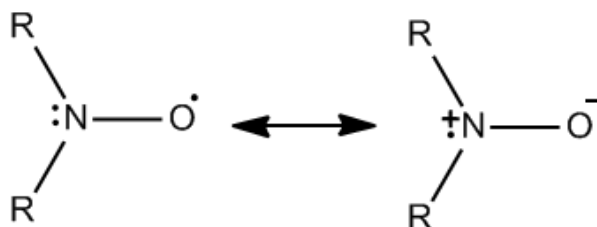
Scheme 1.1. Homolytic (top) and heterolytic (bottom) bond cleavage.

While macroscopic damage to a thermoset network can be detected using a variety of methods, there are no reports of an accurate and efficient method to detect damage at a molecular level with the exception of EPR.<sup>5</sup> However, carbon-centered radicals created by homolytic bond cleavage of the thermoset polymer's backbone enable polymer degradation to be detected at the molecular level by the use of radical probes.<sup>6,7</sup>



### 1.3 NITROXIDES AS RADICAL PROBES

A particularly useful radical for probe purposes is the nitroxyl radical because nitroxides are excellent radical scavengers. The resonance structures of a nitroxide are shown in Scheme 1.2.



Scheme 1.2. Resonance structures of a nitroxide.

Nitroxides are divided into four basic classes depending on the molecule from which they are derived.<sup>2</sup> Figure 1.1 shows the four base molecules: non-cyclic di-tert-butyl nitroxide (1); 2,2,5,5-tetramethylpyrrolidin-1-yloxy (2); 2,2,5,5-tetramethylpiperdin-1-yl-oxy (3); and 1,1,3,3-tetramethylisindoline-2-yloxy (4). Nitroxides derived from **4**, known as isoindoline nitroxides, tend to be more stable than other types of nitroxides.<sup>2</sup>

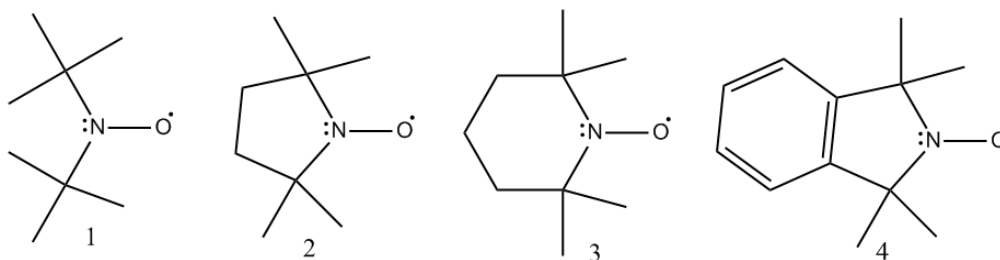
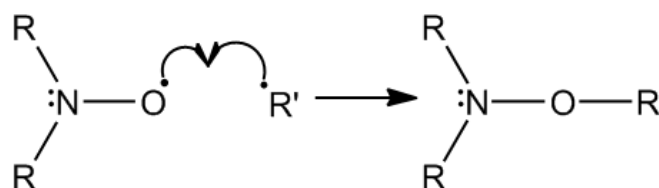


Figure 1.1. Base nitroxide molecules.

Though nitroxides will react with oxygen-centered radicals, stable reaction products are generated only when nitroxides react with carbon-centered radicals.<sup>8</sup> The ability to create stable alkoxyamine species (Scheme 1.3) with carbon-centered radicals is

the reason why nitroxides are excellent radical scavengers and are commonly used as hindered amine light stabilizers (HALS) in coatings.<sup>9, 10</sup> The process by which nitroxide radicals react with radical degradation products is known as the Denisov cycle.<sup>11</sup> A nitroxide radical will only enter the Denisov cycle when presented with a radical caused by some type of degradation or physical damage to the network.



Scheme 1.3. Alkoxyamine formation.

Another important characteristic of nitroxides is their paramagnetism.

Paramagnetism is the property of a molecule that causes it to be susceptible to magnetism and is caused, in the case of the nitroxide, by the unpaired electron.<sup>2</sup> Nitroxide paramagnetism offers two important advantages: a) nitroxides can be detected via electron paramagnetic resonance spectroscopy (EPR),<sup>12, 13</sup> and b) nitroxides can quench excited state fluorescence in fluorophores.<sup>14, 15, 16</sup> If a nitroxide contains a fluorophore, the fluorophore will only fluoresce after the nitroxide has scavenged a radical and created an alkoxyamine because the molecule becomes diamagnetic, and fluorescence can be detected.<sup>17</sup>

#### 1.4 PROFLUORESCENT NITROXIDES

Nitroxides coupled with a fluorophore for indicating the presence of radicals are known as profluorescent nitroxides (PFN). Bottle and colleagues have shown that PFN, specifically isoindoline PFN, are useful in indicating degradation in polypropylene.<sup>6, 9, 18</sup>

The success of using PFN in polypropylene has led to other investigations of the application of PFN, including this study on the use of PFN in thermoset networks.

As previously stated, isoindoline nitroxides are typically more stable than other types of nitroxides; such stability ensures that the addition of an isoindoline nitroxide as a probe would not interfere with the degradation process experienced by the epoxy-amine network. Consequently, the isoindoline nitroxide 10-(phenylethynyl)-9-(1,1,3,3-tetramethylisoindolin-2-yl)oxy-5-ethynylanthracene (TEPEA, Figure 1.2) was chosen for this research. TEPEA was first developed by Fairfull-Smith *et al.* in 2008 and is now available commercially.<sup>19</sup>

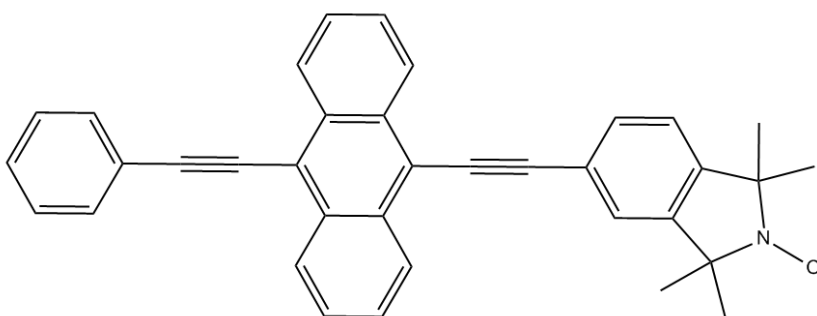


Figure 1.2. TEPEA.

Bottle *et al.* employed less than 0.1% w/w of PFN in testing thermal oxidative degradation in polypropylene.<sup>6</sup> No reports were found that discuss the use of TEPEA (or any other PFN) in an epoxy-amine system to monitor degradation. It is believed that in thermoset (specifically epoxy-amine) networks, homolytic chain scission events occur during macroscopic fracture and that chain scission can be exacerbated by thermal or chemical degradation; such chain scission could potentially be captured and detected by a profluorescent nitroxide probe (TEPEA).

## CHAPTER II. GOALS AND OBJECTIVES

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### *2.1 RESEARCH GOALS*

This study will probe three questions not studied extensively in current literature:

- 1) What is the effect of an oxygen atmosphere on the degradation and chain scission processes in a thermoset network?
- 2) What degradation conditions are most useful and consistent for TEPEA to indicate homolytic chain scission in the thermoset network?
- 3) Does solvent swelling have an effect on the mobility and reactivity of the TEPEA in a degraded network?

Answering these three questions will provide new insights into the degradation processes of thermoset networks and enable the understanding of how thermoset networks must be treated throughout their lifetime for maximum lifespan and effectiveness in use.

## CHAPTER III. EXPERIMENTAL

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### 3.1 INTRODUCTION

An epoxy-amine system based on diglycidyl ether of bisphenol-A (DGEBA), specifically Epon 828, and 2-methylpentane-1,5-diamine (MPMD) was chosen for this study. Figure 3.1 shows the molecular structures of Epon 828 and MPMD.

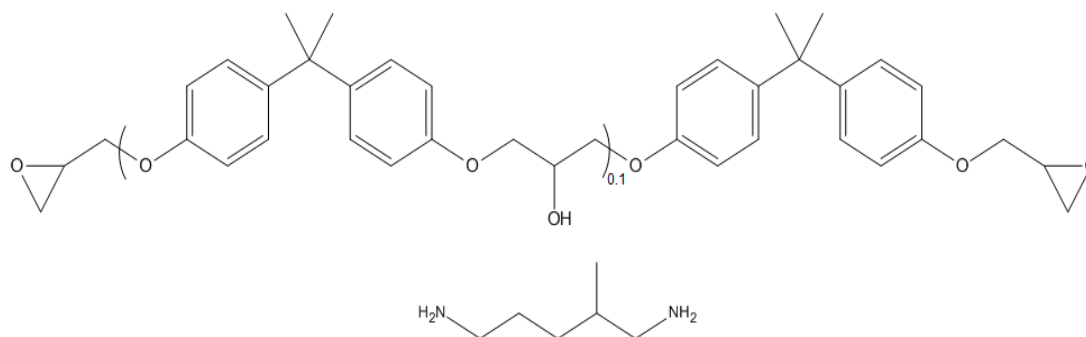


Figure 3.1. Epon 828 (top) and MPMD (bottom)

Epon 828, supplied by Momentive, is a 185 g/mol functional weight epoxy resin with a molecular weight of 380 g/mol.<sup>20</sup> The difunctional amine, MPMD, is supplied by TCI America. TEPEA was procured from SpinFX Probes of Australia—TEPEA is sold as Monofairoxyldiylne. The following methods were employed to evaluate the utility of TEPEA in indicating homolytic bond cleavage in epoxy-amine systems.

### 3.2 EPOXY SYNTHESIS AND PREPARATION

Prior to synthesis, Epon 828 was heated to 90 °C in a vacuum oven and degassed before use. The epoxy-amine system was formulated to stoichiometric equivalency and 0.005% w/w concentration of TEPEA. Table 3.1 lists the formulation weights (Appendix A details the calculations for the formulation).

**Table 3.1. Epoxy-amine Formulation**

<b>Reagent</b>	<b>Amount (g)</b>
Epon 828	5.95
MPMD	0.978
TEPEA	0.000346

TEPEA was incorporated in the form of its solution in acetonitrile (supplied by Fisher Scientific); calculations for the solution are in Appendix B. To formulate the epoxy-TEPEA blend, 1.0 mL of the TEPEA solution was added to 5.95 g of Epon 828 and mixed in the Flacktek<sup>®</sup> speed mixer at 1,700 rpm for two minutes to ensure even distribution of TEPEA into the epoxy. The epoxy-TEPEA blend was then heated to 85 °C for 24 hours to drive off the acetonitrile. All acetonitrile must be driven off before the MPMD can be added to begin the polymerization. Once it was ensured that no more acetonitrile was present in the epoxy, 0.978 g of MPMD was added to the epoxy-TEPEA blend and mixed in the Flacktek speed mixer for five minutes at 1,700 rpm. The epoxy-amine system was then centrifuged at 46,000 xg for four minutes to remove all the bubbles that entered the system during the mixing process. The epoxy-amine system was cast via a syringe injection pump into pre-made silicone molds in the form of eight bars (20 mm x 6 mm x 0.5 mm). The epoxy-amine is injected at 0.03 mL/min for three hours, covered with aluminum foil, and allowed to cure for 24 hours. The injection set up is seen below in Figure 3.2. As can be seen in the image four needles are used to inject the eight samples. A schematic of each injection site into the mold is seen in Figure 3.3.

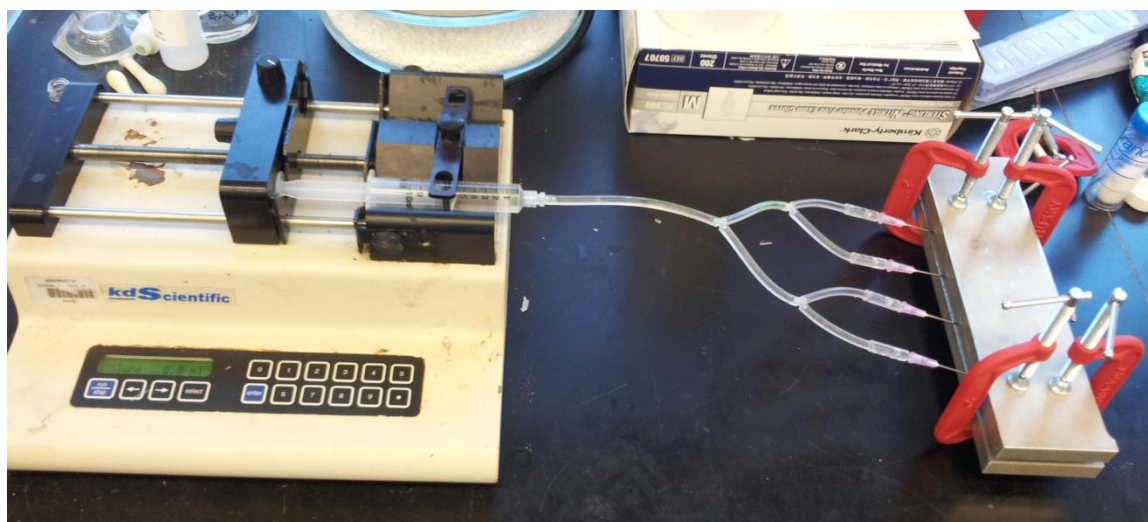


Figure 3.2. Injection pump set up for sample casting.

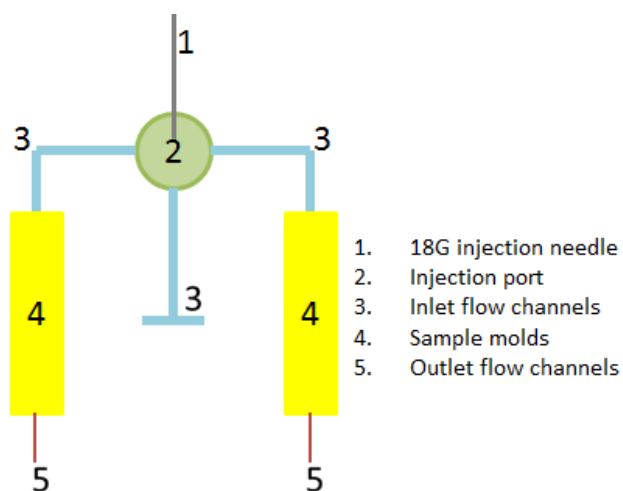


Figure 3.3 Sample injection flow and mold.

The bars were then cured for one hour at 60 °C followed by post-cure for two hours at 120 °C. (The cure and post-cure times do not include the twenty-five minute temperature equilibration times, so the full times are eighty-five and 145 minutes, respectively.) The bars were removed from oven, weighed on an analytical balance, and placed into labeled containers for baseline characterization and conditioning.

### 3.3 SAMPLE CHARACTERIZATION AND CONDITIONING

The samples were analyzed on the TECAN<sup>®</sup> Infinite M1000 UV/Vis fluorimeter at the optimal excitation/emission wavelengths (bandwidth of 5 nm) for TEPEA, i.e., 440 nm and 486 nm, respectively. The fluorimeter was set to 10 flashes (scans) from a z position of 20,000  $\mu\text{m}$  and a gain of 70 during fluorescence intensity testing. The fluorescence intensities were documented as initial (baseline) fluorescence. Table 3.2 indicates the conditions to which the samples were exposed.

**Table 3.2. Annealing Conditions**

<b>Condition Number</b>	<b>Condition</b>
A	Ambient atmosphere annealing at 135 °C (24 hours)
B	Ambient atmosphere annealing at 135 °C (48 hours)
C	Ambient atmosphere annealing at 135 °C (72 hours)
D	Nitrogen atmosphere annealing at 135 °C (24 hours)
E	Nitrogen atmosphere annealing at 135 °C (48 hours)
F	Nitrogen atmosphere annealing at 135 °C (72 hours)
G	Control (No conditioning)

After annealing, the samples were removed from the oven, cooled to ambient temperature, and analyzed again with the TECAN fluorimeter. The non-conditioned control samples were re-evaluated every 24 hours to determine any variation in fluorescence upon storage at ambient conditions.

### 3.4 SOLVENT SWELLING

For solvent conditioning, each sample was placed in its respective vial with 5 mL of acetonitrile for one hour after thermal annealing. The samples were then placed under



vacuum for 24 hours to remove excess acetonitrile. Subsequently, each sample was analyzed again using the aforementioned TECAN fluorimeter settings to note any changes in fluorescence.

### 3.5 SAFETY

A review of the Material Safety Data Sheets of the materials used in this research indicated that the largest health hazard lay in the use of solvents and amines. Therefore, the handling of acetonitrile and MPMD was restricted to the confines of a fume hood. Any unused solvent was disposed of as hazardous organic waste. Solid epoxy samples not considered to be an environmental hazard were disposed of accordingly.

## CHAPTER IV. RESULTS AND CONCLUSIONS

### 4.1 SAMPLE ANNEALING

Due to slight variance in dimensions between sample sets, fluorescence intensity ( $\Delta I$ ) values were normalized to the change in intensity for each sample as seen below.

$$\Delta I = I_{final} - I_{initial}$$

Such normalization allows for comparison between samples of various sets and under different conditions. The annealing results for ambient atmosphere, nitrogen atmosphere, and control samples are seen below in in Figures 4.1, 4.2, and 4.3, respectively.

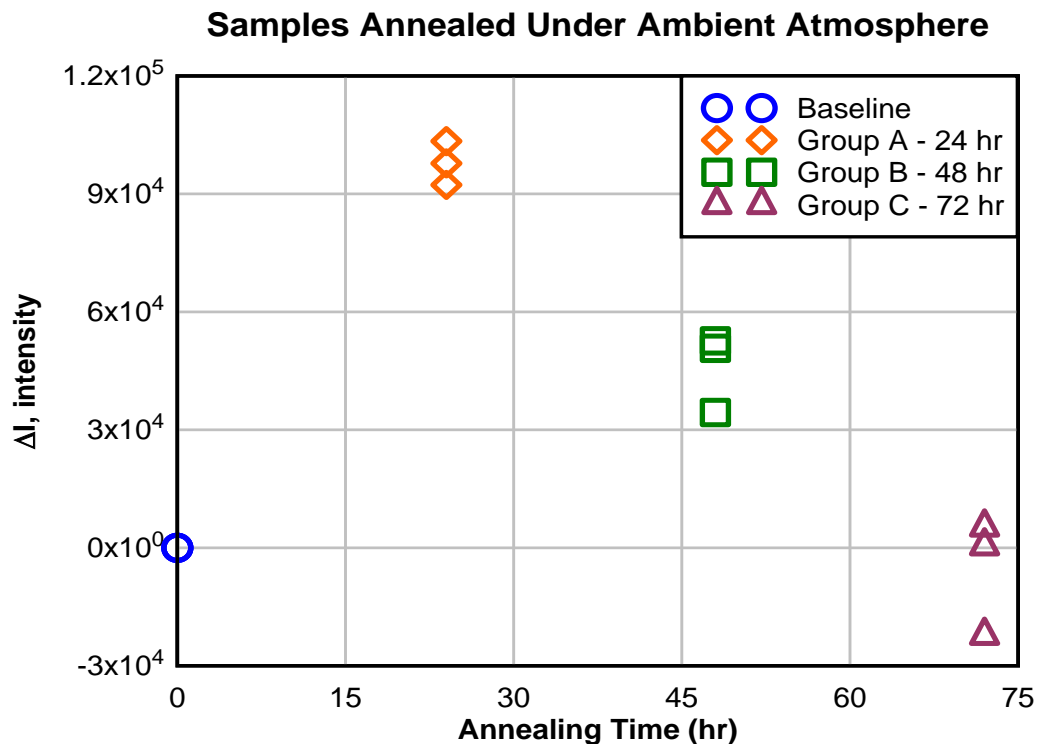


Figure 4.1. Ambient atmosphere annealing fluorescence intensities.

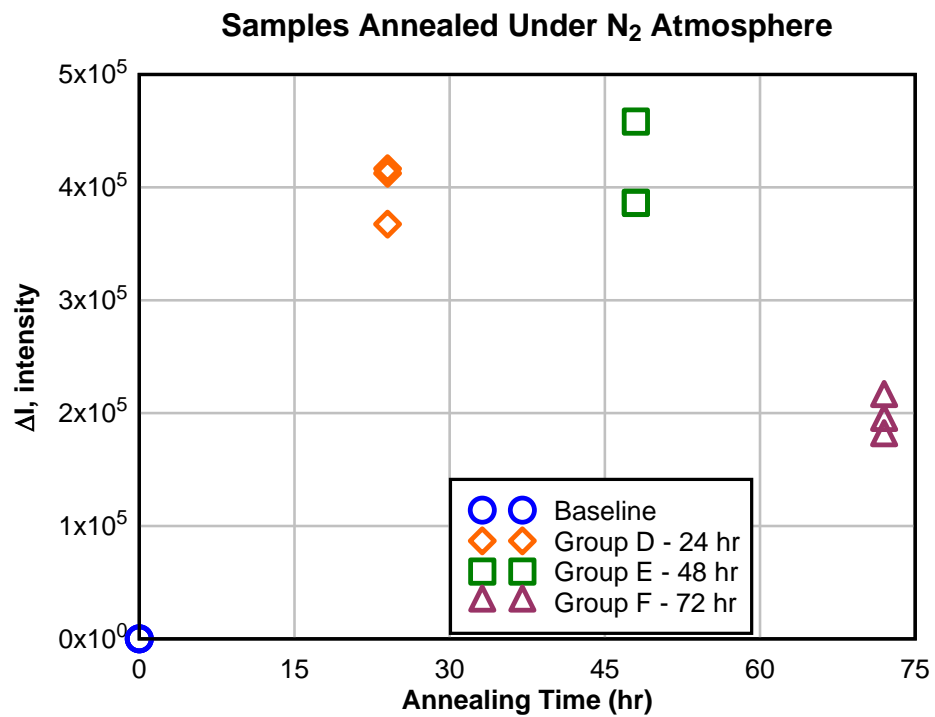


Figure 4.2. Nitrogen atmosphere annealing fluorescence intensities.

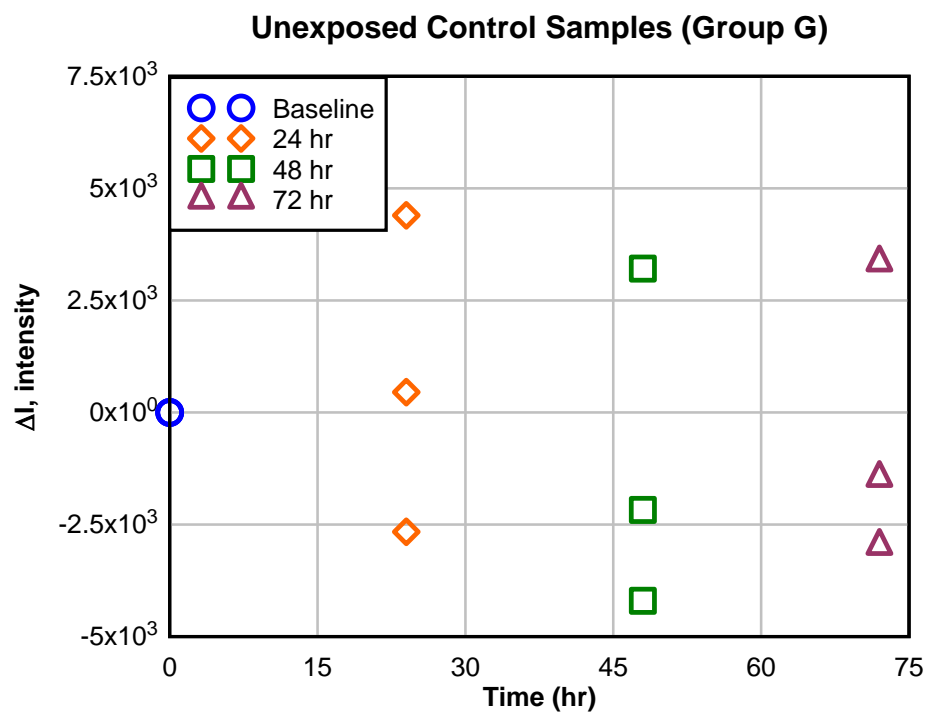


Figure 4.3. Control sample fluorescence intensities.

Figures 4.1 and 4.2 indicate that fluorescence intensity decreased with continued exposure at 135 °C. The initial increase in fluorescence intensities at 24 hours indicates that high temperature causes degradation and bond cleavage in epoxy networks. However, the decrease in  $\Delta I$  as exposure time increases suggests the presence of a second mechanism. The greater changes and steeper slope of the ambient atmosphere data suggests that the aforementioned mechanism is exacerbated by the presence of oxygen. One possibility is the degradation of the TEPEA molecule itself. Exposure to high temperature could cause a change in the electron density of the fluorescent tail and thus affect the fluorescent response of the molecule. Also, thermo-oxidative degradation is known to cause a darkening of color in epoxy samples, and it is expected that such a color change would interfere with fluorescence intensity.

Appendix B shows photographs of the samples soon after they were removed from the oven and the drastic difference in color is apparent. The nitrogen atmosphere samples initially appeared slightly green, which is indicative of the higher fluorescence intensity. The ambient atmosphere samples darkened and changed from clear to brown with increasing exposure at 135 °C. The color change limits the usefulness of TEPEA as an indicator of thermo-oxidative degradation in this system.

The control samples, shown in Figure 4.3, exhibited wide variations in intensity and did not present a clear trend of increase or decrease in  $\Delta I$ . The oxygen content of ambient atmosphere could also affect the sample fluorescence intensity. The similarity of the shape of the each sample's respective plot would seem to indicate that all three samples were exhibiting the same response to the atmosphere even if that response did not show a noticeable trend in relation to the changing intensity.

## 4.2 SOLVENT SWELLING

Figures 4.4, 4.5, and 4.6 show the change in fluorescence intensity of the 24, 48, and 72 hour samples, respectively, after solvent conditioning.

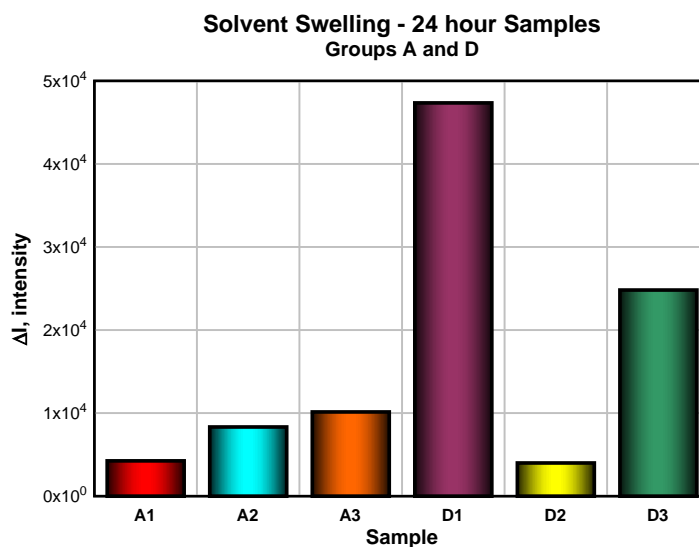


Figure 4.4. Intensity change: 24 hour samples.

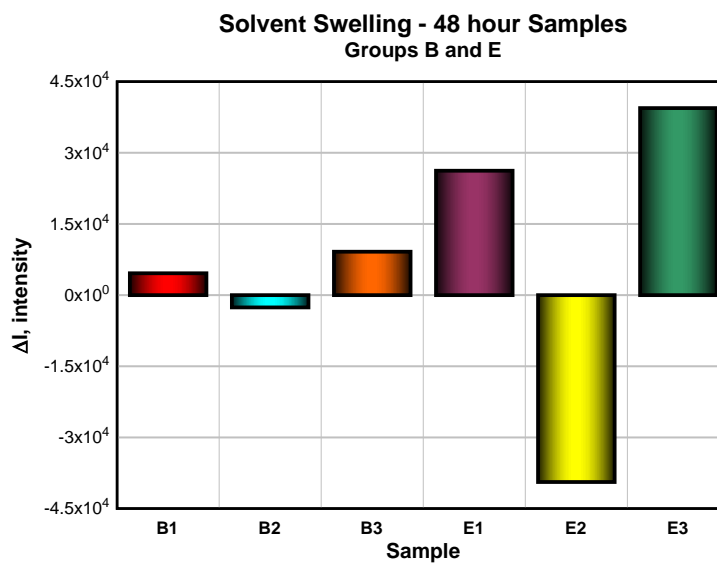


Figure 4.5. Intensity change: 48 hour samples.

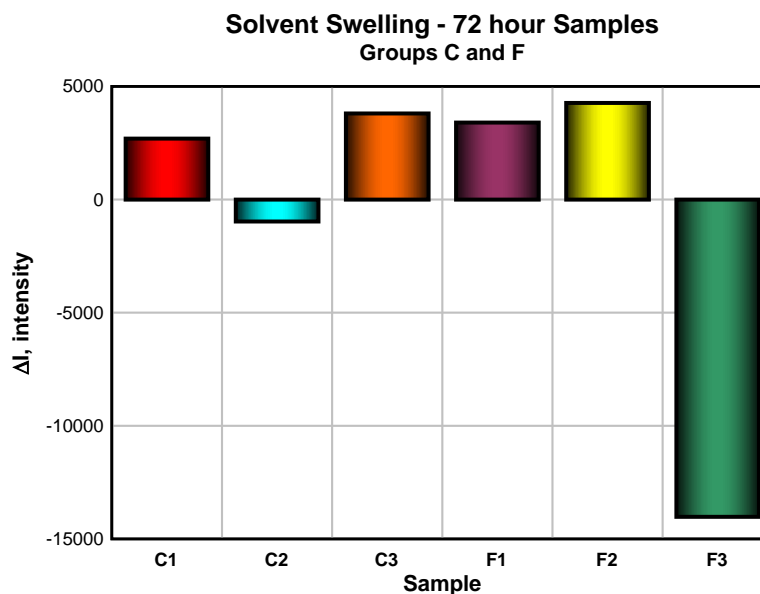


Figure 4.6. Intensity change: 72 hour samples.

Solvent swelling increased the fluorescence intensity in ~ 78% of the samples, most likely due to increased mobility of the TEPEA molecules upon swelling. It is critical to note, however, that just TEPEA mobility is not what increases fluorescence, but rather the increased likelihood that TEPEA will encounter a radical with which it can react and thus fluoresce. Swelling increased the  $\Delta I$  values in all the 24 hour samples, while two samples in each of the 48 and 72 hour sets showed a decrease. Because samples in both the nitrogen and ambient atmosphere showed a fluorescence decrease after swelling, it would seem that whatever caused the decrease in fluorescence intensity is a fundamental aspect of the epoxy network. The increased crosslinking resulting from annealing at 135 °C is expected to limit the ability of the TEPEA to move in the solvent swollen samples.

## CHAPTER V. CONCLUSIONS

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The effectiveness of TEPEA as an indicator of thermal degradation decreases with increased exposure to high temperatures. Color changes caused by degradation in the epoxy network render fluorescence spectroscopy and PFN ineffective in establishing the extent of network degradation. Degradation in an ambient atmosphere occurs more rapidly than in an inert (nitrogen) atmosphere. Solvent swelling increases TEPEA mobility and thus increases the propensity for the TEPEA to encounter a radical within the polymer network with which to react and cause an increase in fluorescence intensity but such an increase is less evident as samples are exposed to higher temperatures.

## CHAPTER VI. FUTURE WORK

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Additional studies are recommended in the areas of exposure at ambient conditions, inert atmosphere as well as high temperature. Also, other thermoset networks need to be employed at high temperatures to determine if other network chemistries are more conducive to the use of TEPEA for the indication of high temperature degradation. Studies into TEPEA diffusion within the network would also be pertinent to gain a complete understanding of the usefulness of this indicator in thermoset networks.



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 APPENDIX A
 

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## FORMULATION CALCULATIONS

Note: Due to constants used in Mathcad 15, the unit of gram is abbreviated “gm” not “g”.

$$\text{epon}_{\text{wt}} := 5.95 \text{ gm} \quad \text{mpmd}_{\text{wt}} := \frac{5.95 \text{ gm}}{185 \frac{\text{gm}}{\text{mol}}} \cdot 1.05 \cdot 29 \frac{\text{gm}}{\text{mol}} = 0.98 \cdot \text{gm}$$

$$\frac{\text{tepea}_{\text{wt}}}{\text{epon}_{\text{wt}} + \text{mpmd}_{\text{wt}} + \text{tepea}_{\text{wt}}} \cdot 100 = 0.005$$

$$\text{tepea} := 0.00005 \cdot \text{epon}_{\text{wt}} + 0.00005 \cdot \text{mpmd}_{\text{wt}} = 0.35 \cdot \text{mg}$$

$$\text{total}_{\text{tepea}} := \text{epon}_{\text{wt}} + \text{mpmd}_{\text{wt}} + \text{tepea} = 6.93 \cdot \text{gm}$$

$$\text{percent}_{\text{tepea}} := \frac{\text{tepea}}{\text{total}_{\text{tepea}}} \cdot 100 = 0.005$$

$$\text{tepea}_{\text{sln}} := \text{tepea} \cdot 10 = 3.46 \cdot \text{mg}$$

$$\text{sln}_{\text{conc}} := \frac{\text{tepea}_{\text{sln}}}{10 \text{ mL}} = 0.35 \cdot \frac{\text{mg}}{\text{mL}}$$

**APPENDIX B**

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*SAMPLE PHOTOGRAPHS*