8-2019

Investigation of Environmental Degradation of Plastic Scintillators

Matthew Loyd

University of Tennessee, mloyd1@vols.utk.edu

Follow this and additional works at: https://trace.tennessee.edu/utk_graddiss

Recommended Citation

https://trace.tennessee.edu/utk_graddiss/5660

This Dissertation is brought to you for free and open access by the Graduate School at Trace: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of Trace: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.
Investigation of Environmental Degradation of Plastic Scintillators

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Matthew Starr Loyd
August 2019
Acknowledgements

The work presented in this dissertation is not only my work, but a result of a collaboration of effort by many people, who I would like to thank here. First and foremost, I would like to thank my advisors Dr. Mariya Zhuravleva and Dr. Charles L. Melcher, who have guided me since my start at the SMRC and have also been extremely patient with me. This includes Merry Koschan, who has personally improved my writing and presenting style, as well as offering wonderful suggestions on how to lead my research. I would also like to thank Dr. Jason Hayward, Dr. Roberto Benson, and Dr. Michael Lance for taking time to be on my committee and offering support and expertise. I would not have been able to accomplish this without the teachings of my lab mentors and friends Adam Lindsey, Luis Stand, and Yuntao Wu. I would also like to thank Camera Foster for being my colleague and friend for eight years. Additionally, this work was finished in a timely manner due to assistance from students Daniel Rutstrom, Cordell Delzer, Josh Smith, Jessee Johnson, Eleanor Comer, and Kaycee Gass. I would especially like to thank my partner in crime for this project, Matheus Pianassola. The lab would not be able to operate without the amazing help of Doug, who makes stuff, and Frank and Randy, who get stuff. I would also like to thank the ladies of the Ferris office: Tracy, Tonya, Ashley, and Carla, and the wonderful support from department mentors Dr. Claudia Rawn, Dr. David Keffer, and Dr. Chris Wetteland.

None of this would be possible without the incredible support from my parents, who worked hard to ensure I would have this opportunity, and my brother and sister, for keeping me grounded and always being my friends. Additionally, I would like to thank my in-laws for making their house a home for me here in Knoxville. Finally, I would like to thank my wife Sydney for being my best friend and putting up with my late night and weekends at the lab and providing me with motivation to work hard and persevere.

This work has been supported by the US Department of Homeland Security, Domestic Nuclear Detection Office, under competitively awarded grant #2017-DN-077-ER0002. This support does not constitute an expressed or implied endorsement on the part of the Government.
Abstract

Scintillators are a class of materials that are used as radiation sensors and are especially useful in national security applications. Plastic scintillator detectors are often deployed due to their availability, relatively low cost, and the ability to be cast in large sizes. In recent years it has been discovered that plastics deployed in high-humidity environments will absorb water, especially at high temperatures. When cooled, this water creates defects in the plastic that scatter light and increase maintenance costs, and often require replacement of the detectors.

In this research, we have investigated fogging by examining both fresh and field-aged PVT and PS-based scintillators. We have developed protocols for producing temporary and permanent fogging using both liquid water and high-humidity environments combined with temperature cycling. Important properties of fogging have been discovered, such as the correlation between cooling rates and defect size. Temporary defects have also been shown to appear in the same location during multiple cycles, confirming a permanent deformation in the plastic. Optical transmission and photoluminescence measurements revealed that fogging does not affect the scintillation mechanism, but merely increases light scattering in the plastic. PS-based compositions are slightly more fog-resistant but perform worse after aging. New compositions produced and provided by collaborators have been testing using an accelerated aging test. Scintillation measurements were taken on the plastics before, after, and during the test to better understand how aging reduces scintillation performance.
# Table of Contents

Chapter 1 Introduction ........................................................................................................ 1  
  1.1 Radiation Detection .................................................................................................... 1  
  1.2 Scintillators ................................................................................................................ 1  
  1.3 Plastic Scintillators ..................................................................................................... 5  
    1.3.1 Properties ............................................................................................................. 5  
    1.3.2 Production ........................................................................................................... 8  
    1.3.3 Practicalities ....................................................................................................... 11  
Chapter 2 Fogging in Plastic Scintillators ........................................................................... 14  
  2.1 The Problem ................................................................................................................ 14  
  2.2. Consecutive Efforts ................................................................................................. 16  
  2.3 Gaps in Current Knowledge ..................................................................................... 16  
  2.4 Goals and Objectives ............................................................................................... 23  
Chapter 3 Properties of Fogging ......................................................................................... 24  
  3.1 Experimental ............................................................................................................ 24  
    3.1.1 Materials ........................................................................................................... 24  
    3.1.2 Methods ........................................................................................................... 27  
  3.2 Results ...................................................................................................................... 29  
    3.2.1 Materials Properties ......................................................................................... 29  
    3.2.2 Producing Fogging ......................................................................................... 33  
  3.3 Conclusions .............................................................................................................. 41  
Chapter 4 New Compositions .............................................................................................. 47  
  4.1 Experimental ............................................................................................................ 47  
    4.1.1 Materials ........................................................................................................... 47  
    4.1.2 Methods ........................................................................................................... 47  
  4.2 Results ...................................................................................................................... 51  
    4.2.1 LLNL/Eljen Compositions .............................................................................. 51  
    4.2.2 Triton-X Compositions .................................................................................. 60  
  4.3 Multiple Cycling ....................................................................................................... 68  
  4.4 Conclusions .............................................................................................................. 75  
Chapter 5 Fogging Kinetics ................................................................................................. 76
5.1 Diffusion of Water in Plastics

5.1.1 Introduction

5.1.2 Modeling Diffusion

5.2 Experimental

5.3 Results

5.4 Conclusions

Chapter 6 Temperature Dependence of Luminescence

6.1 Experimental

6.2 Results

6.3 Conclusions

Chapter 7 Conclusions

7.1 Fogging in Plastic Scintillators

7.2 New Compositions

7.3 Fogging Kinetics

7.4 Temperature Dependence of Luminescence

7.5 Novel Contributions

7.6 Future Work

List of References

Vita
List of Tables

Table 1. Physical Properties of Polyvinyl Toluene and Polystyrene. Asterisks denote values that were calculated in this research. .................................................................................................................................................. 10
Table 2. Common additives for plastic scintillators............................................................................................................................................................................. 12
Table 3. A summary of all experimental parameters used for accelerated aging of plastic samples. ........................................................................................................................................................................... 30
Table 4. Measured $T_g$ values for each sample using two different DSCs and the DMA. ............ 36
Table 5. New Compositions tested in this Chapter ............................................................................. 48
Table 6. Samples’ mass gain and fogging status after saturation and cooling (stage 2). ............ 52
Table 7. Mass change of the Triton-X samples and EJ-200 after soaking in water for 60 days ... 65
Table 8. Compositions chosen for the multiple cycling experiment. ............................................. 71
Table 9. Density of water in different saturated plastics and air at various relative humidities at 55 °C. ........................................................................................................................................................................ 79
Table 10. Activity of H3 water and expected activity in the saturated sample......................... 84
List of Figures

Figure 1. Radiation portal monitor (white panel in yellow casing) [4]. ........................................ 2
Figure 2. A scintillator mated to a photomultiplier tube (PMT). .................................................. 4
Figure 3. A pulse height spectrum from NaI:Tl irradiated by $^{137}$Cs [3]. ............................... 6
Figure 4. Jablonski diagram showing different processes in organic scintillators: 1) Electronic
transition due to ionization; 2) Relaxation due to thermal vibrations; 3) Internal conversion; 4)
Intersystem crossing; 5) Radiative transition (emission); 6) Non-radiative transmission [10]. ... 7
Figure 5. Molecular composition of PVT (left) and PS (right) monomers [20, 21] . .................... 9
Figure 6. A typical $^{137}$Cs spectrum collected with a plastic scintillator. The peak is the Compton
edge maximum. No photopeak is present .................................................................................. 13
Figure 7. PVT (left) and PS (right) samples that have been saturated and cooled to induce fogging
[34].............................................................................................................................................. 15
Figure 8. A permanent defect (center) in an aged PVT block .................................................... 17
Figure 9. Optical microscope image of surface crazing on a field-aged plastic scintillator.
Horizontal lines are polishing defects and were not caused by aging. ................................. 18
Figure 10. A plot of fogging temperature and water concentration in a plastic (left) with the fog-
line reproduced from experimental data (right) [39]............................................................... 19
Figure 11. Water uptake in PVT cubes with varying encapsulations. [41] ................................. 20
Figure 12. SEM images of lab produced defects in PVT (a &c) and defects in a field-aged PVT panel
(b & d). [37]................................................................................................................................. 21
Figure 13. Water concentration in a plastic as a function of temperature in four different
environments with the fog-line overlain [39]........................................................................... 22
Figure 14. Plastic materials selected for accelerated aging experiments a) field-aged block with
visible permanent defects (FA1), b) field aged detector with no visible permanent defects (FA2),
c) fresh EJ-200 (FPVT), d) new formulation (NF) ..................................................................... 25
Figure 15. Full field-aged block of PVT (FA1). A human has been included for scale .......... 26
Figure 16. Slices of FA1 for DSC measurements. Each slice is 3.5 mm thick ............................. 28
Figure 17. Micro-environmental stage placed under the optical microscope lens ................. 31
Figure 18. DSC results of FA1 slices across the sample measured with a Labsys Evo (left) and a TA
Q20 (right). There was no significant change in $T_g$ between slices measured on either DSC .... 32
Figure 19. DSC results of the four different plastics measured with a Labsys Evo (left) and a TA
Q20 (right). FA1-C describes clear sections of FA1, while FA1-D related to those that contain
defects ......................................................................................................................................... 34
Figure 20. Dynamic mechanical analysis (DMA) of FA2, NPVT, and 2 sections of FA1. ......... 35
Figure 21. FTIR absorbance spectra for FPVT, FA1-D, and FA1-C. All three spectra are extremely
similar and lack characteristic water bands in the 1000-2000 cm$^{-1}$ range ................................. 37
Figure 22. Samples before (top) and after (bottom) one cycle of the ECE. All samples except NF
developed temporary fogging ........................................................................................................ 38
Figure 23. Optical microscope images of the samples after one cycle of the ECE. Temporary
fogging defects are represented by white particles. The grid lines are 400 microns. The cloudy
appearance of the NF sample is due to the background.  

Figure 24. Photoluminescence emission recorded at a 279 nm excitation before (black curves) and after (red curves) the ECE.  

Figure 25. Optical transmission of 0.25-inch thick samples before and after the ECE.  

Figure 26. Size of fogging defects for instantly cooled (left) and slowly, 4 °C/hr, cooled (right) PVT. The inset shows the 1" cubes a few days after fogging.  

Figure 27. Optical microscope images of fogging E-VT-4 at 30 minute intervals.  

Figure 28. Optical microscopy images of FA1 after induced temporary fogging (left), 5 days after recovery (middle) and re-fogging (right). The circles and arrows connect temporary defects that appear in the same location. Surface cracks were used as a reference position in order to obtain the same focus and location of the sample after the second fogging.  

Figure 29. Temperature and humidity profile for the accelerated aging experiment. Asterisks mark times when scintillation measurements were taken. Time axis not to scale.  

Figure 30. Samples before the experiment (top), after the rapid cooling step, stage 2 (middle), and after the slow cooling step, stage 5 (bottom). Sample ID numbers are included in the top image. Cube samples are fresh EJ-200, 2 field aged samples, and PMMA, left-to-right.  

Figure 31. Pure PVT (top) and pure PS (bottom) before the experiment and after stage 2, 5, and 6, respectively. The morphology of fogging defects is dependent on cooling rate.  

Figure 32. Optical microscope images of permanent defects in PVT-1 (left), PS-2 (middle), and VT-5 (right). All images are on the same scale.  

Figure 33. N555S-7 (top) and N556S-9 (bottom) before the experiment (left) and after stage 2 (right). N556S-9 yellowed more severely than N555S-7.  

Figure 34. 137Cs gamma spectra for a) VT-5, b) N556V-8, c) N556S-9, and d) N556VS-14 at five points during the experiment.  

Figure 35. Channel number of inflection point on Compton edge (top) and the relative light yield calculated using those values (bottom) as a function of aging experiment stage.  

Figure 36. Gamma-ray spectra of a) N555S-7, b) N556S-9, c) V/M5-11, and d) N556VS-14 fresh samples and after dry annealing for 26 and 50 days. The collected spectra after stage 2 of the accelerated aging experiment are also included for reference (labeled as wet aging).  

Figure 37. 1" cube samples before (top) and after (bottom) one saturation/cooling cycle.  

Figure 38. Photoluminescence of the 1" cube samples before and after the saturation/cooling cycle. All emissions were measured with 370 nm excitation and all excitations were measured at 435 nm emission.  

Figure 39. 137Cs spectra of the 1" cube samples before and after one saturation/cooling cycle.  

Figure 40. 1-inch cube samples after the first temperature cycle.  

Figure 41. 1-inch cube samples EJ-200 and TX7-C after the first temperature cycle. The density of defects is higher in EJ-200 than in TX7-C.  

Figure 42. 1-inch cube samples after soaking in water at 50 °C in the second cycle.  

Figure 43. 1-inch cube samples after the sixth temperature cycle.  

Figure 44. The 9 samples tested in the multiple cycling experiment before (top), after 1 cycle (middle), and after 100 cycles (bottom). The three fogging compositions are EJ-200, V/M5, and
Figure 45. Optical microscope images of EJ-200 after 1 cycle (top), 43 cycles (middle), and 100 cycles (bottom).

Figure 46. Optical microscope image of TX7C.

Figure 47. Water vapor pressure (line) and density (dotted line) in air as a function of temperature. Three relative humidities are plotted: 100%, 75%, and 50%.

Figure 48. A 5-node region of width w. The concentration at each node is represented by the variable C_n.

Figure 49. Water concentration in a PVT plastic as a function of time modeled using a numerical solution to the diffusion equation.

Figure 50. Mass change for all 6 samples as a function of defogging days (left) and detail for the samples with low mass change (right).

Figure 51. Samples after defogging for 7 days (left); defogging rate shown as defogging distance to the surface as a function of days (right).

Figure 52. 1" (2.54 cm) cubes illuminated with a LED light after 30 days of defogging. Permanent defects are visible in all fogged samples.

Figure 53. Schematic representation of sample set-up in the furnace (left); defect size as a function of temperature (right). Defects change morphology from flat to 3D at ~95 °C, which is just above the glass transition temperature.

Figure 54. Optical microscope images of permanent defects after heating samples to 90 °C (left), 95 °C (center), and 155 °C (right).

Figure 55. Heating of a FA1-D sample placed on a ~200 °C hot plate. Images were taken after 0, 5, 10, and 15 minutes.

Figure 56. PMT response of a non-saturated and an H³ saturated sample of N-1-D.

Figure 57. Photoluminescence of a) EJ-200, b) TX7A, c) TX7B, and d) TX7C at 50 K (blue) and 300 K (black).

Figure 58. Photoluminescence emission of a) EJ-200, b) TX7A, c) TX7B, and d) TX7C between -30 °C and 50 °C.

Figure 59. Photoluminescence emission of TX7A (top), TX7B (middle), and TX7C (bottom) under with 370 nm excitation.

Figure 60. Radioluminescence of TX7A at temperatures between -30 and 50 °C in a linear scale (left) and logarithmic right (right).

Figure 61. Integrated intensity of radioluminescence emission for TX7A, TX7B, and TX7C (left) and intensity normalized to the 20 °C measurement (right).

Figure 62. Background subtracted and normalized radioluminescence intensity as a function of temperature. The Y-axis range was chosen as the same as that of the photoluminescence plot.

Figure 63. ¹³⁷Cs spectra of TX7B measured at 50, 300, and 323 K.
List of Attachments

Time-lapse of the growth of a fogging defect ........................................... (DefectGrowth.avi)
Time-lapse of bubble growth ........................................................................ (BubbleGrowth.avi)
Chapter 1
Introduction

1.1 Radiation Detection
Although it may not seem like it, radiation is everywhere. Understanding the universe, medical diagnosis and treatment, power production, and plate tectonics all rely on radiation in some form or another; even the human body contains radioactive isotopes such as $^{14}$C and $^{40}$K. However, radiation is not always friendly. Overexposure to solar UV rays causes the unenjoyable sensation known as sunburn, and higher energy particles increase the chances of healthy body cells mutating into cancerous ones. If radiation sources are lost or misplaced, they can be very harmful. More dangerous still is the threat of a nefarious group obtaining or using $^{235}$U or $^{239}$Pu to produce an atomic weapon. Only small amounts of these isotopes are theoretically required to produce a fission weapon: 25 and 8 Kg, respectively [1]. We should be very thankful, therefore, that these isotopes are radioactive. Their tendency to spontaneously emit x-rays, gamma-rays, alpha particles, and neutrons makes it possible to detect them without visibly seeing them.

One way to detect radiation is to use a scintillator detector. Scintillators are materials that absorb high-energy radiation (gamma-rays, x-rays, alpha particles) and emit visible light. The produced visible photons can then be recorded using a Si-based photosensor or a photomultiplier tube (PMT).

Detecting unwanted radioactive materials is a major aspect of national security. This is accomplished primarily at high-throughput entry points such as airports, docks, and border crossings. At border crossings specifically, a two-step process is used. Cars and trucks are driven through radiation portal monitors (RPM) that contain large, high-efficiency gamma-ray and x-ray detectors as well as $^3$He tubes to detect neutrons. An RPM is pictured in Figure 1. If a radiation is detected, the vehicle is then pulled over and higher resolution hand-held detectors are deployed to locate and identify the source [2].

The majority of radiation devices for national security applications utilize scintillators to detect gamma rays and X-rays. Scintillators work by converting high energy particles into visible photons, which can then be collected with more conventional technologies. Scintillators are generally can be produced larger and cheaper than semiconductors while still retaining high efficiency that is lacking in gaseous detectors. There are two main branches of scintillators: inorganic, which includes oxides and halides, and organic scintillators, which can be split into liquids, single crystal organics, and plastics, which act as gamma ray and X-ray detectors in RPM's [3].

1.2 Scintillators
Scintillators have many advantageous over proportional detectors such as Geiger counters. First, they are typically higher efficiency due to their solid densities and higher-Z components. Secondly, they can offer more information than the number of radiation interactions. The
Figure 1. Radiation portal monitor (white panel in yellow casing) [4].
number of photons generated in a scintillator per deposited radiation energy is known as the scintillators light yield and is often given in units of photons/MeV. Although this light yield is not always proportional to the incoming energy, the non-proportionality of a given scintillator can be measured and corrected for. This allows for even modest and poor resolution scintillators to provide some spectroscopic capabilities.

The scintillation light, once generated, must be collected and detected. One common photosensitive detector used frequently is a photomultiplier tube (PMT). This is a vacuum tube that consists of a photocathode to convert photons into electrons and a series of dynodes with an increasing applied voltage to amplify the photoelectrons into a readable signal. Figure 2 shows schematic of a scintillator mated to a PMT. PMTs have varying spectral responses based on the composition of the photocathode [3, 5-7]. Because of this, the wavelength of a scintillator is extremely important when engineering properties or choosing a PMT.

The electrical signal generated by the PMT is processed by a pre-amp and an amplifier before being binned by a multi-channel analyzer. The resultant histogram is known as a pulse-height spectrum because it displays the distribution of pulse heights generated by the PMT, which themselves are proportional to the number of photons collected from the scintillator.

There are three main ways in which a X-ray or gamma ray can interact with a scintillator. The first occurs when the photon is fully absorbed, and its energy is transferred into an electron due to the photoelectric effect. This typically occurs in X-rays and low energy gamma rays. The second outcome is when a photon collides with an electron in the scintillator, deposits some of its energy, and scatters off at an angle. This phenomenon typically occurs at intermediate energies. There is a maximum energy that can be deposited by a photon that corresponds to a scattering angle of 180°, and this energy is given by:

$$E_{\text{max}} = h\nu \left( \frac{2h\nu/m_0c^2}{1+2h\nu/m_0c^2} \right)$$  

where $h\nu$ is the initial energy of the photon and $m_0c^2$ is the rest mass of an electron [3]. The third type of interaction is called pair production, and only occurs at energies greater than 1.022 MeV, or twice the rest mass of an electron. Pair production is when a high energy photon interacts in a scintillator and produces an electron and a positron. Although each process occurs at different energies, the regions in which they occur overlap. Furthermore, the probability of any of the three happening is a function of energy, scintillator density, and atomic number [3, 6].

After a scintillator has been ionized, it takes some time for all of the luminescence centers to relax and produce scintillation photons. The scintillation intensity versus time plot of the scintillation light forms an exponential decay with one or more components. The time it takes for the intensity to drop by a factor of $e$ (~2.718) is known as the decay time of a scintillator, and is denoted with a $\tau$.

As mentioned before, the number of visible photons emitted by a scintillator is relatively
Figure 2. A scintillator mated to a photomultiplier tube (PMT).
proportional to the energy deposited in the scintillator. Therefore, the shape of the pulse height spectra is influenced by a combination of photoelectric absorption and Compton scattering. The energies of interest in this work are typically well below those required for pair production. A typical pulse height spectrum for NaI:Tl when irradiated with $^{137}$Cs is pictured in Figure 3.

Photons that are fully absorbed either through the photoelectric effect or Compton scattering followed by the photoelectric effect result in a count in the full energy peak. Any Compton scattered photons that escape the crystal result in a count in the Compton distribution according to how much energy was deposited during the scatter event. Because there is a maximum energy possibly deposited by Compton scattering, there is a drop off on the Compton distribution before the full energy peak known as the Compton edge.

Although dense scintillators allow for high-resolution spectroscopic capacities, they are often expensive and difficult to produce in large sizes. For this reason, plastic scintillators are often employed when the application calls for large, cheap detectors.

1.3 Plastic Scintillators

1.3.1 Properties

For locating and identifying unknown sources of radiation, handheld detectors that utilize inorganic metal halide scintillations such as NaI:Tl and semiconductors such as high-purity Ge (HPGe) are used. However, for bulk, high efficiency gamma-ray detection, plastic scintillators are more desirable for several reasons. First, they are cheap; plastic scintillators are < $1/cc, while NaI:Tl, one of the oldest and cheapest metal halides, is ~ $10/cc. Secondly, plastic scintillators are orders of magnitude faster than most inorganic ones. EJ-200, a common PVT based plastic scintillator, has a decay time of 2.1 ns, while LaBr$_3$:Ce, one of the most prompt metal halide scintillators, has a decay time of 30 ns [8, 9]. Finally, plastic scintillators can be produced in large sizes, with many radiation portal monitors (RPM) containing blocks of plastic > 6 ft in length.

The mechanism of scintillation in organic scintillators is slightly more complicated than in inorganic scintillators. In inorganic scintillators, ionization produces an excited state of an atom known as an activator. This activator ion deexcites and produces a visible photon. The two most common activators, Eu$^{2+}$ and Ce$^{3+}$ have one and two emission bands, respectively. This results in clean single and double emission peaks which are influenced by the surrounding crystal field. On the other hand, organic scintillators produce scintillation photons through changing electronic orbitals within a single molecule. Because the electronic orbitals within molecules are only slightly influenced by the surrounding matrix, organic fluors will scintillate similarly regardless of their surrounding compounds or their state of matter [5, 10].

Organic molecules scintillate by deexcitation from higher states to ground states. A Jablonski diagram of optical excitation and emission of organic scintillators is pictured in Figure 4. Ionization caused by X-rays and gamma rays causes electronic transitions from $S_0$ to $S_1$ or $S_2$
Figure 3. A pulse height spectrum from NaI:Tl irradiated by $^{137}$Cs [3].
Figure 4. Jablonski diagram showing different processes in organic scintillators: 1) Electronic transition due to ionization; 2) Relaxation due to thermal vibrations; 3) Internal conversion; 4) Intersystem crossing; 5) Radiative transition (emission); 6) Non-radiative transmission [10].
(singlet states). These very rapidly relax to the lowest level of their respective states or drop to a lower, above ground state via internal conversion (IC). From the lowest level states the electron can relax to the ground state via non-radiative or radiative (photon emission) transitions. It is possible for an electron to transfer to a triplet state (T₁ or T₂) via intersystem crossing, but the transition from the triplet to the ground state is spin-forbidden and only results in phosphorescence, or delayed emission.

One specific type of organic fluorescent compound that scintillates efficiently is one that contain π – bonds. The ionizing process converts bonding π-orbitals into non-bonding π-orbitals. This is common in benzene-ring-containing molecules such as anthracene and stilbene, two efficient scintillator molecules [10-12]. Interestingly, only a small amount of optically active molecules is required to have an efficient scintillator. Although a majority of the incident energy is absorbed by the bulk plastic, there is an efficient transfer of the energy from bulk plastic to fluor molecules, which may make up 1 percent or less of the plastic [7].

Organic scintillators are often orders of magnitude faster than inorganic scintillators. If the deexcitation process occurs through singlet states, it is very prompt and is referred to as fluorescence. As mentioned previously, deexcitation through a triplet state results only in phosphorescence, which can take much longer, and often contributes to any afterglow in the scintillator. Additionally, the decay time of plastic can be tuned by varying concentrations of multiple fluors [13].

Neutron sensors are extremely important in nuclear non-proliferation, and solid-state detectors are continually investigated because of the scarcity of ³He [14]. Due to their high hydrogen concentration, plastic scintillators are being explored as combined neutron-gamma detectors. Specifically, they are utilized due to their ability to differentiate between gamma-ray and neutron interactions through pulse-shape discrimination [15-17]. This process is possible due to the fact that the ratio between multiple components in the decay of a plastic scintillator depend on the deposition of energy across a scintillator dE/dr, and therefore the type of interacting particle [6].

1.3.2 Production

As previously mentioned, organic scintillators have the advantage of being producible as bulk detectors. Often a polymer matrix is chosen due to its promising physical properties and is doped with fluors and wavelength-shifters to produce an efficient plastic scintillator. One important quality of the matrix polymer is its glass transition temperature (Tₙ). Because plastics are amorphous, they may not have a conventional melting point. Instead, at a certain temperature, the plastic undergoes a transition between a solid (“glassy”) state and a softer, rubbery state [18]. If this temperature is below the maximum operating temperature of a plastic, it can negatively affect its physical properties. Two common polymer bases used in plastic scintillators are polyvinyl toluene (PVT) and polystyrene (PS). Monomers of both compositions are pictured in Figure 5, while properties of the two polymers are compared in Table 1.

The process of producing plastic scintillators has been described as early as 1953 [5, 19]. For
Figure 5. Molecular composition of PVT (left) and PS (right) monomers [20, 21].
Table 1. Physical Properties of Polyvinyl Toluene and Polystyrene. Asterisks denote values that were calculated in this research.

<table>
<thead>
<tr>
<th>Property</th>
<th>Polyvinyl Toluene</th>
<th>Polystyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>([\text{CH}_2\text{CH(C}_6\text{H}_4\text{CH}_3)]_n)</td>
<td>([\text{CH}_2\text{CH(C}_6\text{H}_5)]_n)</td>
</tr>
<tr>
<td>Density ((\text{g/cm}^3))</td>
<td>1.02*</td>
<td>1.05*</td>
</tr>
<tr>
<td>(T_g) ((^\circ\text{C}))</td>
<td>~ 70*</td>
<td>~ 100 [22]</td>
</tr>
<tr>
<td>Index of Refraction ((n))</td>
<td>1.59 [8]</td>
<td>1.46-1.59 [23]</td>
</tr>
</tbody>
</table>
large block detectors and laboratory-size samples, the base monomer, initiator, and other additives are mixed and poured into a mold for polymerizing. Chain-reaction polymerization occurs at 70 -120 °C and is typically done in an argon or nitrogen-purged oven to reduce dissolved oxygen [24-27]. Polymerization in general is a fast procedure; it can take around a microsecond for a chain of 1000 monomers to form [18]. The time for complete polymerization depends on the specific composition and thickness of the sample, as the reaction is exothermic. This often limits the thickness of large block detectors to ~ 8 inches or less due to overheating of the bulk. If done correctly, the resultant plastic is solid, uniform, and rigid. Once polymerized the plastic is cut and polished into its desired shape.

In addition to fluors, various chemicals can be added to plastic scintillators before polymerization to improve or change the final plastic’s properties. Typical additives for plastic scintillators are listed Table 2. In addition to final properties, the solubility of each additive must be considered when selecting chemicals for plastic scintillators.

1.3.3 Practicalities
Although plastic scintillators have many positive properties, their low density and effective atomic numbers leave much to be desired. These low values mean that high energy particles have a lower probability of interacting as they pass through a scintillator detector. For increasing detection efficiency, large samples are produced. However, there is another issue with having a low density/low Z scintillator.

As mentioned in the previous chapter, the probability of photoelectric absorption and Compton scattering is a function of these properties. At the energies often used to characterize scintillators, such as the 662 keV gamma from $^{137}$Cs, plastic scintillators have a very low probability of photoelectric absorption and a very high chance of Compton scattering if they interact. Furthermore, the odds of collecting a Compton scattered photon is very low. As a result, pulse-height spectra of plastic scintillators do not have fully energy peaks at higher energies, only a Compton spectrum. Figure 6 shows a typical $^{137}$Cs spectrum for a PVT-based plastic scintillator.

Even without full energy peaks, plastic scintillators can provide meager spectroscopic capabilities. The Compton edge maximum does not have enough resolution for spectrum matching algorithms, but a technique of comparing relative intensities is employed to monitor for certain energy windows known to contain signals from dangerous sources [28, 29]. Additionally, there has been an effort to produce a plastic scintillator loaded with high-Z elements to fully collect gamma rays [27, 30].

Large plastic scintillator detectors act as the gamma-ray and X-ray detector in RPMs. Typically, they are wrapped in a reflective coating and mated to PMTs on two ends to ensure maximum light collection. The completed detector is placed inside of a metal frame, along with a $^3$He tube neutron detector to complete the RPM [2]. The outer metal casing protects the detectors and electronics from direct sunlight and some environmental conditions, but as can be seen in the next section, it is not always enough.
<table>
<thead>
<tr>
<th>Additive</th>
<th>Purpose</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5 diphenyloxazole (PPO)</td>
<td>Primary Dye</td>
<td>[16]</td>
</tr>
<tr>
<td>1,1,4,4-Tetraphenyl-1,3-butadiene (TPB)</td>
<td>Primary Dye</td>
<td>[16]</td>
</tr>
<tr>
<td>1,4-bis(5-phenyl-2-oxazolyl) benzene</td>
<td>Secondary Die</td>
<td>[16]</td>
</tr>
<tr>
<td>$^{10}$B Enriched tetramethyl-2-phenyl-1,3,2-dioxaborolane (MBB)</td>
<td>Neutron Capture</td>
<td>[26]</td>
</tr>
<tr>
<td>Bismuth trupivalate</td>
<td>Gamma capture</td>
<td>[27]</td>
</tr>
<tr>
<td>Bisphenol A dimethacrylate (BPA-DM)</td>
<td>Cross-linker</td>
<td>[24]</td>
</tr>
<tr>
<td>Divinylbenzene (DVB)</td>
<td>Cross-linker</td>
<td>[31]</td>
</tr>
</tbody>
</table>
Figure 6. A typical $^{137}$Cs spectrum collected with a plastic scintillator. The peak is the Compton edge maximum. No photopeak is present.
Chapter 2
Fogging in Plastic Scintillators

2.1 The Problem
Plastic scintillator detectors based on PVT and PS have been deployed heavily in the last 15 years. Although some experiments have been done on the background signatures of portal monitors over a year-long period [32], no long-term performance data has been made public. In recent years a degradation phenomenon called “fogging” has been acknowledged in plastic scintillators deployed in certain environments [33, 34]. This fogging can result in permanent defects in the bulk of the plastic that result in increased light scattering, an increase in maintenance cost, and a decrease in detector lifetime. To study this phenomenon, multiple groups have produced fogging in laboratory settings.

Cameron et al. note that fogging can be induced in PVT via an accelerated aging tests that include exposing the plastic to an environment of high temperature and humidity for a period of time, followed by cooling the sample [33]. Samples of PVT and PS that have had fogging included in laboratory settings are pictured in Figure 7.

Although this method can produce fogging in laboratory-size samples, it is not as useful on full-size detectors due to the increased time required to saturate the plastic. Accelerated aging tests also do not account for the large number of temperature fluctuations that detectors experience in the field. The aforementioned report shows that larger samples, if not sufficiently saturated, will show fogging only on the borders of the plastic. Sword et al. expanded on this research by producing fogging in polystyrene (PS) as well as PVT, and showing that this effect is absent in polymethyl methacrylate (PMMA) [34]. Both of these publications note the temporary nature of at least some of the fogging defects, as well as high humidity environments required to produce fogging.

The currently understood mechanism for fogging is as follows: water diffuses into the plastic at a given temperature and humidity. The time it takes to fully saturate a plastic depends on temperature, relative humidity, detector size, and detector geometry. When the temperature changes, so does the maximum saturation level of water in plastic. If the sample cools significantly, it becomes over saturated, and water condenses into temporary fog defects, similar to water condensing in air [31, 33-40].

This heating, saturating, and cooling process has been seen to produce two types of fogging: temporary and permanent. Temporary fogging appears rapidly after cooling (< 10 minutes), and can be made to disappear, either by allowing the excess water to diffuse out of the plastic, or by heating the plastic to increase its saturation limit. Permanent defects remain regardless the humidity or temperature, within standard environmental ranges (-30 to 55 °C and 0 to 90 % relative humidity (RH)). Large block detectors that have been deployed for extended periods of time often contain permanent defects in their bulk but remain clear on their border. Both temporary
Figure 7. PVT (left) and PS (right) samples that have been saturated and cooled to induce fogging [34].
and permanent defects appear as disc-shaped cracks. An optical microscope picture of a permanent defect inside of an aged PVT detector is pictured in Figure 8.

In addition to bulk defects, surface level defects known as crazing have been observed. Although they are not explicitly explored in this research, they are worth noting. A microscope image of crazing on a field aged plastic sample is pictured in Figure 9.

2.2. Consecutive Efforts

Multiple groups are focused on solving the fogging problem by investigating different aspects such as encapsulation solutions [41], new composition development [31, 36], defect formation [37], and development of a predictive model that can determine whether a plastic will fog in certain environmental locations [39]. One product of these efforts is the “fog-line”, a linear relationship between fogging temperature and water concentration in plastics below which fogging is formed [39]. A plot of the “fog-line” is included in Figure 10.

System level solutions, such as covering the plastic to prevent water penetration, have been researched. One study found that a 2.5 cm PVT cube encapsulated in a Shannon bag material absorbed significant amounts of water after a single pinhole was punctured in the bag [41]. The results of this experiment are summarized in Figure 11.

The formation of defects has also been studied via scanning electron microscopy (SEM) images of permanent defects. Lance et. Al. have hypothesized that water agglomerates during cooling while the saturation limit of a plastic decreases [37]. These spherical regions of water exert a tensile stress on the plastic, which eventually leads to a disk-shaped tear in the plastic. The spheroid and tears in plastic can be seen via SEM in Figure 12.

The ability to predict fogging in certain environments is important for reducing maintenance and replacement costs. A group at Lawrence Livermore National Laboratory (LLNL) has combined temperature and humidity patterns with water uptake data to produce such a model. As can be seen in Figure 13, various environments lead to different water concentration cycles in plastic scintillators, and if this cycles brings the concentration or temperature below the fog-line, the plastic will fog [39].

2.3 Gaps in Current Knowledge

As mentioned in the previous section, fogging in plastic scintillators is a problem being attacked on multiple fronts. However, much is still unknown. For instance, Myllenbeck writes that although a relationship has been established between “environmental aging conditions, moisture uptake, extent of light scattering, and fog-onset temperatures ... [future experiments] will focus on the transition between transient and ‘permanent’ defect regimes, specifically exploring variable cooling rates” [36]. The importance of changing the cooling rates is also mentioned by Lance, who says “In order to predict which environmentally exposed PVT will degrade in performance in the field using only weather data, further experimentation will be performed using hydrothermal cycling that closely matches day-to-night temperature swings,
Figure 8. A permanent defect (center) in an aged PVT block.
Figure 9. Optical microscope image of surface crazing on a field-aged plastic scintillator. Horizontal lines are polishing defects and were not caused by aging.
Figure 10. A plot of fogging temperature and water concentration in a plastic (left) with the fog-line reproduced from experimental data (right) [39].
Figure 11. Water uptake in PVT cubes with varying encapsulations. [41]
Figure 12. SEM images of lab produced defects in PVT (a & c) and defects in a field-aged PVT panel (b & d). [37]
Figure 13. Water concentration in a plastic as a function of temperature in four different environments with the fog-line overlain [39].
cold fronts that last days and seasonal changes in temperature and humidity lasting months” [37].

The presence of liquid water has been confirmed to play a role in fogging of plastic scintillators. Encapsulation efforts have shown that although it is difficult, preventing any moisture from penetrating the plastic will prevent fogging [41]. However, the movement of water in the plastic and whether liquid water is stored in permanent defects have not been experimentally studied.

In addition to better understanding the fogging mechanism, new plastics must be rigorously investigated to determine which compositions are best suited for varying environmental conditions. Scintillation measurements of plastic scintillators that have undergone multiple cycles with varying cooling rates have not been examined. Additionally, little work has been done comparing the scintillation performance of plastics with permanent vs temporary defects.

Plastics that have undergone dry heat cycles have not been measured to confirm scintillation stability, and Payne notes that “it was suggested that other factors might be important such as heating of the portal by direct sunlight”, an effect that could heat detectors higher than normal weather temperatures [39]. Additionally, plastics have been assumed to have no light yield dependence on temperature, something that has not been confirmed for each composition.

2.4 Goals and Objectives
Environmental degradation of plastic scintillators is a broad topic that multiple groups are working on understanding. To further narrow down this research, a few important goals are focused on:

1. Investigate the mechanism of fogging in plastic scintillators
2. Develop an understanding of the effects of fogging on scintillation performance
3. Evaluate the resistance of new compositions to environmental degradation

In order to achieve these goals, specific objectives have been outlined:

- Produce temporary and permanent fogging in a laboratory setting using high humidity and liquid water saturation techniques
- Compare the physical and scintillation properties of field-aged and laboratory-aged plastics
- Correlate the presence of water to the disappearance of temporary fogging
- Explore conditions that produce temporary or permanent fogging
- Study the effects of temporary and permanent fogging on scintillation performance and light collection
- Investigate the effect of temperature on luminescence
- Evaluate the resistance to environmental degradation of novel plastic scintillators provided by collaborators

Details on experiments, materials, and processes are outlined fully in their respective chapters.
Chapter 3
Properties of Fogging

This chapter contains research that was carried out to better understand the properties of fogging including formation, reappearance, and particle size. Many of these results have been published in a peer-reviewed journal by Matthew Loyd. Minor changes have been made to provide a better flow within the larger dissertation.

The full citation for the published manuscript is as follows: Matthew Loyd, Matheus Pianassola, Charles Hurlbut, Kyle Shipp, L. Sideropoulos, Ken Weston, Merry Koschan, Charles L. Melcher, Mariya Zhuravleva, Effects of temporary fogging and defogging in plastic scintillators, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 922, 2019, Pages 202-208 [42]. The author would like to fully acknowledge and thank the efforts of the co-authors for their help.

3.1 Experimental
3.1.1 Materials

Four main types of plastic scintillators were used in this research and a picture of each are included in Figure 14.

1) A field-aged PVT (FA1) block that was used in an RPM supplied by Nucafe [43]. This block has visible permanent fogging defects in its bulk but has an ~ 2 cm clear region on its edges. This clear region was used to obtain samples to ensure that any produced temporary defects would not be obstructed by existing permanent defects. A picture of nearly the full block is included in Figure 15.

2) A second field-aged (FA2) plastic of unknown composition that was used in a dry environment with no temperature control for > 7 years, also provided by Nucafe. This block has no visible permanent defects.

3) Fresh EJ-200 PVT (FPVT) supplied by Eljen Technology [44].

4) A new formulation (NF) developed at LLNL [31] and produced by Eljen Technology. This composition consists of a PVT base with 5% each of PPO, DVB, and PMMA. Although new compositions are discussed in detail in a later chapter, this sample has been included to compare fogging compositions with non-fogging compositions.

In addition to these four materials, pure polystyrene (PS) produced by Eljen and commercially purchased poly methyl methacrylate (PMMA) were used. All samples were cut to desired size and hand polished using 600, 800, and 1200 grit polishing paper and lapping oil. A 0.25 x 1 x 1” piece was cut from each of FA1, FA2, FPVT, and NF for use in the environmental chamber experiment (ECE). This size was chosen for ease of optical and photoluminescence measurements. 1” cubes were cut from FA1, FA2, FPVT, NF, PS, and PMMA for use in the water-soaking experiments.
Figure 14. Plastic materials selected for accelerated aging experiments a) field-aged block with visible permanent defects (FA1), b) field aged detector with no visible permanent defects (FA2), c) fresh EJ-200 (FPVT), d) new formulation (NF).
Figure 15. Full field-aged block of PVT (FA1). A human has been included for scale.
3.1.2 Methods

Physical and Thermal Properties

Although it is readily apparent that fogging affects light transport in plastic scintillators, it is unclear what effects it has on physical and thermal properties of the bulk polymer. To test this, fresh and aged samples were measured using both differential scanning calorimetry (DSC). DSC measures heat flow in and out of a sample as its temperature is changed, and can detect phase transitions, melting points, and glass transition temperatures. Two different DSCs were used in this experiment. The first, a Labsys Evo TG-DSC is capable of reaching 1600 °C and utilizes 150 mL alumina crucibles. The second is a TA Q20 DSC that is often used for plastics and measures samples in aluminum crucibles. A section of FA1 was cut from the bulk and cut into ten slices so that the properties could be analyzed across the entire block. These slices are pictured in Figure 16. Samples weighing ~ 10 mg were broken from each slice, as well as from FA2, FPVT, and NF, and were placed into a crucible. The DSC was then heated from 25 °C to 200 °C at a rate of 10 °C/min.

In addition to DSC, the glass transition temperature of FA1, FA2, and FPVT was measured using dynamic mechanical analysis (DMA). In this technique, a small stress is applied in a cyclic manner over a range of temperatures. When the glass transition temperature is reached, there is a maximum difference between the storage modulus and the loss modulus of a material [45]. A TA Q 800 DMA was used at the Joint Institute of Advanced Materials (JIAM) Polymer Characterization Laboratory (PCL). Samples were cut to a size of 60 x 15 x 1.7 mm, and were strained 0.5 % at a frequency of 1 Hz while being heated to 140 °C at 5 °C/min.

Finally, Fourier transform infrared spectrometry (FTIR) was measured on a fresh PVT sample and an aged PVT sample to look for water resonances. FTIR uses infrared light to measure the molecular vibrations of a material. These vibrations are dependent on the molecular structure being measured [46]. Therefore, if water was present in one plastic sample but not another, there would be a difference in FTIR spectra showing water vibrational bands. Three samples were prepared for measurement, a fresh PVT sample and a piece of each FA1-C (clear) and FA1-D (with defects). An Agilent Cary 610 FTIR microscope with a mercury cadmium telluride (MCT) detector was used to collect spectra on each sample.

Environmental Chamber Experiments

Two environments were used to induce water absorption and produce fogging in the plastics: high-humidity air and liquid water. A Thermotron benchtop environmental chamber was used to produce high-humidity air. The environmental chamber experiments (ECE) utilized a fogging profile developed at PNNL [47], which consists of a soak period at 55 °C and 90% relative humidity, followed by rapid cooling (80 °C/hr) to -30 °C. The samples used in the ECE were 1 x 1 x 0.25”, and a soaking period of 48 hours was used.
Figure 16. Slices of FA1 for DSC measurements. Each slice is 3.5 mm thick.
Water Saturation Experiments
For the water-soaking experiments, 1” cube samples were soaked in deionized water heated to 55 °C. Because of the larger sample volume, a saturation period of two weeks was used. Two cubes of fresh PVT were used to compare the size of fogging defects as a function of cooling rate. The first was cooled instantly by placing it on the lab top at 25 °C, and the second was cooled in water at 4 °C/hr.

Cubes of various compositions were used in the defogging experiments. These samples were cooled in water to room temperature at a rate of 4 °C per hour. A summary of all aging experiments in this chapter is included in Table 3.

Characterization
The four 0.25 x 1 x 1” samples were characterized before and after the ECE to better understand the effects of fogging on light production and collection. The photoluminescence emission was measured in the 200-800 nm range using a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer with an excitation wavelength of 279 nm. Optical transmission was collected using a Varian Cary 5000 UV-VIS-NIR Spectrophotometer. Optical images were taken with a KEYENCE VHX-1000 microscope. Additionally, a micro-environmental stage was developed to control temperature and humidity of plastic samples while imaging on the optical microscope and is pictured in Figure 17.

The micro-environmental stage was used to produce a time-lapse video of fogging particles as they form and evolve. A 1” cube of E-VT-4 was soaked in deionized water at 55˚C for > 14 days to ensure complete saturation, then placed in ambient conditions to rapidly produce fogging. The cube was then loaded into the MES and the optical microscope was focused with high magnification on a temporary defect particle. The MES was heated to 55˚C rapidly, then cooled to room temperature at a rate of 4˚C/hr. An optical microscope image was taken every 2 minutes during this period to produce a time-lapse video of the evolution of the defect particles.

3.2 Results
3.2.1 Materials Properties
Both DSC and DMA were used to compare fresh and aged samples to see if there were any changes in thermal properties of the plastic due to fogging. DSC results for the ten slices of FA1 are plotted in Figure 18. The difference in heat flow intensity is caused by variations in sample size. As can be seen in Figure 16, the presence of permanent defects in the slices of FA1 is dependent on the position in the bulk. Slices 1, 2, 9, and 10 are free of permeant defects, while the other slices contain them. The T_g was calculated from the DSC curves by finding the onset temperature of the endothermic peak. Because there is no change in T_g across all slices of FA1, visible permanent defects do not affect the glass transition temperature. Because of different setups, the glass transition temperature can be measured as different values on different instruments and different methods (i.e. DSC vs DMA) [48].

In addition to comparing across slices of FA1, T_g was measured for each sample discussed in this
Table 3. A summary of all experimental parameters used for accelerated aging of plastic samples.

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Formation of temporary fogging defects</th>
<th>Defogging (fading of temporary defects)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid water</td>
<td>Water vapor (ECE)</td>
</tr>
<tr>
<td>Sample ID</td>
<td>FPVT</td>
<td>FA1</td>
</tr>
<tr>
<td>Sample size</td>
<td>1” cube</td>
<td>5 x 10 x 10 mm</td>
</tr>
<tr>
<td>RH%, T, time for saturation</td>
<td>55 °C, 14 days</td>
<td>55 °C 2 days</td>
</tr>
<tr>
<td>RH%, T to induce fogging</td>
<td>25 °C</td>
<td>25 °C</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>Instant, 4°C/hr</td>
<td>Instant</td>
</tr>
<tr>
<td>RH%, T, time for defogging</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 17. Micro-environmental stage placed under the optical microscope lens.
Figure 18. DSC results of FA1 slices across the sample measured with a Labsys Evo (left) and a TA Q20 (right). There was no significant change in $T_g$ between slices measured on either DSC.
chapter. The DSC results from both instruments are plotted in Figure 19. Exothermic peaks measured at \( \sim 130 ^\circ C \) are present on all scans measured on the Labsys Evo and are instrumental in nature. Both sections of FA1 and FPVT have about the same \( T_g \) (although different values are measured for each instrument), while the \( T_g \) of FPVT and FA2 is about 5-7 degrees cooler. Due to the confidential nature of working with industry partners, the exact composition of the field aged samples is unknown. However, we can deduce that FA2 has a different composition than FA1, FPVT.

In addition to DSC, DMA was measured on all of these materials except NF, which was excluded due to size constraints. As can be seen in Figure 20, similar results to those from the DSC were obtained, with FA2 having a lower \( T_g \) than the other materials. The values obtained for \( T_g \) from all three instruments are listed in Table 4.

FTIR spectra measured on FPVT, FA1-D, and FA1-C are plotted in Figure 21. All three samples have the same absorbance spectra, with only minor differences in intensities. Additionally, none of the samples contain characteristic water H-O-H bending mode bands in the 1300-2000 cm\(^{-1}\) range [46]. Although water is expected in the aged samples, this measurement was only able to probe a very small amount of the surface, and water was not detected. The samples all have the same base polymer (PVT), which explains the similar spectra for all three samples.

3.2.2 Producing Fogging

The environmental chamber experiment was used to compare fogging of fresh and aged samples, as well as to test the new formulation. The ECE profile consists of the most extreme environmental conditions possible; samples are fully saturated and the temperature change (55°C to -30 °C) covers the entire range of reasonable weather fluctuations. The four samples before and after one cycle of the ECE are pictured in Figure 22. Both field aged samples and the fresh PVT were visibly fogged after the ECE, while the new formulation was not. Optical microscope images of each samples after the ECE are included in Figure 23. For the samples that fogged, defects of tens of \( \mu m \) in diameter can be seen, while no such defects appear in the new formulation. Both aged samples with different histories, as well as fresh PVT all produce similar levels of fogging. The density of defects is slightly different in FA2 than in FA1 and FPVT; this is most likely due to some unknown factor in the sample’s history or composition. PVT that has been aged in the field over several years does not fog differently than freshly cast PVT.

Optical properties were measured for all four samples to assess the effects of temporary fogging. Photoluminescence emission when excited at 279 nm was collected for each sample before and after the ECE and is plotted in Figure 24. The difference in emission shape between NF and the other samples is likely due to the difference in chemical composition. Both field-aged samples and fresh PVT show slight change in emission intensity after fogging, but the ECE resulted in no change in emission shape for any of the samples. The change in intensity can be attributed to increased light scattering at the fogging defects.

To quantify the light scattering effect, optical transmission of 0.25-inch thick samples is plotted.
Figure 19. DSC results of the four different plastics measured with a Labsys Evo (left) and a TA Q20 (right). FA1-C describes clear sections of FA1, while FA1-D related to those that contain defects.
Figure 20. Dynamic mechanical analysis (DMA) of FA2, NPVT, and 2 sections of FA1.
Table 4. Measured $T_g$ values for each sample using two different DSCs and the DMA.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Labsys Evo DSC</th>
<th>TA Q20 DSC</th>
<th>TA Q50 DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1-C</td>
<td>88.3</td>
<td>83.3</td>
<td>97.6 °C</td>
</tr>
<tr>
<td>FA1-D</td>
<td>89.4</td>
<td>84.8</td>
<td>96.3 °C</td>
</tr>
<tr>
<td>FA2</td>
<td>81.1</td>
<td>77.5</td>
<td>89.2 °C</td>
</tr>
<tr>
<td>FPVT</td>
<td>88.3</td>
<td>83.3</td>
<td>97.1 °C</td>
</tr>
<tr>
<td>NF</td>
<td>82.9</td>
<td>78.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 21. FTIR absorbance spectra for FPVT, FA1-D, and FA1-C. All three spectra are extremely similar and lack characteristic water bands in the 1000-2000 cm\(^{-1}\) range.
Figure 22. Samples before (top) and after (bottom) one cycle of the ECE. All samples except NF developed temporary fogging.
Figure 23. Optical microscope images of the samples after one cycle of the ECE. Temporary fogging defects are represented by white particles. The grid lines are 400 microns. The cloudy appearance of the NF sample is due to the background.
Figure 24. Photoluminescence emission recorded at a 279 nm excitation before (black curves) and after (red curves) the ECE.
in Figure 25. The transmission intensity decreased by at least 50% in the fogged samples, while the transmission of new formulation was not significantly affected by the ECE. The decrease in transmission intensity is due to optical scattering off temporary defects, an effect will have a significant impact on the light collection of large detectors. The absorption edge of the samples was not shifted due to the temporary fogging.

The effect of cooling rate on the temporary defect size and density in freshly cast PVT is compared in Figure 26. The fogging defects are larger and less densely located in the slowly cooled (4 °C/hr) sample than in the instantly cooled sample. The instant cooling produced defects of 80-100 µm in diameter, while the slow cooling rate produced defects of 150-200 µm. The slower cooling rate allows water in the sample to diffuse into the created fogging defects, which then causes them to “grow”.

The “growth” of fogging defects was visualized using time-lapse photography on the optical microscope. A time-lapse video titled DefectGrowth has been attached with supplemental files. The video covers a total of 3 hours as the sample cooled from 55°C to 21°C. Although the experiment started at 55°C, no defects appeared until the sample was cooled to 36°C. In the video, particles first appear small, then “grow” outward until the sample has completely cooled. Optical images from the timelapse at 30-minute intervals are compared in Figure 27.

Temporary fogging is, as the name indicates, reversible and can be cycled multiple times. A significant question to answer is whether the defects that appear during temporary fogging reappear in the same location with each cycle. If so, one possibility is that the permanent fogging is caused by repeated stress on the same area until a permanent cracks form. Therefore, an experiment was conducted to examine the location of temporary fogging after multiple cycles, in which a sample taken from the clear edge of FA1 was saturated using the described water-soaking conditions and placed in ambient environment to produce fogging. The sample was then allowed to fully defog through water diffusing out in ambient conditions. After it was fully cleared and defects were no longer optically visible, the sample was subjected to a second saturation/fogging cycle. Optical microscope images of the sample after first fogging, recovery, and second fogging are included in Figure 28. The red circles surround temporary fogging defects that were found in the same location relative to the visible cracks used as a reference point. The fogging defects appear in the same location after both fogging cycles, even though the fog visually appeared to have fully recovered between cycles. This has also been observed in fresh, non-field-aged samples. This implies that the fogging, although temporary, either creates or locates in previously existing permanent defects in the plastic matrix that are not visible to the naked eye.

3.3 Conclusions
In this chapter we investigated the properties of temporary fogging and defogging in plastic scintillators. The physical and thermal properties of field aged and fresh plastic scintillators showed that fogging does not affect materials properties such as glass transition temperature.
Figure 25. Optical transmission of 0.25-inch thick samples before and after the ECE.
Figure 26. Size of fogging defects for instantly cooled (left) and slowly, 4 °C/hr, cooled (right) PVT. The inset shows the 1" cubes a few days after fogging.
Figure 27. Optical microscope images of fogging E-VT-4 at 30 minute intervals.
Figure 28. Optical microscopy images of FA1 after induced temporary fogging (left), 5 days after recovery (middle) and re-fogging (right). The circles and arrows connect temporary defects that appear in the same location. Surface cracks were used as a reference position in order to obtain the same focus and location of the sample after the second fogging.
FTIR measurements were not sensitive enough to detect water on the surface of samples after saturation. Samples were saturated in both high-humidity and liquid water environments. An environmental chamber experiment produced fogging in two field-aged samples as well as fresh PVT, while a new formulation was left unaffected. The photoluminescence of the fogged plastics was not changed due to the fogging, but the optical transmission was reduced by at least 50% in the 400-800 nm range. Therefore, fogging negatively affects the performance of plastic scintillators by reducing light collection, an effect that will be exaggerated in larger detectors. Liquid water experiments revealed that the size of the fogging defects is dependent on the rate of cooling, with slower cooling rates producing larger defects. The defects appear in the same location after successive fogging, which is evidence that a single cycle of fogging leaves permanent defects in the polymer matrix.

The distribution of permanent defects in large, aged detectors can be explained by the results obtained in this work. If plastic scintillators become saturated with water in high humidity conditions, they will fog whenever the temperature drops and the saturation limit falls below the current concentration of water in the plastic. However, as the temperature drops and the water vapor content in the surrounding air decreases, the water will diffuse outward from the edges of the plastic, as seen with the rapid mass decrease in Fig. 9, while remaining in the interior for a longer time. Even fogging that was formed rapidly will leave permanent defects in the plastic, as evidenced by Fig. 7. Eventually, long cooling times caused by weather will produce larger defects due to the correlation between cooling rate and defect size (Fig. 6). A large, permanent defect from the center of FA1 is pictured in Fig. 12. Defects are three dimensional and not spherically symmetric. The water in the edges of the plastic will have time to diffuse out during the long cooling periods and will not form large, permanent defects. The “halo” defects will most likely not form in field conditions blocks, as they require a block to become fully saturated at high temperatures, cool sufficiently to produce fogging, then stay at a lower temperature with low humidity for a length of time to defog the entire block.
Chapter 4
New Compositions

As mentioned by Janos et al [40], one solution to fogging of plastic scintillators is to produce new compositions that are resistant to fogging. Although many different additives have been tested, the most promising are those that contain polar molecules [24, 31, 40]. These polar molecules create more bonding sites to which water may bond, preventing the agglomeration that creates fogging defects. However, adding too much of certain molecules, such as PMMA or PPO, can plasticize the scintillators. Therefore, these must be countered with crosslinkers like DVB. In this chapter, new compositions with different origins have been tested for scintillation performance and resistance to fogging. The two sources for these compositions are:

1. Compositions developed at LLNL and produced by Eljen Technology
2. Triton compositions produced by Sandia National Laboratory (SNL)

The author would like to thank all of our suppliers for being generous with ample samples to experiment on.

4.1 Experimental
4.1.1 Materials
New compositions supplied by four different sources were investigated. The composition, source, and same details of each composition are compiled in Table 5. The exact composition of SNL plastics are proprietary and will not be discussed.

4.1.2 Methods
4.1.2.1 Accelerated Aging Experiment
To study the LLNL/Eljen samples, aggressive environmental conditions were simulated using a Thermotron SM 1.0 8200 environmental chamber; temperatures and relative humidities were chosen based on an accelerated aging test that is known to produce fogging in laboratory conditions [47]. Samples were subjected to a six-stage temperature and humidity profile, which is illustrated in Figure 29. The 6 stages are as follows:

1. A 23-day saturation period, in which samples were exposed to water vapor at 90% relative humidity (RH) and 55 °C.
2. The temperature and humidity were decreased to -30 °C and 25 RH%, respectively, over 1 hour. The samples were kept in this new condition for 24 hours.
3. The samples were heated rapidly to 55°C at 0 %RH for a 20-day drying period, during which water diffused out of the samples. Because the drying occurred at an elevated temperature, samples were not fogged during this drying period.
4. The samples were then saturated once more at 55 °C and 90 %RH for 23 days.
5. Another cooling stage was used to induce fogging; this time the cooling rate was much
Table 5. New Compositions tested in this Chapter

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample ID</th>
<th>Composition</th>
<th>Developer</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>VT</td>
<td>1</td>
<td>Pure PVT</td>
<td>Eljen</td>
<td>Ø1.5 x 1”</td>
</tr>
<tr>
<td>PS</td>
<td>2</td>
<td>Pure PS</td>
<td>Eljen</td>
<td>Ø1.5 x 1”</td>
</tr>
<tr>
<td>VT</td>
<td>5</td>
<td>EJ-200 Alternative Primary Fluor</td>
<td>Eljen</td>
<td>Ø1.5 x 1”</td>
</tr>
<tr>
<td>N555V</td>
<td>6</td>
<td>PVT with 5% each of PPO, PMMA, and DVB</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N555S</td>
<td>7</td>
<td>PS with 5% each of PPO, PMMA, and DVB</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N556V</td>
<td>8</td>
<td>PVT with 5% of PPO and PMMA, and 6% DVB</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N556S</td>
<td>9</td>
<td>PS with 5% of PPO and PMMA, and 6% DVB</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>V/M10</td>
<td>10</td>
<td>PVT with 10% PMMA and small amount PPO</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>V/M5</td>
<td>11</td>
<td>PVT with 5% PMMA and small amount PPO</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N556V</td>
<td>12</td>
<td>N556-PVT with a different initiator</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N556S</td>
<td>13</td>
<td>N556-PS with a different initiator</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>N556VS</td>
<td>14</td>
<td>A base of 80% PVT and 20% PS; 5% of PPO and PMMA, and 6% DVB</td>
<td>LLNL/Eljen</td>
<td>Ø2 x 1”</td>
</tr>
<tr>
<td>TX7A</td>
<td>15</td>
<td>PVT with Triton-X blend #2, primary fluor #2, and wavelength shifter #1</td>
<td>SNL</td>
<td>1” cubes</td>
</tr>
<tr>
<td>TX7B</td>
<td>16</td>
<td>PVT with Triton-X blend #2, primary fluor #3, and wavelength shifter #1</td>
<td>SNL</td>
<td>1” cubes</td>
</tr>
<tr>
<td>TX7C</td>
<td>17</td>
<td>PVT with Triton-X blend #3, primary fluor #3, and wavelength shifter #1</td>
<td>SNL</td>
<td>1” cubes</td>
</tr>
</tbody>
</table>
Figure 29. Temperature and humidity profile for the accelerated aging experiment. Asterisks mark times when scintillation measurements were taken. Time axis not to scale.
slower than in stage 2. Samples were cooled over a 48-hour period to -30 °C and 25 % RH.

6. Finally, samples were dried in ambient laboratory conditions for 60 days. Temporary fogging remained in the fogged samples until the excess water diffused out.

All samples were weighed before the experiment and after stage 2. The mass increase at saturation was calculated by dividing the difference between fresh and saturated mass by the initial mass.

Samples were characterized multiple times throughout the experiment to monitor their response to environmental conditions. Photographs were taken of each sample between stages. Gamma-ray excited pulse-height spectra were acquired on the scintillator samples at five different points, highlighted by the asterisks in Figure 29. Samples were brought to room temperature and mounted on a Hamamatsu R877 photomultiplier tube (PMT) with optical grease. The sample was covered with Teflon tape to ensure complete light collection. The signal from the PMT was passed through a Canberra model 2005 pre-amplifier followed by an Ortec 672 amplifier, and finally a Tukan 8k multi-channel analyzer. A $^{137}$Cs source was used for irradiation, and spectra were collected for 600 seconds.

Direct comparison of the gamma spectra is difficult due to variations in the shape of the Compton edge for the different materials. A python script was written to calculate the inflection point on the Compton edge so that this point could be compared across materials and various test stages.

Some of the fog-resistant samples performed worse after the accelerated aging experiment. It was unclear whether the reduction in performance was due to the humidity or simply annealing of the samples. To test this, some of those samples were heated in a low humidity furnace (< 25 % relative humidity) at 55 °C for 26 days and their scintillation performance was compared before and after annealing. Samples were cooled to room temperature before measuring a pulse height spectrum with a $^{137}$Cs source.

4.1.2.2 Triton-X sample testing

Another type of new composition developed at SNL was provided for testing, as well as EJ-200 for comparisons. First, the effect of a single fogging cycle was tested. One 1” cube of each composition was polished, weighed, and characterized using scintillation and photoluminescence techniques. All four cubes were then placed in the environmental chamber at 50°C and 90 %RH for 5 days, then cooled to -30 °C and 25 %RH in one hour. Samples were then weighed and characterized once again. Photoluminescence emission and excitation spectra were acquired with a Horiba Fluorolog with a 450 W Xe lamp and a Hamamatsu R928 photomultiplier.

The effect of multiple fogging cycles on Triton-X samples was also investigated. In order to visually compare the defect production in the Triton-X compositions, 1-inch cubes of TX7A, TX7B,
TX7C, and EJ-200 were soaked in deionized water at 50 °C for 60 days. After saturation with water, the samples were submitted to 6 temperature cycles consisting of 1 h at 50 °C in water and 1 h at 0 °C in air. The samples were transferred immediately from one environment to the other; the cooling and heating rates were not controlled.

4.2 Results

4.2.1 LLNL/Eljen Compositions

4.2.1.1 Fogging

All samples were weighed before the experiment and after the first saturation stage. The percent mass gained in water absorption is included in Table 6, as well as the fogging status of each sample after stage 2 (fogging, no fogging, or yellowing). In general, PS-based samples gained more mass than PVT-based ones. Both pure PVT-1 and PS-2, as well as VT-5 gained 0.06-0.09 % mass after saturation, while new compositions that contain some amount of PMMA absorbed nearly double this amount, which is comparable to previous observations [31, 34, 37, 42]. The N555 and N556 PVT-based compositions showed good resistance to fogging, while the PS-based compositions yellowed to different degrees but did not fog. Both samples that contained an alternative initiator (N556V-12 & N556S-13) also remained transparent.

Pictures of the samples before the experiment, after stage 2, and after stage 5 are included in Figure 30. Four 1" cube samples (EJ-200, two field aged samples, and PMMA) were included in the experiment for reference but were not analyzed in this work. Water absorption and fogging of these compositions have been covered in a previous publication [42]. Five of the cylindrical samples were visibly fogged after stage 2 and stage 5. The fogging defects were smaller and more densely spaced after rapid cooling (stage 2) than after slow cooling (stage 5), as would be expected. Additionally, due to the longer cooling time (24 hours) during stage 5, water was able to diffuse out of the samples near the edges, leaving them clear of fogging.

It has been shown that fogging morphology changes based on cooling rates [31, 42]. Figure 31 highlights this by comparing images of pure PVT and pure PS before the experiment and after stages 2, 5, and 6. Fogging after rapid cooling (stage 2) was dense and the defects were small, while slow cooling (stage 5) produced larger, less densely packed defects. After rapidly drying (stage 3), no visible defects were present in any of the foggable samples. However, foggable samples after slow cooling (stage 6) contained visible permanent defects. These permanent defects were either caused by the formation of larger fogging defects during slow cooling or by the defogging process, which has been shown to produce permanent defects in “halo” formations [37, 42].

Fogging defects after slow cooling were larger in the pure PVT sample than those in pure PS even though PS samples absorb more water. Additionally, pure PVT contained more visible permanent defects after ambient drying. Based on these results, PS is more resistant to larger, permanent fogging defects than PVT. Microscope images of permanent defects in PVT-1, PS-2, and VT-5 are included in Figure 32. The permanent defects in the PS sample are visibly smaller than those in
Table 6. Samples’ mass gain and fogging status after saturation and cooling (stage 2).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mass increase after saturation (%)</th>
<th>Visual Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>VT-1</td>
<td>0.068</td>
<td>Fogged</td>
</tr>
<tr>
<td>PS-2</td>
<td>0.088</td>
<td>Fogged</td>
</tr>
<tr>
<td>VT-5</td>
<td>0.062</td>
<td>Fogged</td>
</tr>
<tr>
<td>N555V-6</td>
<td>0.109</td>
<td>No Fogging</td>
</tr>
<tr>
<td>N555S-7</td>
<td>0.120</td>
<td>Slight Yellowing, No Fogging</td>
</tr>
<tr>
<td>N556V-8</td>
<td>0.107</td>
<td>No Fogging</td>
</tr>
<tr>
<td>N556S-9</td>
<td>0.125</td>
<td>Heavy Yellowing, No Fogging</td>
</tr>
<tr>
<td>V/M10-10</td>
<td>0.087</td>
<td>Fogged</td>
</tr>
<tr>
<td>V/M5-11</td>
<td>0.093</td>
<td>Fogged</td>
</tr>
<tr>
<td>N556V-12</td>
<td>0.106</td>
<td>No Fogging</td>
</tr>
<tr>
<td>N556S-13</td>
<td>0.134</td>
<td>No Fogging</td>
</tr>
<tr>
<td>N556VS-14</td>
<td>0.127</td>
<td>No Fogging</td>
</tr>
</tbody>
</table>
Figure 30. Samples before the experiment (top), after the rapid cooling step, stage 2 (middle), and after the slow cooling step, stage 5 (bottom). Sample ID numbers are included in the top image. Cube samples are fresh EJ-200, 2 field aged samples, and PMMA, left-to-right.
Figure 31. Pure PVT (top) and pure PS (bottom) before the experiment and after stage 2, 5, and 6, respectively. The morphology of fogging defects is dependent on cooling rate.
Figure 32. Optical microscope images of permanent defects in PVT-1 (left), PS-2 (middle), and VT-5 (right). All images are on the same scale.
PVT. Although VT-5 is PVT-based, the permanent defects are larger, less densely packed, and have a different morphology than those in pure PVT. This means that the additives that allow it to scintillate have an impact on fogging. The samples that turned yellowed before and after stage 2 are pictured in Figure 33. Neither sample fogged but both were visibly yellowed when compared to the fresh samples, with N556S-9 yellowing more severely. Yellowing only occurred in PS-based compositions.

4.2.1.2 Scintillation Results
Gamma-ray excited pulse-height spectra were taken five times during the experiment as shown in Figure 29. All samples except pure PVT and pure PS scintillate. Gamma spectra for VT-5, N556V-8, N556S-9, and N556VS-14 are plotted in Figure 34 to highlight the variation in scintillation performance for different materials. As it can be seen, gamma response to the environmental aging experiment varied based on sample composition. For instance, the gamma spectrum for VT-5 was only slightly affected by the experiment. Conversely, N556V-8 and N556S-9 suffered both in light yield (channel number) and shape of the Compton edge. N556VS-14 degraded in light yield but the Compton shape was unchanged. VT-5 responded similarly to previously measured plastic compositions in this size sample, with slight reduction in light yield due to increased scattering after fogging but returned to the initial performance after fogging disappeared. Although the yellowed samples are still transparent, their scintillation performance was negatively affected by the degradation.

Because there was such variation in the shape of spectra, the inflection point on the Compton edge was used as a reference point for each measurement. Relative light yield was calculated by dividing the channel number of the inflection point of the Compton edge by the channel number of the inflection of the Compton edge measured on the fresh sample of each composition.

The channel number of the inflection point on the Compton edge and relative light yield using this value are plotted in Figure 35. Samples that fog (plotted in black) have a higher light yield and only suffer a minor loss of light output after fogging. These losses due to light scattering on fogging would surely be exaggerated on full-size panels like those used in radiation portal monitors. The VT-5 sample finished with a slightly higher channel number (~1%) than the initial measurement. This is most likely due to slight changes in sample coupling and Teflon reflector application. In general, the PS-based compositions performed worse both absolutely and relatively after aging, with the sample that had the most yellowing suffering the most. Both N555V-6 and N556V-8 maintained 90% of their light output after rapid cooling and seemed to remain stable after their initial decline.

As can be seen in Figure 35, even the fog-resistant compositions (those colored in red and blue) were susceptible to reduction in scintillation performance after the accelerating aging experiment. However, is it not immediately clear if this is caused by the high humidity, high temperature, or both. To better understand this, four of the new compositions with different responses to the aging experiment were chosen to undergo a dry annealing experiment. One fresh sample of N555S-7 (no fogging), N556S-9 (yellowing), V/M5-11 (fogging), and N556VS-14
Figure 33. N555S-7 (top) and N556S-9 (bottom) before the experiment (left) and after stage 2 (right). N556S-9 yellowed more severely than N555S-7.
Figure 34. $^{137}$Cs gamma spectra for a) VT-5, b) N556V-8, c) N556S-9, and d) N556VS-14 at five points during the experiment.
Figure 35. Channel number of inflection point on Compton edge (top) and the relative light yield calculated using those values (bottom) as a function of aging experiment stage.
(no fogging) were placed in a dry furnace at 50 °C and pulse height spectra were acquired at room temperature after 26 days and after 50 days. Although humidity was not controlled during the dry annealing, it was monitored at below 25% RH. Additionally, V/M5-11, a foggable composition, contained no fogging after 50 days of dry annealing.

The $^{137}$Cs spectra for these samples, as well as the $^{137}$Cs spectra for the same compositions after the first saturation stage of the accelerated aging experiment are plotted in Figure 36. Just as with the high-humidity aging, all samples performed worse after dry annealing. However, all compositions still performed better after 26 days of dry annealing than after 23 days of wet annealing. After an additional 24 days, all samples’ Compton inflection points were similar to those of the wet heated ones. This experiment shows that the scintillation response of the new compositions can be reduced by annealing alone but is accelerated in high humidity.

4.2.2 Triton-X Compositions

4.2.2.1 Single fogging cycle

Triton-X samples and the EJ-200 sample are pictured in Figure 37 before and after the fogging cycle. Photoluminescence excitation and emission of the Triton-X blend samples were measured before and after aging. Figure 38 compares PL emission and excitation of TX7A before and after aging. All emission spectra were excited at 370 nm, while all excitation spectra were measuring for 435 nm emission. The photoluminescence of the Triton-X samples was not changed after the saturation and cooling. The excitation of the EJ-200 changed slightly after fogging, with more intensity in the 250-370 nm range. Light in this range produced in the bulk of the sample is below the absorption edge of the PVT, causing it to be self-absorbed. In the fresh sample, most light in the 400 nm peak leaves the sample, while the lower wavelengths are reabsorbed. In the fogged sample, the fogging causes scattering of any light produced in the bulk, so the relative intensity of the 400 nm peak is reduced. A similar effect is seen when PL of different sized samples are measured.

Each sample was measured for scintillation response using a $^{137}$Cs source. The collected gamma spectra for all four 1” cubes are plotted in Figure 39. EJ-200, TX7B, and TX7C all showed similar levels of reduction in light yield, while TX7A was almost unchanged.

4.2.2.2 Multiple fogging cycles

The mass change for those samples after the 60-day soaking period are shown in Table 7. EJ-200 had a typical water absorption of 0.04 % in mass, which is in the same order of magnitude as the water absorption for TX7C. A larger mass change was observed for TX7-A and TX7-B, indicating that those samples absorb more water than the commercially available composition EJ-200.

After the first temperature cycle, TX7A and TX7B were the only ones that did not fog as seen in Figure 40. It is believed that TX7C was not fully saturated after the first cycle discussed in the previous section. The fogged samples are also shown in Figure 41 with a higher amplification; it is possible to see that EJ-200 had a higher density of defects than TX7C after one cycle. All the four samples were put back in water at 50 °C to initiate the second cycle.
Figure 36. Gamma-ray spectra of a) N555S-7, b) N556S-9, c) V/M5-11, and d) N556VS-14 fresh samples and after dry annealing for 26 and 50 days. The collected spectra after stage 2 of the accelerated aging experiment are also included for reference (labeled as wet aging).
Figure 37. 1” cube samples before (top) and after (bottom) one saturation/cooling cycle.
Figure 38. Photoluminescence of the 1” cube samples before and after the saturation/cooling cycle. All emissions were measured with 370 nm excitation and all excitations were measured at 435 nm emission.
Figure 39. $^{137}\text{Cs}$ spectra of the 1” cube samples before and after one saturation/cooling cycle.
Table 7. Mass change of the Triton-X samples and EJ-200 after soaking in water for 60 days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass before soaking (g)</th>
<th>Mass after soaking (g)</th>
<th>Mass change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EJ-200</td>
<td>14.27628</td>
<td>14.28193</td>
<td>0.04</td>
</tr>
<tr>
<td>TX7A</td>
<td>14.69167</td>
<td>14.70815</td>
<td>0.11</td>
</tr>
<tr>
<td>TX7B</td>
<td>15.21871</td>
<td>15.24450</td>
<td>0.17</td>
</tr>
<tr>
<td>TX7C</td>
<td>14.88023</td>
<td>14.88873</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure 40. 1-inch cube samples after the first temperature cycle.
Figure 41. 1-inch cube samples EJ-200 and TX7-C after the first temperature cycle. The density of defects is higher in EJ-200 than in TX7-C.
We observed that after 1 h in hot water the EJ-200 sample was clear but TX7C still had defects as shown in Figure 42; in this Figure, the defects seen on the edges of EJ-200 started appearing when the sample was removed from water and put on the bench top, while the defects in TX7C could be seen when the sample was still immersed in hot water. The larger defects in TX7C are a possible reason why this sample did not defog as fast as EJ-200, since it would take longer for the water molecules to diffuse out of big defects into the polymer matrix; we would expect that the smaller defects in EJ-200 would fade out quicker. Another possibility is that the water diffusion rate in TX7C is lower than in EJ-200, which would make the defogging process slower in the first composition.

Figure 43 shows the samples after the sixth temperature cycle. No major differences were observed between the visual aspect of the samples after the first and the sixth temperature cycles. The samples TX7A and TX7B remained free of defects while EJ-200 and TX7C had similar concentrations of temporary defects. It is possible that TX7-A and TX7-B can still fog but require cooling to below 0 °C or more fogging cycles.

4.3 Multiple Cycling

Although new compositions were tested after a few aging cycles, multiple cycles are required to better simulate environmental conditions. In this experiment, the three Triton-X compositions, fresh EJ-200, and 5 of the most promising LLNL/Eljen compositions were chosen. Table 8 includes a list of these compositions. 1” cubes were cut from each composition and placed in the environmental chamber, where they were saturated for seven days. The samples were then cycled between 50 °C / 90% RH and -30 °C / 20 % RH. A 1-hour ramp was used, and samples were held at each condition for 1 hour. Samples were exposed to 100 total cycles, with photographs and microscope images taken periodically. After the experiment, samples were returned to 50 °C and 90% RH and then cooled to -30 °C over 48 hours.

Photographs of the fresh samples, as well as after 1, 48, and 100 cycles, are included in Figure 44. All of the samples are transparent before the experiment, and three compositions are fogged after 1 cycle, EJ-200, V/M5 and V/M10. V/M10 was not fully saturated after the first cycle (as is evident by the lack of fogging defects in the center of the sample) but was nearly fully fogged after all 100 cycles. Microscope images of the defects in EJ-200 are compared in Figure 45. The size and density of defects in EJ-200 are not significantly different after 100 cycles than after 1 cycle.

The cubes were saturated once more and cooled to -30 °C over 48 hours. No new compositions fogged as heavily as EJ-200, V/M10, or V/M5, but TX7C did contain some sparse defects that can only be seen under the optical microscope, one of which is pictured in Figure 46. The density of these defects is much less than those produced in the previous section when TX7C was saturated in water. In this experiment, the TX7C sample gained 0.042 % mass in water, only slightly less than in the water saturation experiment (listed in Table 7).
Figure 42. 1-inch cube samples after soaking in water at 50 °C in the second cycle.
Figure 43. 1-inch cube samples after the sixth temperature cycle.
Table 8. Compositions chosen for the multiple cycling experiment.

<table>
<thead>
<tr>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>EJ-200</td>
</tr>
<tr>
<td>TX7A</td>
</tr>
<tr>
<td>TX7B</td>
</tr>
<tr>
<td>TX7C</td>
</tr>
<tr>
<td>N555V</td>
</tr>
<tr>
<td>N556V</td>
</tr>
<tr>
<td>V/M10</td>
</tr>
<tr>
<td>V/M5</td>
</tr>
<tr>
<td>N556VS</td>
</tr>
</tbody>
</table>
Figure 44. The 9 samples tested in the multiple cycling experiment before (top), after 1 cycle (middle), and after 100 cycles (bottom). The three fogging compositions are EJ-200, V/M5, and V/M10.
Figure 45. Optical microscope images of EJ-200 after 1 cycle (top), 43 cycles (middle), and 100 cycles (bottom).
Figure 46. Optical microscope image of TX7C.
4.4 Conclusions

In this chapter, water uptake, fogging status, and scintillation performance of various new compositions was tested. An environmental chamber was used to simulate aggressive environmental conditions with varying cooling rates to produce different types of fogging. Compositions that contain PMMA, DVB, and PPO absorb more water, but can be resistant to fogging, with compositions N555V-6, N555S-8, N556V-12, N556S-13, and N555VS-14 remaining un-fogged after two saturation-cooling cycles. Scintillation measurements revealed a reduction in relative light yield after these cycles in most new compositions, an effect that has been recreated using dry annealing. It is possible that an optimization in production processes could prevent this in the future.

Triton-X compositions were also tested using saturation-cooling cycles. Of the three new Triton-X compositions, TX7A and TX7B remained un-fogged after multiple cycles, and TX7A especially retained light yield after heating. Compositions were also tested with 100 cycles of rapid heating and cooling (1 hour ramps) in the environmental chamber. Fogging samples were not drastically changed between 1 cycle and 100 cycles, and out of the compositions that did not fog after cycle 1, only TX7C contained defects (albeit only a few). It is possible that TX7C fogs differently after saturation in water than in high-humidity, or it requires maximum saturation to produce many fogging defects, like those seen in Figure 43.
Chapter 5
Fogging Kinetics

This chapter contains research that was carried out to better understand the properties of moisture uptake and fogging disappearance. Some of these results have been published in a peer-reviewed journal by Matthew Loyd. Minor changes have been made to provide a better flow within the larger dissertation.

The full citation for the published manuscript is as follows: Matthew Loyd, Matheus Pianassola, Charles Hurlbut, Kyle Shipp, L. Sideropoulos, Ken Weston, Merry Koschan, Charles L. Melcher, Mariya Zhuravleva, Effects of temporary fogging and defogging in plastic scintillators, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 922, 2019, Pages 202-208 [42]. The author would like to fully acknowledge and thank the efforts of the co-authors for their help.

5.1 Diffusion of Water in Plastics
5.1.1 Introduction
One important aspect of fogging is the absorption of water into plastics and the movement of absorbed water during heating and cooling. Fresh-cast plastic scintillations should be moisture free but will still contain microscopic pores. In the case of polystyrene, positron annihilation spectroscopy has been used to measure a free volume fraction of 5.7% at room temperature and average pore sizes of 2.88 Å [49], while more recent studies have calculated pore sizes as large as 10 Å at room temperature for PS [50]. However, both reports agree that the pore size of PS should increase as temperature increases. Although there are no current measurements for pore size or free volume in polyvinyl toluene, both plastics have a similar molecular structure.

As mentioned in chapter 1, water movement in plastics is controlled by Fickian diffusion which can be explained by Fick’s second law [35, 51]:

$$D \frac{d^2C}{dx^2} = \frac{dC}{dt}$$

where $C$ is the concentration of water, $x$ is the distance into the plastic, and $D$ is the diffusion coefficient, which for PVT is $1.3 \times 10^{-7}$ cm$^2$/s at 23 °C [52, 53]. The diffusion coefficient is almost always a function of temperature, and changes based on the Arrhenius equation [54]:

$$D = D_0 e^{-\frac{E_A}{RT}}$$

where $D_0$ is the theoretical limit of the diffusion coefficient, $E_A$ is an activation energy, $R$ is the gas constant, and $T$ is the Temperature. Using this relationship and experimental data, the diffusion coefficient of water in PVT was calculated to be $1.11 \times 10^{-6}$ cm$^2$/s and $4.44 \times 10^{-7}$ cm$^2$/s at 55 °C and 20 °C, respectively [39]. Another experiment yielded a value of $5.8 \times 10^{-6}$ cm$^2$/s for $D_0$ [35].

Because the plastic initially contains no water, any humidity in the surrounding environment will create a concentration gradient, which is the driving force for diffusion. Relative humidity of air
is the percentage of total saturation of water in air at a given temperature. The saturation vapor pressure of water in air can be estimated using the Arden Buck equations [55, 56]:

\[
P(T) = 0.61121e^\left(18.678 - \frac{T}{234.5}\right)\left(\frac{T}{257.144} + 1\right), \text{for } T > 0 \, ^\circ C
\]

\[
P(T) = 0.61115e^\left(23.036 - \frac{T}{333.7}\right)\left(\frac{T}{279.824} + 1\right), \text{for } T < 0 \, ^\circ C
\]

where \( P \) is the saturation vapor pressure in kPa and \( T \) is the air temperature in Celsius. Once the pressure has been calculated, it can be converted to water concentration using the ideal gas law [57-59]:

\[
PV = nRT
\]

where \( P \) is pressure, \( V \) is volume, \( n \) is the mols of a gas, \( R \) is the ideal gas constant, and \( T \) is the temperature. Although the law can be used with unit systems, the typical SI units are pascals for pressure, m\(^3\) for volume, moles for amount of a gas (\( n \)), and Kelvin for temperature. Using these units, the correct gas constant is 8.314 J/K*mol. The saturation vapor pressure and density of water in air as a function of temperature is plotted in Figure 47. Additionally, multiple relative humidities have been calculated and plotted to demonstrate how water concentration varies with temperature.

As can be seen in Figure 47, both vapor pressure and density of water in air increase with temperature. Because density is a function of temperature, it is not directly correlated with the vapor pressure.

5.1.2 Modeling Diffusion

As we saw in the previous section, an increase in temperature yields both higher maximum concentrations of water vapor and faster diffusion of water in plastics. Combined, these create a condition in which water uptake and retention in plastics leads to fogging defects. However, even plastics with minimal water uptake, such as pure PVT, will absorb more water per volume than the air surrounding it. The density of water in air at different relative humidities, as well as the saturation density of water in various plastics at 55 °C are compared in Table 9. This discrepancy can be explained by the bonding of water molecules on plastic molecules. As the water diffuses into the plastic, there is a small, ~ 1 mm thick layer where the concentration of water increases further into the plastic [41]. Although this complicates the absorption of water into plastics, the movement of water in plastics in one direction can be modeled relatively well using the diffusion equation and an assumption of an infinite thickness [35, 36, 41]. While an analytical solution to this scenario has been found [60, 61], a more simple method is to solve the equation numerically using a programming language like Python [62].

To solve the diffusion equation numerically, a model has to be set up that contains boundaries...
Figure 47. Water vapor pressure (line) and density (dotted line) in air as a function of temperature. Three relative humidities are plotted: 100%, 75%, and 50%.
Table 9. Density of water in different saturated plastics and air at various relative humidities at 55 °C.

<table>
<thead>
<tr>
<th>Environment/Material</th>
<th>Water Density (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air at 100 % RH and 55 °C</td>
<td>104.12</td>
</tr>
<tr>
<td>Air at 75 % RH and 55 °C</td>
<td>78.09</td>
</tr>
<tr>
<td>Air at 50 % RH and 55 °C</td>
<td>52.06</td>
</tr>
<tr>
<td>Pure PVT</td>
<td>693.97</td>
</tr>
<tr>
<td>Pure PS</td>
<td>921.32</td>
</tr>
<tr>
<td>N555V</td>
<td>1133.05</td>
</tr>
<tr>
<td>TX7A</td>
<td>459.04</td>
</tr>
<tr>
<td>TX7B</td>
<td>451.78</td>
</tr>
<tr>
<td>TX7C</td>
<td>377.47</td>
</tr>
</tbody>
</table>
and initial conditions. An extremely simple 5-node model is pictured in Figure 48. The concentration (in this case, the water concentration in the plastic) at each node is represented by the variable $C_n$, and the width between nodes is $dx$. Using this model, the width of $dx$ can be calculated using

$$dx = \frac{w}{N-1}$$  

where $N$ is the number of nodes. Using the fundamental theorem of calculus, we can estimate the first derivative of concentration with respect to distance $x$ at point $i$ with the equation

$$\frac{dC}{dx} = \frac{C_{i+1} - C_i}{dx}$$  

as long as $dx$ is relatively small. We can take this one step further to estimate the second derivative by plugging in $dC/dx$ at points $i$ and $i-1$ for $C$ in equation 7 to get

$$\frac{d^2C}{dx^2} = \frac{1}{dx} \left[ \left( \frac{C_{i+1} - C_i}{dx} \right) - \left( \frac{C_i - C_{i-1}}{dx} \right) \right]$$  

which simplifies into

$$\frac{d^2C}{dx^2} = \frac{C_{i+1} - 2C_i + C_{i-1}}{dx^2}$$  

Finally, we can plug in equation 9 into the diffusion equation (eq 1) and multiply both sides by $dt$ to get

$$dC = D \left( \frac{C_{i+1} - 2C_i + C_{i-1}}{dx^2} \right) dt$$  

Because we know the initial values for $C$ at each position (based on boundary and initial conditions) and $dx$, we can solve for the concentration at a given point after a time step $dt$ with

$$C_i = C_{i0} + D \left( \frac{C_{i+1} - 2C_i + C_{i-1}}{dx^2} \right) dt$$

Therefore, the concentration of water at each node can be solved relatively simply using for loops in Python. For these models, the assumption has been made that the concentration of the boundary nodes rapidly reaches the maximum saturation when surrounded by high humidity environments and similarly rapidly reaches 0 when in a dry environment. Additionally, the concentration at every node except the boundaries have been set to 0 for the first time-step. Using this model and these assumptions, the water concentration of a 5 cm thick PVT plastic while saturating has been plotted in Figure 49.

5.2 Experimental

The materials used in this chapter are the same (and follow the same naming convention) as those in section 3.1.1. From each of FA1, FA2, FPVT, NF, as well as pure PS and pure PMMA, 1” (2.54 cm) cubes were cut and polished to investigate the process of defogging. Defogging (or
Figure 48. A 5-node region of width w. The concentration at each node is represented by the variable $C_n$. 
Figure 49. Water concentration in a PVT plastic as a function of time modeled using a numerical solution to the diffusion equation.
fading of the induced temporary fogging) occurred after the water in the samples was allowed to diffuse out in ambient conditions over time. To monitor the progression of water diffusion, both visual observations and gravimetric analysis were used. The distance from the clear edge of the sample to the fogged area (defogging front) as well as the sample mass were measured daily over a period of 30 days.

It has been assumed that once defects are permanent, water will fill these voids when a plastic is saturated. In order to test this, 10x10x5 mm samples from the block FA1-D (with defects) were subjected to a range of temperatures from 25 to 175 °C. The samples were placed on a glass plate in a furnace for 20 min and a thermocouple recorded the temperature of the sample. A KEYENCE optical microscope and ImageJ were used to measure the size of the defects.

In addition to monitoring defogging in plastics to study diffusion of water, an experiment was planned to visualize water in plastic scintillators. The goal was to image water location in permanent and temporary defects using tritiated water to saturate plastic samples. The radioactive water would then produce scintillation photons near the water due to the low decay energy of H³ (5.7 keV average). A 10 x 10 x 5 mm permanently fogged piece of FA-1-D was saturated at 55 °C in H³ water for 14 days. N-1-D was chosen to learn if liquid water was stored in permanent defects. Table 10 includes the radioactivity of the tritiated water and the expected activity of the saturated sample. The number of scintillation photons was calculated using equation 1.

\[ N = A \times m \times SL \times LY \times E \]  

A is the activity of the H³ water, m is the mass of the sample, SL is the saturation limit of water in the plastic, LY is the light yield of the sample, and E is the average electron energy of H³ decay (5.7 keV). Because of the small mass of water absorbed in the sample, the relatively low light yield of plastic scintillators (~10,000 Ph/MeV), and the low average energy of H³ radioactivity (5.7 keV), the saturated sample will only produce ~ 125 photons per second.

5.3 Results
The water uptake during saturation and water desorption during defogging were investigated via optical microscopy and gravimetric analysis. The 1” (2.54 cm) cubes of FA1, FA2, FPVT, NF, PS, and PMMA were saturated in a liquid water environment and cooled to room temperature to produce temporary fogging. The mass of each sample was measured immediately after cooling to represent the water uptake, which corresponds to the mass at day zero in Figure 50. At day zero, PMMA had the highest water uptake (0.56 wt %) of all 6 samples, which can be associated with its strong interaction with water through hydrogen bonds. The high retention of water in the PMMA sample has been observed in similar previous measurements [34]. As expected, NF had the second highest water uptake (0.074 wt%) most likely due to the 5 wt% of PMMA in its formulation. The other four samples (FA1, FA2, FPVT, and PS) absorbed almost equal amounts of water upon saturation (0.039, 0.038, 0.038, and 0.05 wt%, respectively) and produced temporary fogging defects with different densities. Interestingly, PMMA absorbed > 5 times as
Table 10. Activity of H3 water and expected activity in the saturated sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity of H(^3) water</td>
<td>44,220 Bq/g</td>
</tr>
<tr>
<td>Mass of saturated sample</td>
<td>~0.5 g</td>
</tr>
<tr>
<td>Expected mass of H(^3) water in sample</td>
<td>&lt; 0.5 mg</td>
</tr>
<tr>
<td>Activity of Sample</td>
<td>~ 22 Bq</td>
</tr>
<tr>
<td>Expected # of Photons</td>
<td>~125 ph/s</td>
</tr>
</tbody>
</table>
Figure 50. Mass change for all 6 samples as a function of defogging days (left) and detail for the samples with low mass change (right).
much water as NF and the other samples; however, neither PMMA nor NF fogged. These observations indicate that the amount of water uptake for each material is not correlated with its tendency to develop temporary fogging under given environmental conditions.

Water desorption profiles for FA1, FA2, FPVT, NF, PS, and PMMA during defogging over a period of 30 days is plotted in Figure 50. The mass never drops fully to zero, indicating that there is some residual moisture remaining at ambient conditions. The mass change of all samples drops rapidly during the first 5 days then slows down over the next 25 days. This non-linear water desorption profile is expected with Fickian diffusion, as there is a large gradient when the samples are first removed from the water but as the water content at the surface drops, so does the diffusive flux.

The distance from the clear edge of the sample to the fogged area (defogging front) was measured to determine the defogging rates. The clear edges surrounding a fogged interior that formed after 7 days of defogging are pictured in Figure 51 (left); the black lines exemplify how the defogging front was measured. The average of the 4 distances for each sample is plotted as a function of defogging days in Figure 51 (right). It became difficult to accurately measure a defogging front in the PS sample after day 8, so no more measurements were plotted. Based on the slope of the curves we conclude that the defogging rate is similar for FA1, FA2, and FPVT, and PS. However, the defect density for PS was much less than the other fogged samples. Since the field-aged samples defog at the same rate as the fresh PVT, we speculate that the invisible permanent defects that may be present in the field-aged samples do not affect the diffusion of water out of the plastic.

After the four fogged samples were allowed to defog in ambient conditions, some permanent defects remained. The appearance of all six cubes after defogging for 30 days is shown in Figure 52. These permanent defects are believed to have formed during the defogging process with a different mechanism from temporary fogging. As the dense, temporary defects disappear starting at the edge of the sample, some permanent defects remain in a “halo” that is the same shape as the defogging interface. A mechanism for the formation of these halos has been proposed by researchers at Oak Ridge National Laboratory (ORNL) [37].

When pieces of FA1 were heated to temperatures above 90 °C, permanent defects were transformed into bubbles. The size of bubbles as a function of temperature is plotted in Figure 53. The morphology of the permanent defects was disc-like and flat for temperatures below 90 °C as seen in Figure 54 (left). Above 95 °C the defects were no longer flat but started having a 3-D morphology as seen in Figure 54 (center). The bubbles seen in the samples heated above 95 °C had similar morphologies with an increase in diameter as the temperature increased; this morphology is shown in Figure 54 (right) for the sample heated at 155 °C. The bubbles keep the disc-like shape from the permanent defects but with a larger volume that originates from the expansion of moisture trapped in the defects. A time-lapse video of the transformation from disc-like defects into bubbles as a sample is heated from room temperature to 200 °C was
Figure 51. Samples after defogging for 7 days (left); defogging rate shown as defogging distance to the surface as a function of days (right).
<table>
<thead>
<tr>
<th>FA1</th>
<th>FA2</th>
<th>FPVT</th>
<th>NF</th>
<th>PS</th>
<th>PMMA</th>
</tr>
</thead>
</table>

*Figure 52. 1” (2.54 cm) cubes illuminated with a LED light after 30 days of defogging. Permanent defects are visible in all fogged samples.*
Figure 53. Schematic representation of sample set-up in the furnace (left); defect size as a function of temperature (right). Defects change morphology from flat to 3D at ~95 °C, which is just above the glass transition temperature.
Figure 54. Optical microscope images of permanent defects after heating samples to 90 °C (left), 95 °C (center), and 155 °C (right)
recorded with images taken every 15 seconds. Images from this time-lapse are shown in Figure 55. The entire video has been attached and is entitled BubbleGrowth.

Only samples that had permanent defects from field-aged plastics formed bubbles when submitted to high temperatures without any previous soaking in water. This means that the bubbles do not originate from volatiles in the plastic composition. FPVT and FA1-C samples formed bubbles when previously soaked in water, which indicates that the expansion of trapped moisture may be responsible for the formation of bubbles from permanent defects.

To confirm the presence of H\textsuperscript{3} in the saturated sample, it was coupled to an R 877 PMT and covered in Teflon tape. Figure 56 compares the PMT response of a saturated sample as well as an un-saturated sample. There is a slight increase in counts in the saturated sample, however it is still minor compared to the background signal of the PMT with no source.

Although the calculated number of visible photons produced by H\textsuperscript{3} per unit area is very low, we attempted to image the saturated sample using two optical microscopes. The first is a KEYENCE VHX-1000. The microscope light was turned off and covered in a blanket to prevent ambient light from hitting the sample. The microscope was set to measure for the longest exposure (16 s), but no scintillation light was detected on the optical microscope.

The second optical detector used was a pixelated CCD camera designed for detecting low levels of light. An image was taken of the sample over 10 hours, but the generated image was indistinguishable from the background. At this point, we have not been able to image the defects in plastic samples using tritiated water due to the small number of visible photons produced per unit area.

5.4 Conclusions

In this chapter we investigated the diffusion driven water uptake and desorption in plastic scintillators. The water uptake in one dimension across 5 cm was modeled using a python code and a diffusion coefficient experimentally determined at 50 °C by Payne et al [39]. The mass and defogging distance in 1” cubes of fresh and field aged samples was measured for 30 days, and the results show suspected a diffusion-driven rate of change. Samples that defogged at room temperature due to diffusion (as opposed to heated to remove fogging) contained permanent “halo” defects. Samples that have been saturated in water or contain permanent defects produce bubbles when heated above 90 °C, confirming the presence of liquid water in permanent defects.
Figure 55. Heating of a FA1-D sample placed on a ~ 200 °C hot plate. Images were taken after 0, 5, 10, and 15 minutes.
Figure 56. PMT response of a non-saturated and an H³ saturated sample of N-1-D.
Chapter 6

Temperature Dependence of Luminescence

One of the reasons plastic scintillators have been chosen for deployment in a variety of environments is due to their stability in relation to temperature changes. Many single crystal scintillators have mild to severe fluctuations in light yield at different temperatures [63-66]. Additionally, measurements have shown that non-proportionality and pulse shape discrimination are strongly correlated with temperature [67, 68]. Plastic scintillators, however, are known to essentially have little to no temperature dependence [69, 70]. These studies are typically done either by measuring x-ray excited radioluminescence while a sample is mounted to a liquid helium cooled cold finger, or by building a way to control the temperature of a sample while mounted to a PMT. In this chapter, Triton-X samples, as well as an EJ-200 reference are excited with visible light and x-rays in the temperature range of -30 to 50 °C to determine their temperature dependence, if any.

6.1 Experimental

Two different size samples were measured in this chapter. The intensity of emission is much higher on the photoluminescence measurement than on radioluminescence due to limitations on x-ray intensity and geometry constrains. In general, a larger sample will result in a higher measured intensity. However, a larger size sample takes longer to enubilate at different temperatures. For photoluminescence, 5 mm cubes were chosen, while 10 mm cubes had to be used for radioluminescence to ensure enough emission intensity.

Both size cubes were cut from TX7A, TX7B, and TX7C, as described in section 4.1.1. These compositions were selected for temperature dependence measurements due to their promising resistance to fogging and their variation in primary fluors and Triton-X blends. Additionally, samples of commercially available EJ-200 were tested for comparison. Samples were mounted on to a copper sample holder with a two-part thermally conductive epoxy and set at 50 °C overnight. The sample holder was then screwed onto a liquid helium-cooled cold finger.

For photoluminescence, emission and excitation spectra were measured at 50 K and room temperature (300 K). The excitation wavelength that produced the maximum emission wavelength was chosen for each sample, and the same for the emission wavelength when measuring excitation.

The luminescence of each composition was studied over the maximum environmental temperature ranges of -30 °C to 50 °C. For PL, emission was measured at 5 °C increments in the range of 415 to 550 nm with a 1 nm step size. RL emission measurements were taken every 10 °C degrees in a wavelength range of 300 to 600 nm also with a 1 nm step size. The total emission intensity for PL and RL was calculated by summing up the total intensity over the entire measured range.

In addition to RL and PL measurements, a $^{137}$Cs spectra was measured for TX7B at different
temperatures. A 10 mm cube sample was mounted on to the copper sample holder and cold finger. $^{137}$Cs sources were then placed closed to the sample and a Hamamatsu R0259 PMT was placed next to the quartz window of the cold head. The signal from the PMT into a Canberra model 2005 Pre-amplifier, an Ortec 672 amplifier, and a Tukan 8K multi-channel analyzer.

6.2 Results
The photoluminescence emission and excitation of all four compositions at 50 K and 300 K are plotted in Figure 57. The excitation and emission of all compositions were extremely similar. All four samples had a lower total emission intensity at 50 K than at room temperature. Additionally, the emission was slightly red shifted and peaks were narrower. TX7B had the most severe reduction in intensity at lower temperatures.

The emission of each sample was also measured at 5 degree increments between 50 °C and -30 °C and are plotted in Figure 58. EJ-200 had a maximum excitation wavelength of 399 nm, while the other three compositions all had a maximum excitation of 402 nm. The emissions were not red shifted or significantly narrowed in the temperature range of -30 °C to 50 °C, but the emission did decrease as temperature decreased. The three Triton-X samples were measured again, this time starting at -30 °C and heating during the measurement. The emission spectra for all thee samples when excited with 370 nm excitation are plotted in Figure 59. The change in intensity as a function of temperature was not consistent across compositions, or even across multiple samples of the same composition at 280, 370, or 402 nm excitation. It is possible that there is an instrumental factor affecting the intensity.

Radioluminescence emission spectra for each sample was measured between -30 °C and 50 °C in 10-degree increments. The RL spectra for TX7A at each temperature are plotted in Figure 60. The shape and intensity of emission is unchanged throughout this temperature range. However, the background counts in the 300-350 nm range increase as temperature decreases, which is the direction that the measurement was taken in. The cause of this increase in background counts is unclear. A similar effect was seen on the other samples measured in this fashion. To correct for this, the average background value in the range of 300-350 nm was calculated for each temperature and subtracted out. The normalized, background subtracted intensities are plotted versus temperature in Figure 62. Once the background has been subtracted, it is clear that if there is any temperature dependence for RL intensity, it is less than the noise of this measurement.

The relative intensity at each temperature was calculated by summing the total intensity at each temperature and dividing by the sum intensity at room temperature. The relative RL intensity for each sample as a function of temperature is plotted in Figure 61. When the integrated intensity is plotted in raw counts, all three samples seem to have a similar temperature dependence with a slight decrease as temperature increases, the opposite effect measured on photoluminescence. However, when normalized, the rate of dependence varies greatly between
the three compositions. In fact, the slope of the dependence is much higher for TX7C, the sample

Figure 57. Photoluminescence of a) EJ-200, b) TX7A, c) TX7B, and d) TX7C at 50 K (blue) and 300 K (black).
Figure 58. Photoluminescence emission of a) EJ-200, b) TX7A, c) TX7B, and d) TX7C between -30 °C and 50 °C.
Figure 59. Photoluminescence emission of TX7A (top), TX7B (middle), and TX7C (bottom) under 370 nm excitation.
Figure 60. Radioluminescence of TX7A at temperatures between -30 and 50 °C in a linear scale (left) and logarithmic right (right).
Figure 61. Integrated intensity of radioluminescence emission for TX7A, TX7B, and TX7C (left) and intensity normalized to the 20 °C measurement (right).
Figure 62. Background subtracted and normalized radioluminescence intensity as a function of temperature. The Y-axis range was chosen as the same as that of the photoluminescence plot, Error! Reference source not found.
with the least intense emission, while it is nearly flat for TX7A, the sample with the highest emission. It is possible that this dependence measured is due to the increased background counts as the measurement was carried out, an effect that would be exaggerated on low intensity measurements.

A final test was measured on TX7B using a $^{137}$Cs source at different temperatures, and the resultant spectra are plotted in Figure 63. Due to geometry and source strength, the spectra were worse than those measured with a sample mounted to a PMT. Similar to RL results, there is no change in relative light yield as a function of temperature. The reason

6.3 Conclusions
In this chapter, the effect of temperature on luminescence (both optically and X-ray excited) of Triton-X compositions and EJ-200 was measured. Photoluminescence results show that all four compositions measured contain a positive correlation between PL emission and temperature, the opposite effect of many single crystal scintillators. Conversely, radioluminescence measurements showed that there is little effect of temperature on scintillation response. The mechanism for the PL change with temperature, and the reason for the lack of change when the plastic is ionized, is not understood at this time.
Figure 63. $^{137}$Cs spectra of TX7B measured at 50, 300, and 323 K.
Chapter 7
Conclusions

7.1 Fogging in Plastic Scintillators
In this research we investigated the properties of temporary fogging and defogging in plastic scintillators. The physical and thermal properties of field aged and fresh plastic scintillators showed that fogging does not affect materials properties such as glass transition temperature. The thermal properties of the polymer matrix are unaffected by fogging; the glass transition temperature of fresh and aged samples was the same in both DSC and DMA measurements. Temporary fogging negatively affects light transport in plastic scintillators, with visible light in the emitted range of plastics reduced by up to 75% over a 0.25 in thickness. However, the shape of radioluminescence and photoluminescence are unchanged in aged versus fresh samples. Additionally, field aged plastics did not behave significantly differently than laboratory aged samples.

Plastic samples were saturated in both liquid water and high humidity environments. Temporary fogging was formed by cooling saturated samples rapidly (< 1 hour). These temporary fogging defects are fairly small (~ 20-300 µm in diameter) and will disappear as water diffuses out of the plastic or when the plastic is heated. However, repeating this process on the sample samples reveals that defects appear in the same location, confirming that fogging produces invisible permanent defects in the polymer. Defects will “grow” larger if the plastic is cooled slowly. Larger, permanent defects (100-500 µm in diameter) have also been produced by cooling saturated samples slowly (> 24 hours) or by allowing water to diffuse out of temporarily fogged plastics, which produces defects in “halo” rings.

For the first time, a time-lapse video of a defect growing was produced using a micro-environmental stage on an optical microscope. This can be used to better understand the progression of fogging defects and the transition from temporary to permanent defects.

7.2 New Compositions
New composition plastics developed and provided by collaborators have been studied. Compositions that contained polar molecules were shown to absorb more water but some were resistant to fogging. Two-inch diameter cylindrical one-inch thick samples were saturated at 90% RH and 55 °C and underwent two cooling cycles, one rapid and one slow. The presence of fluors has been shown to affect on the morphology of fogging defects. Defects in pure PVT are smaller and more symmetrical than those in doped plastics, as can be seen in Figure 32. PVT and PS-based scintillators also have different fogging defects, with PS forming fewer, smaller permanent defects. Although PS plastics may be more promising, aside from yellowing of certain compositions, production of PS introduces more technical challenges than PVT.

The scintillation relative light yield was measured after each step to quantify the effect of fogging. The most promising compositions according to this experiment are N556V and N556VS; neither
composition fogged, and their scintillation response was not significantly reduced due to the high
temperature annealing. One-inch cubic samples of compositions containing a Triton-X blend
have also been tested, with TX7A being the most promising.

7.3 Fogging Kinetics
The diffusion driven water uptake and desorption in plastic scintillators was investigated. The
water uptake in one dimension across 5 cm was modeled using a python code and a diffusion
coefficient experimentally determined at 50 °C by Payne et al [39]. The mass and defogging
distance in 1” cubes of fresh and field aged samples was measured for 30 days, and the results
show suspected a diffusion-driven rate of change. Samples that defogged at room temperature
due to diffusion (as opposed to heated to remove fogging) contained permanent “halo”
defects. Samples that have been saturated in water or contain permanent defects produce
bubbles when heated above 90 °C, confirming the presence of liquid water in permanent
defects.

7.4 Temperature Dependence of Luminescence
The effect of temperature on luminescence (both optically and X-ray excited) of Triton-X
compositions and EJ-200 was measured. Photoluminescence results of 5 mm cubes show that
all four compositions measured contain a positive correlation between PL emission and
temperature, the opposite effect of many single crystal scintillators. Conversely,
radioluminescence measurements on 10 mm cubes showed that there is little effect of
temperature on scintillation response. The mechanism for the PL change with temperature, and
the reason for the lack of change when the plastic is ionized, is not understood at this time.

Based on these results, new compositions N556V, N556VS, and TX7A are all promising for
replacing fogging plastic scintillators in high-humidity environments that undergo temperature
cycles. The TX7A composition has been confirmed to have little to no scintillation temperature
dependence, making it ideal for all temperature environments.

7.5 Novel Contributions
The result of this research includes many results simultaneously collected at Oak Ridge National
Laboratory, Sandia National Laboratory, Pacific Northwest National Laboratory, and Lawrence
Livermore National Laboratory. Additionally, novel contributions to the literature have been
presented.

Although collaborators studied fresh plastics, this was the first work comparing field-aged
samples to fresh and laboratory-aged plastics. Time-lapse study of defects is unique to this work.
An accelerated aging experiment that included multiple cycles of varying cooling rates was using
to study the scintillation performance of new compositions, which compliments the research
done by Lance, Myllenbeck, and Zaitseva [31, 36, 37]. Measuring the temperature dependence
of plastic scintillations is important for calibration and troubleshooting of detectors.
7.6 Future Work

Although much has been discovered in this research, much is still unknown. Future work towards understanding fogging in plastic scintillators would involve measuring scintillation properties and light collection in full-size panels, an extremely time-consuming endeavor. The connection between physical properties of the plastic, such as tensile strength, has not been correlated with fogging defects, but would almost certainly have an effect on defect size and amount of pressure required to make defects. If polystyrene has a higher tensile strength than polyvinyl toluene, it could accommodate more water molecules without producing permanent defects.

Long term, multiple cycling experiments are required to fully confirm that new compositions are resistant to environmental degradation in terms of both physical fogging and scintillation light yield reduction. Although the scintillation performance of studied plastics is stable in environmental temperature ranges, the photoluminescence does change. The cause of this change in visibly excited emission spectra is not currently understood. It is possible that there is an instrumental effect, such as a change of the ambient temperature of the PMT, that is causing the photoluminescence change. A study of the absorption and transmission of plastics at different temperatures might yield more results to help understand this phenomenon.

Although the movement of water in plastics was studied using gravimetric measurements and visibly observing the disappearance of temporary fogging defects, attempts to image water in plastic samples was unsuccessful. Neutron imaging may allow for water detection due to the different in hydrogen density. The use of heavy water may also aid in this endeavor.
List of References


[34] E. D. Sword, "Humidity-induced damage in polyvinyl toluene and polystyrene plastic scintillator," in 2017 IEEE International Symposium on Technologies for Homeland Security


[50] A. Wiezorek, "Development of novel plastic scintillators based on polyvinyltoluene for the
hybrid J-PET/MR tomograph," Ph.D., Institute of Metallurgy and Materials Science


Vita

Matthew Starr Loyd was born in Florida but was raised and lives Tennessee. He was raised in Germantown, his residence through high school. In 2011 he moved east where received his Bachelors in Materials Science and Engineering in 2015 and his Masters in Nuclear Engineering in 2017 at the University of Tennessee, Knoxville. There, he met his wife Sydney, with whom he is a happy father to a Goldendoodle, Penny. Matthew was driven to engineering by his passion of math and building Legos, as well as his parents Jon and Mary, who always pushed him to succeed and instilled in him a love of knowledge. Outside of research, he enjoys sports, music, playing basketball, and taking walks with his dog and wife.