POLYVINYL TOLUENE AND LITHIUM GLASS COMPOSITES FOR NEUTRON DETECTION

A Dissertation in
Materials Science and Engineering

by
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ABSTRACT

Neutron detectors are required for effective detection of special nuclear materials (SNM). In the past, gaseous neutron detectors, such as He-3, were utilized as the primary means of SNM detection. The expansive deployment of the detectors for Radiation Portal Monitors (RPM) has put a strain on the He-3 stockpile. Since the start of the He-3 shortage, there has been a renewed effort by researchers to identify or fabricate novel alternates to combat this pressing issue. Composite detectors offer a promising avenue to address this crisis and have the potential for added functionalization to detect a wide range of radiation types and energies.

In this dissertation, two types of composite detectors are fabricated using polyvinyl toluene as the matrix and Li-glass fillers in the form of rods and shards. Both materials are scintillators, which means light is emitted after radiation interactions. The polymer has a shorter decay time and sensitivity to gammas and fast neutrons, while the glass has a longer decay time and is sensitive to thermal neutrons. The coupling of the different decay times allow for discrimination between gammas, thermal neutrons, and fast neutrons which is necessary for neutron detection. Additionally, the hydrogenous polymer matrix thermalizes the incident neutrons to realize a wider range of neutron energy. When two materials are coupled in a single detector, challenges arise due to the dissimilar material properties. The mismatched optical properties result in increased light scattering as the scintillated light propagates through the composite. This lowers the optical transmission of the composite, which could be detrimental to detection efficiency.

Three main objectives are considered to address the realization of composite detectors and the effect of light scattering due to added material interfaces. First, a fabrication process is developed for the rods and shards-based composite designs. The composites are then characterized using optical and nuclear techniques. The effect of interfacial surface area on detector performance is quantified experimentally, along with the role that glass volume content plays on light output of the detectors. Second, the role of dopants on the matrix properties is examined using thermal, mechanical and optical characterization techniques. The higher the dopant concentration, the more sensitive the polymer is to fast neutrons. The fabricated detectors in the first objectives only have sensitivities to thermal neutrons and gammas. This highly doped polymer is then used as the matrix to realize triple-pulse-shape discrimination capable composites. Third, an optical light simulation software is utilized to better understand the effect of interfacial surface area of light on light transport. The transmission is modeled for composites with varying glass contents, sizes, shapes, and composite thicknesses.

In this study, all three objectives were addressed and studied to achieve a better understanding of using polyvinyl toluene and Li-glass composites for neutron detection. A facile and scalable fabrication method for rods and shards detector was developed. Additionally composites with high interfacial surface area were found to detrimentally affect both the light transmission and the figure of merit of the composite. These results informed the design of the triple-pulse-shape discrimination capable composite detector. The dopants used to realize fast
neutron sensitivity in the polymer matrix were found to act as plasticizers, creating a mechanical soft material at 25°C. Crosslinking molecules were added to mitigate the plasticizer effect, and storage modulus of matrix with the same dopant concentration increased by an order of magnitude. Therefore a more structurally sound polymer was synthesized without a decrease in detection performance. Finally, the optical light transport model was successfully validated which allowed for accurate simulation of transmission through the composite. The goal of the model was to better understand the relationship of the glass filler parameters, such as interfacial surface area, glass content, and detector thickness, with the propagation of optical light. The model could eventually be used for predicting the transmission through a theoretical composite without the need of a physical sample. It could also be used to guide the experimental fabrication of the composite to maximize nuclear and optical performance. Findings from the model confirmed that interfacial surface area and glass content had an inverse relationship on the composite’s light transmission in a roughly linear trend. The thickness of the composite also had an inverse relationship, and followed an exponential decay.

The important findings of this work to the neutron detection community are wide ranging. First we have identified that filler size and shape have a measureable effect on the gamma rejection and light transmission, which informs future composite detector design. Second, the PSD capable crosslinked PVT resin offers an avenue for the fabrication of a scalable triple PSD composite detector. Third, the ability to model light transport through a composite provides researchers with a tool to simulate optical light transmission without fabricating a physical detector. The model can accurately simulate the light transmission through a composite detector for a wide range of detection parameter such as filler size, shape, content, and composite thickness. Additionally this model can be used in conjunction with nuclear simulations to quantify effect of filler parameters on detection performance.
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<td>$^6\text{Li} + n \rightarrow ^3\text{H}(2.05 \text{ MeV}) + ^4\text{He}(2.73 \text{ MeV})$</td>
<td>1-1</td>
</tr>
<tr>
<td>$PSP = \frac{\int_{t_1}^{t_2} b - Q(t) dt}{\int_{t_0}^{t_2} b - Q(t) dt}$</td>
<td>1-2</td>
</tr>
<tr>
<td>$FOM = \frac{FWHM_g + FWHM_n}{\text{FWHM}_n + \text{FWHM}_g}$</td>
<td>1-3</td>
</tr>
<tr>
<td>$^3\text{He} + n \rightarrow ^3\text{H} + ^1\text{H} + 0.764 \text{ MeV}$</td>
<td>1-4</td>
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<tr>
<td>$^{10}\text{B} + n \rightarrow ^7\text{Li} + ^4\text{He} + 2310 \text{ keV}$</td>
<td>1-5</td>
</tr>
<tr>
<td>$^6\text{Li} + n \rightarrow ^4\text{He} + ^3\text{H} + 4.78\text{MeV}$</td>
<td>2-1</td>
</tr>
<tr>
<td>$%T = \frac{I}{I_0}$</td>
<td>2-2</td>
</tr>
<tr>
<td>$A = -\log \left( \frac{%T}{100%} \right)$</td>
<td>2-3</td>
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<tr>
<td>$FOM = \frac{\text{Centroid}_n - \text{Centroid}_g}{\text{FWHM}_n + \text{FWHM}_g}$</td>
<td>3-1</td>
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<tr>
<td>$R = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2$</td>
<td>4-1</td>
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<tr>
<td>$S = 4\pi \left( \frac{(ab)^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3} \right)^{1/1.6}$</td>
<td>A-1</td>
</tr>
<tr>
<td>$V = \frac{4}{3} \pi abc$</td>
<td>A-2</td>
</tr>
<tr>
<td>$b = a/1.58$</td>
<td>A-3</td>
</tr>
<tr>
<td>$c = a/4.39$</td>
<td>A-4</td>
</tr>
<tr>
<td>$y = \frac{1}{\chi \sigma \sqrt{2\pi}} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}}$</td>
<td>A-5</td>
</tr>
<tr>
<td>$V_{\text{glass}} = \frac{m_{\text{glass}}}{\rho_{\text{glass}}}$</td>
<td>A-6</td>
</tr>
<tr>
<td>$N_{\text{shards}} = \frac{1.65 \times 10^{-5} \text{cm}^3}{V_{\text{glass}}}$</td>
<td>A-7</td>
</tr>
<tr>
<td>$S_{\text{glass}} = N_{\text{shards}} \times 106771 \mu m^2$</td>
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>HEU</td>
<td>Highly Enriched Uranium</td>
</tr>
<tr>
<td>SNM</td>
<td>Special Nuclear Material</td>
</tr>
<tr>
<td>SSNM</td>
<td>Shield Special Nuclear Material</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>PSD</td>
<td>Pulse-Shape-Discrimination</td>
</tr>
<tr>
<td>PSP</td>
<td>Pulse Shape Parameter</td>
</tr>
<tr>
<td>FOM</td>
<td>Figure of Merit</td>
</tr>
<tr>
<td>PVT</td>
<td>Polyvinyl Toluene</td>
</tr>
<tr>
<td>PPO</td>
<td>2,5-diphenyloxazole</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>LGB</td>
<td>Lithium Gadolinium Borate</td>
</tr>
<tr>
<td>CLYC</td>
<td>Cs₂LiYCl₆</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster Resonance Energy Transfer</td>
</tr>
<tr>
<td>VT</td>
<td>Vinyl Toluene</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>Bis(MSB)</td>
<td>1,4-bis(2-methylstyryl)benzene</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic Acid</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>APTES</td>
<td>(3-aminopropyl)triethoxysilane</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectrometer</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analyzer</td>
</tr>
<tr>
<td>CR</td>
<td>Crosslinker</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
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### Nomenclature

<table>
<thead>
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<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>Q</td>
<td>Charge</td>
</tr>
<tr>
<td>b</td>
<td>Baseline</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width Half-Max</td>
</tr>
<tr>
<td>d</td>
<td>Distance</td>
</tr>
<tr>
<td>T</td>
<td>Transmission</td>
</tr>
<tr>
<td>I</td>
<td>Intensity</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>T_g</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>Centroid</td>
<td>Center of Mass for an Object</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive Index</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface Area</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Pi</td>
</tr>
<tr>
<td>$a, b, c$</td>
<td>Semi-axis length of an ellipse</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$\mu, \sigma$</td>
<td>Parameters of Log Gaussian fit</td>
</tr>
<tr>
<td>$y$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$x$</td>
<td>Shard Size, Surface Area, Volume</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of Shards</td>
</tr>
<tr>
<td>$R$</td>
<td>Reflectance</td>
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ACKNOWLEDGEMENTS

During the writing of this dissertation, I have received an immeasurable amount of support and encouragement from many people. First, I would like to thank my advisor Dr. Zoubeida Ounaies for all the guidance and mentoring she has provided me during my graduate research. Her expertise and counsel were invaluable in the formulation of my research and thesis topic.

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Chapter 1

Introduction

1.1 Introduction

1.1.1 Motivation

Detecting neutrons is essential to a wide variety of disciplines like particle physics, cosmic ray detection, materials science, and, in the case of this dissertation, special nuclear material (SNM) detection. All SNM, like highly enriched uranium (HEU) and plutonium, emit neutrons with a unique energy signature. The neutron is a neutral particle, therefore it is much more penetrative through matter than protons or electrons. This characteristic can be exploited to detect shielded special nuclear material (SSNM) that is obscured by material meant to absorb the emitted radiation [4]. There are several different types of shielding that must be discussed in order to understand which radiation detector types are necessary for SSNM identification. Three main types of radiation are emitted by SNM; alpha/beta particles, gammas, and neutrons. Alpha (\(^{4}\)He) and beta (electrons) particles have low to medium penetration of a few mm for aluminum [5]. Thus an alpha and beta detector would not be practical since the radiation would be absorbed well before reaching the detector. Gamma radiation has long penetration depth through low atomic number materials, therefore high atomic number materials, such as lead (Pb) is effective as shielding for gamma radiation [6]. Neutrons have a long attenuation length through high atomic number materials, however, materials with low atomic number materials, like borated polyethylene, are effective at blocking neutron propagation [7]. Therefore radiation detectors for SSNM must have sensitivities to multiple types of radiation, like gammas and neutrons, to increase the likelihood of detection through shielding. Neutrons can also provide information about nuclear reaction dynamics, isotope, and elemental identification necessary for SSNM detection [8]–[10]. The
motivation behind this dissertation focuses on utilizing neutrons to detect SSNM. Neutron detectors can be split into three different categories; liquid, gaseous, and solid. Liquid and gaseous are prone to mechanical failure, therefore solid-state are chosen due to their robustness.

Detection of SSNM has been of upmost importance in recent years due to continued threat of nuclear terrorism [11], [12]. A large number of SSNM detection systems, known as radiation portal monitors (RPM), have been deployed at international border crossings throughout the country [13], [14]. If neutrons are detected by a RPM, then it is possible to garner information about the SSNM without the need to physically search the container or truck. The main requirements for effective detectors of the neutron signature from SSNM are sensitivity to fast and thermal neutrons, high intrinsic efficiency, and the ability to discriminate between gamma rays and neutrons to decrease the nuisance or false alarms. The intrinsic efficiency is defined as the ratio of the number of neutrons detected by the system to the number of neutrons incident on the detector as calculated by the solid angle formula. The final requirement is important because gamma rays are ubiquitous and therefore the detector must have the ability to differentiate between gamma radiation and neutrons. Composite neutron detectors have the potential to meet all the discussed requirements. These types of detectors have unique challenges that arise from the mismatch of material properties, which must be characterized and addressed to further composite detector research. Therefore the focus of this dissertation is developing a composite detector for fast neutrons, thermal neutrons, and gammas along with understanding the role that the interfacial surface area of the filler plays in detector performance.

1.1.2 Neutron Detection Background

Neutrons are one of three particles that compose an atom, along with electrons and protons. The number of protons determines the type of atom and the number of neutrons determines the
isotope of the element. While protons and electrons are charged particles, neutrons are neutral and thus interact with media differently. Therefore methods like the cloud chamber are not sensitive to detection of neutrons since ionization is required [15], [16]. Due to this reason the existence of the neutron was not confirmed until after the proton and electron. James Chadwick used a polonium (Po) source to produce alpha (α) particles that bombarded a beryllium target [17]. An alpha particle is composed of two protons and two neutrons, thus just a helium nucleus stripped of the electrons. When the beryllium (Be) target was irradiated with an alpha particle, a neutron was produced and penetrated paraffin wax (Figure 1-1). The wax then ejected protons which were observed using an ionization chamber. The measured protons had energies much higher than what could be produced by gamma rays therefore it was reasoned that a neutral particle of a similar mass must exist. Since its discovery, a variety of methods have been developed to characterize the neutrons and the next paragraph will focus on such techniques.

Figure 1-1: A schematic of the experimental setup by James Chadwick for the discovery of the neutron [1].

Neutron detection and spectrometry are usually classified in seven unique categories[18]
1. Measuring the energy of a nucleus recoiling from a neutron scattering event
2. Measuring the charged particle’s energies after a nuclear reaction induced by incident neutrons
3. Measuring the neutron velocity, known as time-of-flight (ToF)
4. Detecting the occurrence of an effect like radioactivity that can only be produced by a neutron with a minimum energy is called the threshold method
5. Utilizing the diffraction of the neutron through a certain material
6. Unfolding the energy distribution of the neutrons using a set of detectors and their readings
7. Measuring the time-distribution of high energy neutron retarded in an acceptable medium

For this work, the first and second methods will be the methods used by the fabricated composite to detect via active interrogation. Active interrogation relies on a radiation source, usually mono-energetic photons or neutrons, to induce nuclear reactions in SNM [19]–[21]. The other technique relies on radiation emission resulting from natural decay of the SNMs and is known as passive interrogation [22].

1.1.3 Gamma and Neutron Detection Mechanisms

It is important to understand the detection mechanisms for different types of neutrons, fast and thermal, and gamma radiation to fulfill the design requirements posed in the Section 1.1.1. Fast and thermal refer to the energy of the emitted neutron and correspond to kinetic energy of 0.025 eV and $\geq 0.5$ MeV respectively [23]. Thermal neutrons have lower kinetic energy thus travel slower through materials compared to fast neutrons. This fact results in a higher probability of thermal neutron capture on an element’s nucleus. There are a number of nuclides, such as $^6$Li, $^{10}$B, $^3$He, and Gd, which have relatively large absorption cross-sections and thus are good candidates
for thermal neutron detectors [24]. The absorption cross-section is a measure of the likelihood that an incident neutron will be absorbed by the target nucleus. An example neutron capture reaction on $^6$Li isotope is shown below in Equation (1-1). The capture reaction releases a set amount of energy and is quantified as the reaction’s Q value. An alpha ($^4$He) and triton ($^3$H) particles are produced and travel in opposite directions through the material. The particles can then interact with the material causing a measurable signal that can be correlated to a neutron capture.

$$ ^6\text{Li} + n \rightarrow ^3\text{H}(2.05 \text{ MeV}) + ^4\text{He}(2.73 \text{ MeV}) \quad (1-1) $$

For neutrons with higher energies such as fast neutrons, a moderating material is needed. Moderators, usually composed of hydrogenous materials, help dissipate the fast neutron kinetic energy by elastic scattering with hydrogen nuclei. Water and some polymers are excellent candidates for moderating materials since their chemical structure could contain a large amount of hydrogen. Once moderated, the nuclides with large absorption cross-sections, efficiently capture the incoming neutrons. Fast neutrons can also be detected due to their creation of large amounts of triplet states produced as it travels through a scintillation detector as postulated in Birks’ book “The Theory and Practice of Scintillation Counting” [25]. These triplet states annihilate when two interact with each other resulting in a singlet ground and excited state. This excited state then relaxes and emits light with a decay time on the order of nanoseconds but slightly longer than gamma interactions [26]. Another term for this process is called delayed fluorescence [27]. The higher the density of triplet-triplet states the longer the decay time of the fluorescent light. Since the energy of this delayed fluorescence is lower than prompt fluorescence, the difference in wavelengths can also be taken advantage of when differentiating between radiation types [28].
Gammas are measured when a high energy photon travels through the scintillation detector exciting the surrounding material. The material then relaxes from the excited state and emits photons in the process [29]. These emitted photons then undergo multiple absorption and reemission processes depending on the types of dopants used to ensure that visible light is collected at the end of the process. Dopants must be carefully chosen to ensure adequate but not total overlap of absorption and emission wavelengths. The primary dopant transfers the energy from the excited polymer base to the secondary dopant, also known as a wavelength shifting fluor. This process is extremely fast and the light is produced in a pulse with a decay time of a few nanoseconds. The wavelength shifter then emits in the wavelength range where the photomultiplier tube (PMT) is most sensitive, usually 400 – 600 nm [30]. The PMT functions by accelerating photoelectrons created by the scintillation pulse to the anode and the output is read as an electrical signal [31]. Therefore the intensity of the electrical signal is proportional to the energy of the incident gamma meaning one can measure the energy of the gamma particle interacting with the material.

All the discussed mechanisms produce light with varying decay time and energies, which can be taken advantage of to discriminate between the types of radiation. This is known as pulse-shape-discrimination (PSD). PSD is determined by analyzing the differences in scintillation pulses and energy generated from gamma rays and neutrons interacting with the material. Figure 1-2 shows an example PSD plot obtained using a commercially available neutron detector (EJ-270) with three radiation signatures: gammas, fast neutrons, and thermal neutrons [32]. Gamma radiation is ubiquitous and cover a wide range of energies thus their signature in the PSD plot arises as a band usually centered on the lowest PSD value. The low value is attributed to the fast decay time of the light produced by the gamma interaction with the surrounding material. Fast neutrons are also represented in Figure 1-2 in the form of a band at a slightly higher PSD value.
compared to the gamma band. The thermal neutrons are represented with a localized ellipse in both PSD and energy value (Figure 1-2). This unique shape arise from the thermal neutron capture mechanism on a high absorption cross-section nuclide as discussed in previous paragraphs. Therefore the ellipse shape or neutron island is an excellent indicator of thermal neutron capture and can be used to discriminate between thermal and fast neutrons in the terms of energy. It is also worth noting that there is no physical meaning to the negative PSD values. This is an artifact that arises from the PSD values calculations.

![Figure 1-2: Example Pulse-Shape Discrimination plot of commercially available lithium-doped polyvinyl toluene from Eljen Technology (EJ-270).](image)

It is worth explaining the key features of this PSD plot and how they can be utilized to measure the detector’s figure of merit, gamma rejection, and intrinsic efficiency. The x-axis is basically the energy of the detected light pulse. The units of keVee refers to the electron equivalent
of the recoil energy that is measured by the scintillation light. The y-axis is the measure of pulse shape and is denoted as PSD and sometimes PSP (Pulse Shape Parameter). This PSP value is calculated for each pulse using Equation (1-2).

\[
PSP = \frac{\int_{t_0}^{t_2} b - Q(t) dt}{\int_{t_0}^{t_2} b - Q(t) dt}
\]  

(1-2)

The charge is calculated using the baseline, b, subtracted and integrated over the full pulse from the start time of \(t_0\) (or start of the pulse’s tail, \(t_1\)) to the end time of \(t_2\). A graphical representation of this calculation can be seen in Figure 1-3, which shows a simulated pulse of a neutron capture event. In general, a faster light pulse will produce a lower PSP value than a longer light pulse which will have a higher PSP value.

![Graphical representation of pulse signal integration used to calculate a PSP value.](image)

Figure 1-3: Graphical representation of pulse signal integration used to calculate a PSP value.
Using the energy of each pulse and the PSP value a plot is produced with each point corresponding to a specific event. The graphs are usually represented as heat maps to better visualize the density of events since they tend to happen around the same PSP and energy values. This density distribution can help quantify a parameter known as the figure of merit (FOM) of a detector. An energy range is defined then the frequency of events or counts are projected on to the PSP axis. A graphical representation of how the FOM is calculated can be found in Figure 1-4.

Figure 1-4: A graphical representation of the gamma and neutron events projected on the PSP axis.

The FOM is essentially a measure of the separation between a neutron event and a gamma event. The equation used to calculate this value is shown in Equation (1-3) where $d$ is the distance between the centroids of the two peaks and the $\text{FWHM}_g$ and $\text{FWHM}_n$ is the full-width half-max of the distribution for gammas and neutrons respectively [33].
\[ FOM = \frac{d}{FWHM_g + FWHM_n} \]  

(1-3)

This PSD plot can also help calculate the gamma rejection of the composite. This measurement requires the use of a two separate sources, one is the neutron source and the other is a purely gamma source. A neutron event region is first defined on the PSD plot using a neutron source, such as \(^{252}\text{Cf}\), which also emits gammas. Then events are collected by the detector with only a gamma source, such as \(^{60}\text{Co}\). The number of gamma events within the region previously defined for neutrons is used to calculate the gamma rejection. Kouzes et. al. have set a standard way of calculating the gamma rejection and can be referred to for specific requirements [34]. Additionally the intrinsic efficiency can be calculated using this PSD plot as well. This experiment had a neutron source with a shadow cone, usually composed of iron and borated polyethylene, between the source and detector to block incident neutrons from the \(^{252}\text{Cf}\) [35]. Therefore the only neutrons that are recorded in the defined region are due to room return or neutrons scattering off the surrounding walls. The difference in the neutron events without and with the shadow cone corresponds to the response from only the source. These events from the source along with the solid angle is used to calculate the intrinsic efficiency of the detector.

1.1.4 Neutron Detector Literature Review

Since the 1980s, gas-based \(^3\text{He}\) detectors have been the primary means of neutron detection [11]. These detectors function by neutron capturing on a helium nucleus and the reaction products are shown in Equation (1-4). The tritium and proton (\(^1\text{H}\)) travel through the gaseous detector creating a charged cloud which is then detected with a proportional counter or Geiger-Muller tube.

\[ ^3\text{He} + n \rightarrow ^3\text{H} + ^1\text{H} + 0.764 \text{ MeV} \]  

(1-4)
The output pulse that is measured is proportional to the radiation energy that the detector absorbs. This inherently allows for differentiating between different types of radiations such as alpha or beta, purely using the energy of the particle. While these $^{3}\text{He}$ detectors have excellent intrinsic gamma rejection and neutron efficiency, there is an increased need for viable alternatives due to the scarcity of $^{3}\text{He}$ isotope [36], [37]. Since $^{3}\text{He}$ is only produced as a byproduct of the United States nuclear weapons program, the amount produced is dependent on the need for the program. Therefore other gas-based detectors, for example, $\text{BF}_3$ proportional counters, were developed and exhibited comparable detection efficiency to $^{3}\text{He}$ proportional counters [38]. $\text{BF}_3$ detectors function by taking advantage the capture reaction of a neutron on $^{10}\text{B}$ and is shown in Equation (1-5).

\[ ^{10}\text{B} + n \rightarrow ^{7}\text{Li} + ^{4}\text{He} + 2310 \text{ keV} \]  

(1-5)

However, health and environmental risks exist, especially if $\text{BF}_3$ gas escapes due to mechanical damage of the detector [39]. Additionally the gaseous detectors must be operated under pressure, which add another layer of safety and mechanical requirements. This concern is prevalent in all gas-based detectors and leads to the development other detector types, namely liquid and solid-state detectors.

Most liquid neutron detectors are organic and scintillate meaning they contain hydrocarbon or water solvents and light emitting phosphors. These liquid detectors function by measuring the energy of a nuclear recoiling from a neutron scattering event and are known as scintillation detectors. Liquid detectors are attractive alternative to gas-based detectors since they allow a homogeneous dispersion of different elements to create a detector that is sensitive to fast or thermal neutrons [40], [41]. An example of a liquid thermal neutron detector are water-based Cerenkov
detectors. Dazeley et al., developed a Cerenkov detector that utilized trace quantities of Gd compound suspended in the solution [42]. Cerenkov radiation is produced when charged particles travel through water and produce light. For fast neutron detection, organic liquids are used because the solvent contains a high amount of hydrogen. As opposed to the water-based Cerenkov detectors, these fast neutron detectors rely on phosphors, or fluors, to create the scintillation pulse. In most scintillation fast neutron detector there is a primary and secondary fluor. The primary fluor absorbs a large amount of the deposited energy and the secondary fluor re-emits the energy as light in a wavelength that the PMT can detect. Liquid detectors typically possess fast response times, gamma ray/neutron discrimination capabilities, and thermal neutron sensitivities [43]. Another advantage of liquid-based detectors is the easier scalability compared to gaseous detectors. However, the main drawback for liquid detectors is that the most effective solvents are harmful, such as toluene and 1,2,4-trimethylbenzene that could be detrimental to the environment [44], [45]. They are also susceptible to mechanical damage and therefore costly to maintain. Solid-state detectors offer an attractive safer and more robust alternative to both liquid and gas-based detector and are usually composed of crystals, polymers, or glass materials [46], [47].

With solid-state detectors, there have been numerous advances in the field to synthesize homogeneous materials with sensitivity to a wide range of different particles. One important advancement was the fabrication of a homogenous solid-state polyvinyl toluene (PVT) polymer was developed by Zaitseva et al., exhibiting good pulse shape discrimination performance [48]. By using a high weight percent of the fluorescent dopant, 2,5-diphenyloxazole (PPO), the detector could discriminate between gammas and fast neutrons. This study postulated that by loading the polymer with a large amount of PPO, a higher density of triplet-triplet states were created thus facilitating a delay fluorescence with a longer decay time, which corresponds to a larger PSD.
value. This detector however is not sensitive to thermal neutrons because of the lack of thermal neutron capture isotope like $^6$Li or $^{10}$B. As discussed previously these nuclides are required to allow the detector to be sensitive to a wider range of neutron energies. Zaitseva et al. improved this detector by loading PVT matrix with a Li-salt of 3-phenylsalicylic acid [49]. Their results showcased the improved detector’s sensitivity to thermal neutrons due to the presence of a high absorption cross-section nuclide. However, the amount of lithium that can be added is limited at about 0.135-0.27wt%, due to its insolubility in the polymer. Inorganic materials, like glass, are more stable at higher lithium loading of up to 6.6wt%. Therefore coupling organic and inorganic materials into a composite could increase the lithium content of the detector, which leads to an increase in detector performance.

The first composite neutron detector was developed by Knoll et. al who fabricated the detector using $^3$He filled glass spheres embedded in a polyvinyl toluene matrix [50]. The polyvinyl toluene matrix allowed for the thermalization of the incident neutron for more efficient capture in the glass spheres. Recent researchers have also focused on utilizing hydrogenous materials (such as PVT or polystyrene (PS)) to thermalize neutrons for capture on a variety of different neutron sensitive materials. For example Iwanowska et. al. fabricated a composite detector with organic crystals, like p-terphenyl and stilbene, and successfully discriminated between neutrons and gamma-rays [51]. By dispersing these crystal particle throughout the matrix one could achieve homogeneous dispersion throughout the moderating material. There have been several other groups focused on different types of fillers such as lithium gadolinium borate (LGB) glass, and more recently Cs$_2$LiYCl$_6$ crystals (CLYC) [52]–[55].

CLYC are inorganic crystals that have excellent gamma, thermal and fast neutron discrimination capabilities [56]. Another advantage of CLYC is that it remains stable over a wide
range of temperatures which is important if this detector is deployed in high or low temperature regions of our country [57]. However, CLYC is expensive to synthesize and difficult to produce in bulk therefore neutron sensitive glass in a gamma polymer matrix could meet all the requirements for a neutron detector at a lower cost. There are different types of thermal neutron sensitive glass, but the one considered in this dissertation is commercially known as GS20 [58], [59]. This glass has a total lithium wt% of 6.6 and a $^6\text{Li}$ enrichment of 95% which allows for efficient thermal neutron capture. Cerium is added to facilitate scintillation after the neutron capture occurs. Therefore the Ce must remain in a reducing atmosphere during the melt because the Ce$^{4+}$ state will not scintillate while the Ce$^{3+}$ does [60]. While this glass has poor discrimination properties between gamma’s and thermal neutrons it is much less expensive to produce the CLYC.

Thus heterogeneous glass/polymer detectors have the potential to replace homogeneous solid detectors because of the promise for robustness, fast and thermal neutron energy sensitivity, high intrinsic efficiency, and PSD capabilities. Rich et al. successfully demonstrated this possibility by manufacturing a PSD-capable composite detector using PVT and lithium gadolinium borate (LGB) cubes [52]. However when coupling two materials with dissimilar characteristics there will inevitably be some drawbacks. For example the optical properties of the composite could be compromised due to the mismatch of the material’s index of refraction. This interaction between the glass filler and polymer matrix is commonly neglected area of research. Overall there is a fundamental lack of understanding about how the parameters and properties of the filler can affect the nuclear detection and optical properties of the composite. The next section in this chapter will clearly outline the motivation of this dissertation with the aim of answering specific questions to help further understand and quantify how neutron composite design effect performance.
1.2 Focus of Dissertation

The first question this dissertation proposal aims to answer is: *how do the shape of the filler and the presence of internal interfaces in a polymer composite neutron detector affect its light output and efficiency?* Previous simulations using GEANT4.10.0 p1 code reveal that differences in the glass filler size and shape have a measureable effect on the efficiency and gamma rejection of the composite detector, as summarized in Table 1-1 [2], [61]. The paper investigated several different glass geometries such as spheres, rods, and layers with a fixed glass content (at 7wt%). The weight content was chosen because it produced a reasonable neutron efficiency without compromising optical clarity in lithium gadolinium borate glass (LGB) and polyvinyl toluene polymer (PVT) composite [55]. If the weight content is increased, the thermal neutron detection efficiency will increase as well because of the large volume of thermal neutron sensitive material. For a triple PSD detector the increasing glass weight content would adversely affect the fast neutron detection efficiency because of a lower PSD capable PVT matrix volume. It is also worth noting that the model did not consider the propagation of optical photons and only simulated the amount and location of the deposited energy in the material. The different glass geometries had a slight effect on the neutron intrinsic efficiency and a major effect on the number of misidentified gammas (also known as gamma rejection) determined via simulations. $10^7$ gamma rays from $^{208}$Tl and $10^6$ fission neutrons from $^{252}$Cf were simulated. The neutron energies ranged from 1meV to 15MeV. Spheres were determined to be the optimal glass geometry for the relatively high neutron intrinsic efficiency of 6.63% and lowest gamma rejection at 0%. The low gamma rejection is a result of the characteristic path length of the gamma traveling through the glass. Using the NIST ESTAR database, the CSDA range in plate glass is 0.53 g/cm$^2$, or 2.1 mm for the glass density of 2.5 g/cm$^3$ [62]. A 1-MeV electron therefore deposits only a fraction of its energy in 1-mm thick
glass, and higher energy electrons deposit increasingly smaller fraction of their energy. Therefore the size and shape must be considered when designing the composite. The length of the glass in all directions should be smaller than the travel distance of the electron. This will minimize the gamma rejection leading to a more efficiency neutron detector. According to the simulation, misidentification of gammas is eliminated when the glass sphere size is around 280μm in diameter (Table 1-1) [2]. On the other hand, if the glass sphere size increased while keeping the weight constant the thermal neutron efficiency would decreased. Since the lithium is only contained within the glass, the lithium would be localized to a smaller volume of the composite with the increased glass sphere size. Therefore there would be a lower probability that matrix moderated thermal neutrons would be captured in the glass, which would lower the efficiency of the detector. If the neutron sensitive glass was homogeneously dispersed throughout the composite, then the probability of thermal neutron capture anywhere in the detector would increase, thus increasing the thermal neutron efficiency. One limitation is that lithium glass spheres are difficult to manufacture and expensive to purchase therefore the sphere geometry is approximated in this dissertation by crushing bulk glass into shards of similar dimensions. Throughout the dissertation the composites will be referred to using the 0-3 and 1-3 nomenclature. The first number refers to the dimensional connectivity of the composite’s filler. For example the “0” in 0-3 refers to the glass spheres while the “1” in 1-3 represents the glass rods. The second number is the dimensional connectivity of the matrix, which is “3” dimensions in both the rods and spheres composite.
The first aspect of this question will focus on fabricating and experimentally measuring the neutron efficiency and gamma rejection of the composites. The fabrication of rods and shards based detectors will be explored to create scalable and quickly produced composites. Additionally the composites will be characterized with neutron and gamma sources to determine detector properties. The second part is determining the effect of interfacial surface area to volume ratio of the glass filler on the composite’s optical and detection properties.

As stated earlier, PVT can also be doped with fluors to become sensitive to fast neutrons. When coupled with lithium glass, a detector could be fabricated with excellent discrimination between fast neutrons, thermal neutrons, and gammas. This is known as a triple PSD detector. However, for PVT, a loading of 30 wt% PPO is needed to realize this discrimination [48]. The fluors are expected to act as plasticizers, which detrimentally effects the mechanical and thermal properties of the material for neutron detection applications. Loading polystyrene with high amounts of plasticizers have resulted in a lower glass transition temperature making the polymer softer and less structurally stable [63]. The chemical structure of polystyrene is very closely related polyvinyl toluene and has similar mechanical and thermal properties. Addition of crosslinking agents could allow the polymer to be structurally robust and PSD capable. The next question that

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Neutron Efficiency (%)</th>
<th>Gamma Misidentified* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Disks (450μm)</td>
<td>6.67</td>
<td>0.1</td>
</tr>
<tr>
<td>Rod (1x1x150mm)</td>
<td>6.66</td>
<td>0.044</td>
</tr>
<tr>
<td>Sphere (280μm)</td>
<td>6.13</td>
<td>0.0</td>
</tr>
<tr>
<td>Sphere (500μm)</td>
<td>6.63</td>
<td>0.00017</td>
</tr>
</tbody>
</table>

*Values are of $10^7$ gamma events
This dissertation will answer is: *does doping the polymer matrix with fluors and crosslinking molecules help realize a structurally sound triple PSD detector?*

This second question will be answered by fabricating polyvinyl toluene samples with varying amounts of PPO and characterizing the effect on the mechanical, thermal and fast neutron detection properties. A crosslinking agent will then be added and the same characterization techniques will be performed to elucidate any extraneous effects. The well characterized matrix will then be combined with the lithium glass rods and shards to fabricate a triple PSD detector. The detector will be tested with radiation sources to determine the figure of merit, intrinsic efficiency, and pulse shape discrimination capabilities. The fluorescence and optical properties of the composite and matrix will also be explored.

The third and final question that this dissertation aims to answer is as follows: *how does the interfacial surface area affect the light transport through a composite detector explored with optical modeling software?* As mentioned previously, the GEANT4.10.0 simulation that was performed in [2] does not include optical photon propagation. Therefore a different model is required to understand how the glass interfaces could affect the optical photon transport. GEANT4 does have modules that can simulate optical photons however it is limited in what material properties it can model and has a steep learning curve. Other software, like TracePro, are much more intuitive to use and can model complex material properties such as surface coating and bulk material scattering [64]. TracePro utilizes Monte Carlo simulation to randomly generate rays from user input sources. The rays have a specified amount of power and can be visualized as they propagate through the composite. The power loss of incident rays to exiting rays can be related to properties such as fluorescence and transmission. Therefore TracePro is an excellent optical modeling software to help answer the above question.
This final aspect of the dissertation will utilize TracePro optical modeling software to model light transport through composite detectors. The composite built in the software will use experimentally obtained properties such as fluorescence, absorption, refractive index, and scattering coefficient to accurately simulate the transport. After this step is completed, then the models will be validated with experimental results. Lastly the tradeoff between interfacial surface area and light transport through the detector will be explore by modeling different scattering coefficients and shard size without the need to fabricate physical detectors.

1.3 Problem Statement

1.3.1 Dissertation Objectives

Polymer and lithium glass composite neutron detectors offer added benefits when compared to homogeneous neutron detectors. By coupling two materials with dissimilar characteristics such as scintillation decay time, it is possible to have added functionality as compared to the separate components. The additional functionalities include detection of wider neutron energy range, increased mechanical robustness, and better pulse shape discrimination (PSD) due to the inherent difference in material properties. The goal of this dissertation is to explore the relationship between composite materials and neutron detection performance. The study will focus on three main objectives:

The first objective is to successfully fabricate the two detector geometries, 1-3 and 0-3 (defined in section 1.2 page 16), and determine the relationship between glass filler geometry and efficiency.
The second objective is to study the effect of additives like fluors and crosslinking agents on the mechanical, thermal and nuclear properties of PSD-capable PVT. The PSD-capable PVT will then be combined with lithium glass rods and shards to realize a triple PSD detector.

The third objective is to focus on the role that polymer/glass internal interfaces play in the detector performance by utilizing optical modeling software and its validation with experimental results.

### 1.3.2 Expected Outcomes

There are several expected outcomes that will be revisited at the end of the study. First, the shape and size of the glass fillers will be related to the optical transmission and nuclear detection properties of the composite. This will be accomplished by fabricating composite detectors with different filler geometries and weight content, and characterizing their different properties. More specifically, the light transmission through the detector and light output generated by radiation sources will be quantified and related to the original statement.

Another important outcome of this dissertation is to garner an understanding of the efficacy of crosslinking agents in highly doped PVT to realize a triple PSD composite detector. The crosslinking agents are expected to mitigate the plasticizer effect from the high dopant concentration by increasing the glass transition temperature of the polymer. This should result in a more mechanically stable polymer matrix material while hopefully maintaining the same fast neutron detection properties. After the development of the robust PSD matrix is successful, a triple PSD detector will be fabricated and tested to determine its viability as a composite neutron detector.
The final outcome is understanding how polymer and glass interfaces affect light transport through a composite detector. The relationship between these two parameters will be simulated using TracePro optical modeling software. The expected results from this study will be a quantitative relationship between the efficiency of light transport through the composite and the number of interfaces. Additionally by using this relation, the maximum size of a composite with a specific glass filler shape can be a practical outcome that is applicable to the general composite detector community.

1.4 Organization of Dissertation

This section of the dissertation will outline how each chapter is organized.

Chapter 1 describes the history, motivation, and background of this dissertation. Additionally the main objectives for the research and the expected outcomes are discussed. This chapter serves to provide the reader with the requisite knowledge to understand the research and accomplishments for the future chapters.

Chapter 2 introduces the experimental methods that are utilized throughout this work. It focuses mostly on introducing the reader to different characterization tools and how the techniques probe the important properties of the materials. Optical, thermal, mechanical, and nuclear characterization techniques are covered. This chapter also describes the fabrication process of the 0-3 and 1-3 composites. The process includes the polymerization steps of the commercial and in-house synthesized polyvinyl toluene.

Chapter 3 outlines the characterization of 0-3 and 1-3 composites fabricated with commercially available PVT and Li-glass. The effect of the added interfaces is explored using optical and nuclear characterization techniques. The interfacial surface area is related to the
decrease in light transmission and the glass volume content is shown to effect the light output. Additionally the adverse effect of high interfacial surface area on the PSD properties of the composite detector is discussed along with proposed solutions.

Chapter 4 builds on the work done in Chapter 3 by fabricating triple-pulse-shape-discriminating composite. The detector has the ability to discriminate between fast neutrons, thermal neutrons, and gammas. This is accomplished by doping the polymer matrix to high weight percent of fluorescent compounds. The polymer matrix is synthesized in-house in order to control the components and understand the structure-property relationship. The plasticizer effect of the dopants is quantified using thermal and mechanical characterization techniques. Crosslinking molecules are added to mitigate the plasticizer effect. Once the matrix is characterized, a 1-3 and 0-3 triple PSD composite are fabricated. The detector performance of both composites are explored using various radiation sources.

In Chapter 5, a process to generate glass ellipsoids in different weight contents and sizes with randomized spatial orientation and location is developed. The composite is then exported to an optical ray tracing software called TracePro. The light transmission through the individual materials is checked and the composite transmission is validated with experimental data. Several studies are conducted to explore the relationship between glass volume content, interfacial surface area, and composite thickness with optical light transport.

Chapter 6 summarizes all the previous three chapters and highlights the major contributions of each study. It concludes with the future work and how the research could impact the future of neutron detection with composites.
Chapter 2

Processing and Characterization of Composite Neutron Detectors

2.1 Introduction

This chapter will introduce the materials (both in-house and commercially synthesized) used in this dissertation along with the characterization techniques utilized to probe their properties. Polyvinyl toluene is the polymer matrix for the composite detectors and lithium glass is the glass filler in these composites. The synthesis and structure-property relationship of the materials will be discussed along with the fabrication of the various composite configurations. A variety of characterization tools are used in this dissertation, therefore a brief introduction on their theory and analysis is provided.

2.2 Synthesis and Processing of Polyvinyl Toluene

This section will focus on the polymer component of the composite neutron detector. Vinyl toluene (VT) is the monomer of polyvinyl toluene (PVT) and is purchased from Tokyo Chemical Industry (TCI). VT is a derivative of styrene. Styrene is an organic molecule that consists of a ring of six carbons with alternating double and single bonds. Additionally there are two double bonded carbons attached to one of the carbons in the ring (Figure 2-1 (a)). VT has a similar structure as styrene, however it has an additional carbon singed bonded to the carbon ring (Figure 2-1 (b)). The single bonded carbon is known as a methyl group and the carbon ring is a phenyl group. The methyl group can either be in the meta- or ortho- position on the phenyl ring. The meta- position is the position of the methyl group as pictured in Figure 2-1 (a). The ortho- position refers to the structure when the methyl group is bonded to the carbon in the ring that is directly adjacent to the two double-bonded carbons. When polymerized, the phenyl rings extend from a carbon chain backbone, the repeat unit of which is shown in Figure 2-1. In PVT the phenyl rings allow for
efficient energy transfer or FRET (Förster Resonance Energy Transfer) from the polymer base to the fluorescent dye [65].

Figure 2-1: The chemical structure of vinyl toluene (a) and styrene (b).

In this dissertation two types of PVT (in-house and commercial kit) are synthesized for use as the composite detector’s matrix material. The first part of this section will focus on synthesis of the in-house PVT to help the reader understand the polymerization process. As mentioned before VT is the monomer, or a single repeat unit, of the poly vinyl toluene. In this form the VT is a liquid, but after it undergoes polymerization the resulting material is solid. The in-house synthesis technique is known as bulk free radical polymerization. An initiator is activated with the addition of heat, creating a molecule or element with an unpaired electron, known as a free radical. The free radical is very reactive and promotes bonding between the vinyl toluene monomers. Specifically the double bonded carbons that extended from the phenyl are broken and reform to create single bonds to other vinyl toluene monomers. The process continues until the chain forms a polymer, which can be millions of monomers long. A segment of polyvinyl toluene is visualized...
in Figure 2-2. For simplicity the carbons and hydrogens are not shown, just the carbon-carbon bonds. Additionally these individual chains can bond with other chains when certain chemicals are added during the polymerization process. This is known as crosslinking and it increases the connectivity of the matrix leading to a more robust material. PVT is also completely amorphous meaning it does not organize into larger scale structures like crystalline and semi-crystalline polymers. A crosslinked amorphous polymer is also called a thermoset [66].

The polymerization process is sensitive to the surrounding environment and contaminations, therefore the constituent chemicals must be filtered and the curing is conducted in an inert atmosphere. For this reason, the filtration and curing were all done in a glovebox backfilled with nitrogen. The chemicals that require filtration consist of vinyl toluene monomer (VT) from Tokyo Chemical Industry the initiator 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231) from Sigma Aldrich, and the crosslinked divinylbenzene (DVB) from Alfa Aesar. All are filtered through a column chromatography system filled with sand, silica gel, and basic alumina. The silica is necessary to remove any water molecules that may be dispersed in the liquid. The basic alumina removes any oxygen and inhibitors that would prevent complete polymerization. The sand is used to pack the column down so the silica and basic alumina are not agitated when the liquid is poured through the column. Gravity draws the liquid chemicals
through the column to a frit and stopcock which regulates the flow. Each chemical is filtered independently and a new column is packed each time. For the actual polymer synthesis, the weight content of the initiator is around 0.01wt% and, if crosslinked PVT is desired, then crosslinker is added at 5wt%. The primary fluor is 2,5-diphenyloxazole (PPO) and the secondary fluor shifter is 1,4-bis(2-methylstyryl)benzene (Bis(MSB)), which is obtained from Eljen Technologies and is used as received. For pulse-shape-discriminating PVT, the PPO is added at < 30wt% and the Bis(MSB) has a content of 0.5wt%. All the chemicals are mixed using magnetic stirring in a glass vial for 30 minutes until completely dissolved. The glass vial is tightly capped and placed in a silicon oil bath at 55°C for 5 hours. The stir bar is removed and the capped glass vial is placed back in the bath at 60°C for 4 days, 65°C for 2 days, 70°C for 4 days, and 55°C for 4 hours. Figure 2-3 shows a flowchart of the entire synthesis process.

Figure 2-3: The process flow chart of in-house synthesized PVT

The commercial thermoset PVT resin kit (EJ-290) is purchased from Eljen Technologies. This type of PVT contains a scintillating dye that makes the polymer sensitive to gamma rays as discussed in section 1.1.3 in Chapter 1. The components of the PVT kit are the catalyst, monomer,
and resin. The catalyst is similar to the initiator discussed in an earlier part of this chapter, however it does not take part in the actual chemical reactions, it only helps facilitate them. The catalyst is usually an organic solid such as lauroyl peroxide and benzoyl peroxide [67]. The monomer is liquid vinyl toluene and used to dissolve the catalyst so that it can be properly dispersed in the resin. The resin is partially cured polyvinyl toluene. In this state the resin is a viscous liquid that is stable up to a couple of months if stored at temperature range of 2°C to 4°C. When the resin is mixed with the catalyst and monomer solution, it starts to polymerize. This process is accelerated when thermal energy is applied. The material properties of the cured PVT have been summarized in Table 2-1 and are adapted from Eljen Technologies [3]. The EJ-290 kit is chosen as the composite matrix because of its sensitivity to gamma radiation, refractive index, and wavelength of maximum emission.

<table>
<thead>
<tr>
<th>PVT Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Emission (nm)</td>
<td>423</td>
</tr>
<tr>
<td>Decay Time (ns)</td>
<td>3</td>
</tr>
<tr>
<td>Light Output (% Anthracene)</td>
<td>58</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.02</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.58</td>
</tr>
</tbody>
</table>

The commercial PVT is cured following a modified version of the original synthesis process. As stated in the above paragraph, the solid catalyst is first dissolved in the vinyl toluene monomer liquid. This solution is then mixed with the resin using a magnetic stirrer for 30 minutes. A mold is used to cure the polymer in the desired shape and is made out of glass or a toluene resistant plastic, like acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). A Teflon mold release spray is used to ensure the mold can be separated from the polymer without any
damage. The liquid resin, monomer, and catalyst solution are poured into the treated mold, placed in a vacuum oven, and allowed to degas for 30 minutes or longer depending on the volume. For volumes larger than 100 mL, the degassing time is increased to 12 hours. This length of time was determined via trial and error. The PVT is then cured at 65°C for 30 hours and post-cured at 85°C for 24 hours while under a N₂ gas flow for the entire duration. The nitrogen gas displaces oxygen and moisture in the ambient environment, which helps to mitigate adverse effects. Oxygen and water inhibit polymerization and chemically alter the monomer which could cause clouding and yellowing of the cured polymer. Once the curing process is complete, the oven cools to 25°C with the PVT sample inside. When 25°C is reached the cured PVT inside the mold is removed. If the mold is glass then it is carefully broken and the solid polymer is carefully removed and cleaned so that no glass shards remain. If the mold is plastic, a razor is used to cut the surrounding mold away and the solid polymer is removed. At this point the sample might not have flat faces or could be too large for the desired geometry therefore a diamond saw is used to cut the excess polymer. This cutting process introduces scratches into the polymer surface which is detrimental to the optical clarity. Thus the polymer surface is polished using progressively finer silicon carbide grit paper to mitigate the damages from the cutting.

2.3 Synthesis of Lithium Glass

The commercial glass used for this work was purchased from Scintacor under the name GS20. The glass contains multiple different compounds as follows: aluminum oxide, magnesium carbonate, silica oxide, lithium oxide and cerium oxide. The relative amounts of each compound are unknown for the commercial glass but can be approximated by using various characterization tools such as Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy.
(XPS). The material properties of the lithium glass are summarized in Table 2.2 and adapted from Scintacor [58].

Table 2.2: Important Material Properties of Li-glass

<table>
<thead>
<tr>
<th>PVT Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Lithium (wt%)</td>
<td>6.6</td>
</tr>
<tr>
<td>Isotopic Enrichment (% 6Li)</td>
<td>95% 6Li</td>
</tr>
<tr>
<td>Light Output (% Anthracene)</td>
<td>20-30</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.5</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.55</td>
</tr>
<tr>
<td>Maximum Emission (nm)</td>
<td>395</td>
</tr>
</tbody>
</table>

The synthesized lithium glass was melted with varying amounts of the above chemicals and the composition and properties were compared to those of the commercial glass. The lithium compound allows for neutron capture reaction on $^6$Li, which is shown below in Equation (2.1). The reaction produces an alpha ($^4$He) and triton ($^3$H) particle that travel in opposite directions through the material. The resulting energy is converted to scintillation light which is emitted at 395 nm.

$$^6Li + n \rightarrow ^4He + ^3H + 4.78MeV$$  (2.1)

The in-house synthesized glass required additional steps to allow for the cerium to be in the correct oxidation state. A furnace was modified with a ceramic tube connected to gas cylinders to flow a 50:50 mixture of CO:CO$_2$ into the molten glass. The gas ensures the cerium is surrounded by a reducing atmosphere, which is required for the cerium to remain in the correct oxidation state. The cerium must be in the Ce$^{3+}$ state in order to scintillate when the neutron is captured on lithium.
To begin, the appropriate amounts of each compound were thoroughly mixed until no clumps remain. The powder was then transferred to a platinum crucible and heated to 1550°C. The gas mixture was flowed over the top of the molten glass for 2 hours. The melt was poured onto a metal slab in ambient atmosphere and allowed to cool naturally to room temperature. Next, the glass samples were cut and polished to appropriate sizes for characterization. Figure 2-4 shows the as-poured glass under ambient (a) and ultraviolet (b), demonstrating the glass’ scintillation properties.

![Figure 2-4: As-poured lithium glass illuminated with ambient (a) and UV (b).](image)

### 2.4 Fabrication of Composites

For this work there were two types of composites fabricated, glass rods and shards based composites. The nomenclature used to denote the type of composite is based off of the dimensionality of the filler and matrix connectivity. The filler dimensions of the rods is 1 since the filler propagates through the composite in one direction. The glass shards is 0 since they can be thought of as point homogeneously dispersed in the matrix. Since the matrix, in both cases, is
connected in all dimensions then the number is 3. Therefore the rods is denoted as a 1-3 composite and the shards is a 0-3 composite [68].

All steps of the general fabrication process for the 1-3 composite can be seen in Figure 2-5. The glass rods for all the 1-3 composites were all obtained from a commercial vendor. The first step for fabricating the 1-3 composite was to chemically treat the glass with (3-aminopropyl)triethoxysilane (APTES), which promotes polymer adhesion to the glass surface. The APTES was purchased from Sigma-Aldrich. The glass rods were placed in a 5wt% APTES and 95wt% ethanol bath for 24 hours then removed, rinsed with ethanol, and cured in an oven at 110°C for 10 minutes. A 3D printed ABS and PLA mold was used to stabilize the glass rods in the specific pattern for the 1-3 composite. A glass tube was used to hold the liquid PVT until fully cured. The appropriate amount of PVT was mixed using a vibrational mixer until fully incorporated and poured into the assembled mold. For the larger volume composite, i.e. 12.5cm x 12.5cm, the mixing and curing needed to be performed for volumes less than 150 mL. Any amount greater than this would result in unwanted bubbles in the plastic due the insufficient degassing. The mold was placed in a vacuum oven and degassed for 1 hour or longer depending on the volume of the PVT. The composite was cured at 65°C for 30 hours and post cured for 24 hours at 80°C. Once the composite detector was completely cured it was cut from the mold and polished to optical transparency.
Fabricating the 0-3 composite involved a different approach and the process flow can be seen in Figure 2-6. The bulk glass for the 0-3 composite was both purchased from commercial vendors and synthesized in-house. Since spheres are difficult to process without the needed infrastructure of a drop tower, shards are fabricated instead by crushing bulk glass with a ball mill. The shards were then sieved to a particle size distribution of around 250 and 500 µm. The shards were rigorously washed to remove small glass particles by sonicating and rinsing in ethanol 15 times, and again in water with the same procedure.

The shards were then dried and treated with the APTES/ethanol solution using the process described previously. A given amount, 275 ml, of the PVT kit was mixed using the vibrational mixer. The liquid PVT was then placed in the vacuum oven and allowed to cure for 4-5 hours. The
shards were gradually mixed into the PVT and dispersed with the vibrational mixer. This process was repeated until all the shards were mixed and well dispersed in the PVT resin. Then the mixture was placed back in the oven and allowed to cure for the remaining time as specified in the 1-3 fabrication process. The shards detector has been fabricated with different glass contents of up to 7wt% with a particle size distribution around 250-500μm. The particle’s average size was determined using Scanning Electron Microscopy which is further explain in Appendix I.

2.5 Imaging Techniques

A Zeiss Axio Vert.A1 Optical Microscope (OM) is used to visualize microscopic features in the materials and composites. A Nova NanoSEM 630 Scanning Electron Microscope (SEM) is used to visualize those features smaller than the resolution of the OM. This is necessary when characterizing the effect of aging or the glass/polymer interface. Figure 2-7 shows an example of an SEM image of a shard embedded in the PVT matrix.
Figure 2-7: An SEM image of a Li-glass shard embedded in an in-house synthesized PVT matrix.

Additionally the SEM has a tool called Energy Dispersive Analysis (EDS) that can quantify and identify elemental compositions in the bulk material. EDS measures characteristic x-rays that emit from the sample when stimulated with a beam of high energy electrons. The energy of the characteristic x-ray corresponds to the energy difference between electron orbitals with is unique to each element. This is useful when probing the chemical composition of an unknown sample like commercial lithium glass. Another elemental characterization tool that is used in this dissertation is the Physical Electronics VersaProbe II X-Ray Photoelectron Spectroscopy (XPS). The XPS functions similarly to the EDS however it is a surface sensitive technique. XPS utilizes x-rays to probe the sample and measure the emitted photoelectrons. This technique is useful when the surface chemistry needs to be identified like in the case of determining the efficacy of glass surface functionalization, which is performed in this research. Another important characterization tool is the Bruker V70 Fourier Transform Infrared Spectrometer (FTIR). The FTIR functions by passing
a beam from an interferometer through the sample to determine the chemical structure. This is only used for organic materials like polymers, because of their transparency to infrared light.

### 2.6 Optical Characterization

Optical transmittance measurements of PVT and lithium glass were carried out using a LAMBDA 950 UV/Vis/NIR spectrophotometer. Based on the absorption characteristics provided by the materials vendors, the wavelength range was 250-600 nm. The UV/Vis functions by measuring the intensity difference between two beams of light with the same wavelength. One is the reference beam that does not interact with the sample and the other is transmitted through or reflected off the sample. The percent transmission, \( \%T \), is calculated using Equation (2-2) which is shown below with \( I \) being the intensity of the beam interacting with the sample and \( I_0 \) being the intensity of the reference beam.

\[
\%T = \frac{I}{I_0}
\]  

(2-2)

The absorbance, \( A \), is then calculated based on the percent transmittance and can be found described in Equation (2-3). This technique is useful for determining many different material properties such as wavelength of max absorption, color, extinction coefficient, effect of dopants and determining optical band gap.

\[
A = -\log\left(\frac{\%T}{100}\right)
\]  

(2-3)

Figure 2-8 shows an example UV/Vis transmission scan of the in-house synthesized PVT material with the x-axis being wavelength in nanometers and y-axis being \% transmission.
Additionally when coupled with a center mounted integrating sphere, the scattering coefficient can also be calculated. An integrating sphere is a piece of equipment that allows the UV/Vis user to collect almost all of the transmitted or reflected light from the sample. This is useful when the sample scatters or emits light isotropically. Several experiments in this dissertation makes use of the integrating sphere to decouple the scattering coefficient and fluorescence from other optical properties inherent to the material. For measuring the maximum emission of a material or composite, a Shimadzu RF150X spectrofluorophotometer was utilized at a range of 250-600 nm with varying excitation wavelengths. For this tool, the detector is positioned 90° from the excitation beam in order to ensure only the light emitted from the sample is measured. Figure 2-9 below shows an example of the spectrofluorophotometer curve of the in-house synthesized PVT and an excitation wavelength of 350 nm.
2.7 Thermal/Mechanical Characterization

For the thermal and mechanical property characterization a Q20 TA Instrument Differential Scanning Calorimeter (DSC) and Ares G2 Dynamic Mechanical Analyzer (DMA) are utilized. The DSC functions by measuring the heat flow in and out of the material over a range of temperatures. It can help determine material properties such as glass transition temperature ($T_g$), degree of curing, crystallization temperature ($T_c$), and melting temperature ($T_m$). Figure 2-10 shows an example of what a DSC curve looks like with in-house synthesized PVT. For endothermic transitions, like $T_g$, where heat flows into the sample, the resulting curve will have a downward trending feature. For exothermic transitions, like residual curing, the feature will point
upwards on the graph signifying heat flow out of the sample. The heating rate for all experiments in this dissertation is 10°C/min which is standard.

Figure 2-10: DSC spectra of in-house synthesized PVT.

The DSC is solely a thermal characterization technique, therefore the DMA is useful for testing the mechanical properties as well. The DMA has several different fixtures that are used depending on the material dimensions. The two used in this dissertation are the tensile and three-point bending fixtures. The tensile fixture is useful for thin film samples and for testing the tensile strength of the polymer film. The three-point bending fixture allows for the characterization of bulk materials. Additionally, an environmental chamber can be used to test the materials mechanical properties under a range on temperatures. The DMA can help determine the storage and loss modulus of the sample, Tg, and effects of crosslinking and plasticizers. Figure 2-11 shows an example of a DMA spectra of the in-house synthesized PVT. The run was performed with the three-point bending fixture with a heating rate of 2°C/min and 1Hz. The low heating rate is used
to minimize thermal lag in the sample because of its thickness and 1Hz is a standard frequency for dynamic testing. The downward slope of the storage and loss modulus along with the peak in the tan delta curve indicates the glass transition of the polymer.

Figure 2-11: DMA spectra of in-house synthesized PVT.

2.8 Nuclear Measurements

The neutron intrinsic efficiency and gamma rejection of the composites were measured following the procedure detailed in reference [69]. The composite detectors were coupled to a Hamamatsu R6231-100 photomultiplier tube (PMT) with optical grease and surrounded with Tyvek from DuPont to ensure the scintillating light was reflected towards the PMT. A layer of black Tedlar from DuPont surrounded the entire assembly to ensure all light collected by the PMT originated from the composite. A CAEN DT5533 supplied -1200 V to the PMT. The PMT signals
were digitized using a CAEN DT5730 digitizer. The data were stored in ROOT format for post processing and analysis [70].

The composite-PMT detector assembly was exposed to a 1 μCi $^{60}\text{Co}$ gamma source at 2 cm away for 24 hours to measure gamma rejection. No artificial neutron source was in the immediate vicinity during this measurement. An 8.06 mCi $^{252}\text{Cf}$ neutron source was used for neutron intrinsic efficiency measurements. Figure 2-12 shows the experimental set-up for the neutron and gamma experiments that were performed at Pennsylvania State University (PSU). Additional experiments were performed at University of Michigan by several graduate students in Dr. Igor Jovanovic’s lab, and the group’s website can be found in reference [71]. Therefore, the sources utilized for those experiments were different than the ones used at PSU. The decay rate and dosage were not consistent, which could lead to issues such as gamma pile up. Thus the distance between the source and the composite was adjusted in order to maintain same dosage at the surface of the composite no matter the radiation source. The dosage was 12 mR/hr to ensure the test followed the standard for gamma rejection measurements [34]. A source-detector separation of 1.4m was used to acquire a 15-minute measurement. A shadow cone was placed between the source and detector to remove neutrons directly incident from the source onto the detector, thus effectively subtracting the incident neutrons from room scattering.
Figure 2-12: Image of the experimental setup for measuring the composite’s (black assembly in the center) neutron efficiency using a $^{252}$Cf source (right side) and digitizer (left side).

2.9 Optical Modeling Simulations

For the optical modeling of the composite detector, a software from LAMDA Research Corporation called TracePro is used. TracePro uses SolidWorks to build devices with complex geometries and a variety of materials. It also has the ability to simulate light absorption, bulk scattering, transmission, and fluorescence of the built devices. TracePro functions by using Monte Carlo ray tracing to randomize light as it propagates through a medium. The glass filler’s effect on light scattering can therefore be simulated and optimized without the need for tedious and difficult processing of many different designs. Additionally TracePro allows the user to input custom material properties to simulate the in-house synthesized PVT, which have different properties from default materials available in the software. This allows the user to optimize the detector design and
quantify the efficiency of optical light transport before fabrication, thus decreasing cost and research time.

2.10 Summary

By taking advantage of the material properties such as decay time, index of refraction, and sensitivity to different types of radiation, a composite can be fabricated for neutron detection applications. While the individual properties are important to characterize and understand, it is also worth exploring how the structure of the glass filler affects the detection and optical capabilities of the composite. Therefore the next chapter will focus on the interplay between detector design and composite performance.
Chapter 3

Effect of Interfacial Surface Area on Neutron Detection

3.1 Introduction

In heterogeneous composite neutron detectors, materials with dissimilar characteristics are optically coupled to achieve functionalities that extend beyond those enabled by intrinsic properties of constituent materials. However, the mismatched optical properties, such as refractive indices, of the dissimilar materials introduce light scattering inside the detector, which could potentially affect its performance. Understanding the effects of the glass filler shape and content on light transport and light output is crucial for developing high performance composite detectors. For this chapter detectors with glass rods and shards were fabricated and characterized using UV/Vis, gamma, and neutron sources. The dimensions of the rods detector are 12.7cm x 12.7cm and those of the shards detector are 7cm x 3.8cm. The neutron intrinsic efficiencies of the fabricated detectors were also measured for $^{252}$Cf spontaneous fission neutrons along with gamma rejection. It is worth noting that the PVT used in this chapter was not synthesized in-house but commercially obtain from Eljen Technology. Therefore the matrix is only sensitive to gamma recoil, not neutrons. Future chapters will focus on further functionalization of the PVT then integrate the PSD capable matrix with the glass filler.

The following parts of this chapter focus on the glass/PVT interfacial surface area effect on the light transmission and answer the question posed in “Motivation for Dissertation” section in Chapter 1. How do the shape of the filler and the presence of internal interfaces affect the light output and efficiency of a polymer/glass composite detector? The light output is also studied since this is a better measure of detector performance in terms of radiation detection, with a higher light

[1] – Portions of this work was published in Nuclear Instruments Methods Physics A 2018 [80]
output meaning the detector is more sensitive to neutron capture and gamma recoil. The objectives for this chapter is to fabricate two detector geometries, 1-3 and 0-3, and determine the relationship between glass filler geometry and detector performance. There are three specific tasks of this chapter, 1) study the effect of filler and shape on the optical light transport through composite detector, 2) investigate the effect of the glass filler and shape on light output, 3) calculate interfacial surface area of the composite and relate it to pulse shape discrimination properties.

3.2 Characterization of Lithium-Glass and Polyvinyl Toluene Heterogeneous Composites with Varying Geometries for Fast Neutron Detection

As a brief reminder, heterogeneous composite neutron detectors are an emerging alternative to conventional homogeneous detectors. These detectors couple materials with dissimilar characteristics to create a device with additional functionality. The combination of dissimilar materials allows for a higher degree of flexibility when tailoring the detector properties, such as the degree of sensitivity and specificity to thermal and fast neutrons, and gamma radiation. A seminal composite neutron detector was developed by Knoll et. al using $^3$He filled glass spheres embedded in a polyvinyl toluene matrix [50]. Since then several other groups have focused on different types of fillers such as lithium gadolinium borate (LGB) glass, cerium activated lithium glass (GS20), nanoparticles, silicon pillars, lithium fluoride crystals, and, more recently, $\text{Cs}_2\text{LiYCl}_6$ crystals (CLYC) [52]–[54], [69], [72]–[77]. While recent advances proved the viability of these detectors, there is generally a lack of detailed understanding of how filler shape, size and content affect the detector properties. For example, the addition of the fillers with optical properties different from those of the matrix introduces light scattering interfaces within the detector. The scattering could reduce the light transmission as well as output by increasing the mean path length through the detector, leading to increased light absorption. This chapter discusses the results of an
experimental study that reveals how the filler shape, i.e. interfacial surface area, and content impact the composite’s optical properties and PSD capabilities.

Before fabrication of the detectors, the curing of the PVT matrix was optimized to ensure minimal synthesis time with a reasonable degree of cure. Originally, the Eljen EJ-290 PVT kit required 14 days of curing at 45°C, however this long amount of time was not conducive for the rapid prototyping of the detectors. To decrease the curing time, the temperature of the cure was increased. The maximum curing temperature that the kit could withstand without showing signs of degradation or partial curing was 65°C. These signs manifested themselves in the form of yellowing, cracking, bubbles, and clouding, all of which are detrimental to the transparency of the detector. Three different curing times were chosen and the samples were tested with a tweezer indentation test and differential scanning calorimetry (DSC). For the indentation test, the samples were removed from the molds and allowed to cool to room temperature. The samples that were not completely cured indented when pressure was applied from the tweezers while cured samples experienced no indentation. By examining the glass transition temperature ($T_g$) extracted from the DSC measurements, a reasonable assessment of the extent of cure can be determined. $T_g$ is a temperature range at which the polymer transitions from glassy to rubbery state and it reaches its maximum value when the polymer is fully cured [78]. Figure 3-1 shows the DSC data for three samples prepared with a 14 days cure (dashed and dotted line), 72 hours cure (dashed line), and 30 hours cure (solid line).
Figure 3-1: The DSC plot of PVT cured at 14 days, 72 hours, and 30 hours.

The $T_g$ for the 14 days, 72 hours, and 30 hours samples were around $89^\circ\text{C}$, $87^\circ\text{C}$, and $85^\circ\text{C}$ respectively. The glass transition temperatures of the 30 and 72 hours cure are slightly lower than that of 14 days cure; this can be associated with lower crosslink densities. However since the difference in $T_g$ is within the resolution of the instrument, the 30 hours cure can be considered robust enough for the purpose of our application. This section focused on the need for the matrix to be structurally stable while cured in a limited amount of time; therefore, an indentation test and determination of $T_g$ was deemed sufficient justification for the change of processing parameters. Additionally the environment of the curing was also an important area of improvement. Early trials yielded extremely opaque PVT, which was likely due to the presence of moisture in the curing atmosphere (See Figure 3-2). When cured in a nitrogen rich environment, the PVT sample was transparent, which allowed for excellent visible light transport.
The geometric design for each composite discussed in this paper is inspired from the work by Mayer et al. [2]. The rods and shards geometries were selected because of their simulated higher efficiency and low gamma rejection compared to a two-dimensional layered geometry. Two types of composites were fabricated using steps that were described in prior work [69]. The schematics for each composite are shown in Figure 3-3 (a and b). Images of the fabricated samples and their dimensions are shown in Figure 3-3 (c and d).
Figure 3-3: 6wt% rod (a) and 3wt% shard (b) composite with dimensions and corresponding schematics (c and d respectively).

The PVT polymer matrix was made using an EJ-290 kit manufactured by Eljen Technology. PVT has a peak emission wavelength of 423 nm, a refractive index of 1.58, and decay time of 3 ns. The rods and shards were made of $^6$Li loaded lithium glass, namely GS20, manufactured by Scintacor, Inc. This glass is a cerium-activated lithium silicate glass containing 18% lithium oxide by weight and is enriched to 95% of the $^6$Li isotope. The lithium glass has a refractive index of 1.55, a decay time of 50-70 ns, and the peak of its fluorescence spectrum is at 395 nm as discussed in Chapter 2, Section 2.3, “Synthesis of Lithium Glass”. The glass rod
dimensions were 0.1x0.1x7.7 cm³. The rods composite was prepared with 6wt% glass rods. The shards were obtained by crushing and sieving a lithium glass block to a size distribution around 250 µm. Shards composites with two different weight contents, 1 and 3wt%, were characterized. The difference in the weight content was due to the difficulty in suspending a higher weight percent of shards in the PVT. The PVT and lithium glass were selected for several reasons 1) different decay times allow for pulse shape discrimination between gamma radiation and neutrons, 2) refractive indices are relatively close to ensure minimal Fresnel reflection, which arises from refractive index contrast between different materials, 3) PVT is a hydrogenous material that efficiently moderates fast neutrons while Li-glass is an excellent capture agent for moderated neutrons.

Each composite tested was compared to a pure PVT sample of the same dimensions. Optical transmittance measurements were performed with a LAMBDA 950 UV/Vis/NIR spectrophotometer. Neutron intrinsic efficiency and gamma rejection of both composites were measured following the procedure detailed in [69]. The neutron detection steps were described and can be found in Chapter 2, page 38 and 39. First a 2-hour measurement was collected in an environment isolated from the neutron source, in order to determine the neutrons present in the background. Then another 2-hour measurement with a 42.7 µCi ⁶⁰Co gamma source was performed and the events were subtracted from the background. The remaining neutron events in the defined neutron regions were counted as misidentified gammas. This procedure was repeated twice to increase the number of events and reduce the error. A ²⁵²Cf neutron source was used for neutron intrinsic efficiency measurements. The number of neutrons incident on the detector surface was calculated using the solid angle from the source. A 1.4 m source-detector separation was used to acquire four measurements lasting 15 minutes each. These measurements were performed twice.
For the second measurement, a shadow cone was placed between the source and detector to remove neutrons directly incident from the source onto the detector, thus effectively subtracting the incident neutrons from room scattering according to a method described in reference [79].

The optical transmission spectra of all composites were measured with the flat cylinder face normal to the incident light path. For the rods detector, the light transmission path was parallel to the rods orientation through the composite. Figure 3-4(a) shows a comparison between the transmission spectra of 12.7 cm-long pure PVT detector and the rods composite. At wavelengths shorter than 410 nm, the light is absorbed for all the samples. For the sake of comparison, the changes in transmission are calculated at 500 nm wavelength. The rods composite (6wt%) has a transmission decrease of 10% compared to the pure PVT. This is due to the light scattering from polymer and glass interfaces, which disperses the incident light traveling through the composite. Figure 3-4(b) shows a comparison of the shards composites transmission to that of pure PVT. At 500 nm, the composites’ transmissions decreased 10% and 92% compared to the pure PVT for 1 and 3wt% shards content, respectively. The 500 μm shards composite with a weight content of 7wt% has a transmission decrease of about 30% compared to the pure PVT.

The total interfacial surface area per unit volume of the composite calculations (found in Appendix A) include the experimentally determined distribution of shard sizes. The total interfacial surface values were 0.35 cm²/cc and 1.04 cm²/cc for the 1wt% and 3wt% 250 μm composites respectively. This same calculation was performed with the 7wt% 500 μm shard composite and the total interfacial surface area was 0.72 cm²/cc. The total interfacial surface areas followed the same trend as the decrease in transmission measured from the UV/Vis (Figure 3-4 (b)). The composite with the lowest interfacial surface area (1wt% 250 μm) had the smallest decrease in transmission at 10% and the one with the highest interfacial surface area (3wt% 250 μm) had the largest decrease, as expected.
μm) had the largest decrease in transmission at 92% (Table 3-1). The 7wt% 500 μm composite had a transmission decrease of 30%, which was between transmission decreased for the 1wt% and 3wt% 250 μm composites. The interfacial surface area of the 7wt% 500 μm composite was also in between the 1wt% and 3wt% 250 μm composites, which followed the same trend as the transmission decrease (Table 3-1). This indicated that the interfacial surface area is the driving factor behind the decrease in transmission. This holds true when compared to the 6wt% rods composite as well. The transmission decrease for the rods composite was 10% which was similar to the 1wt% 250 μm shards composite (Table 3-1). The interfacial surface areas for the two detectors are also relatively close at 0.30 cm²/cc and 0.35 cm²/cc for the rods and shards respectively. It is worth noting that the interfacial surface areas might differ slightly from the actual composite due to their approximation as ellipsoids.

Figure 3-4: Transmission spectra of (a) rods and (b) shards composites compared to pure PVT with the same dimension.
Table 3-1: Tabulated interfacial surface area per unit volume and transmission decrease for all detectors.

<table>
<thead>
<tr>
<th></th>
<th>Rods (6wt%)</th>
<th>250 μm Shards (1wt%)</th>
<th>250 μm Shards (3wt%)</th>
<th>500 μm Shards (7wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial Surface Area per Unit Volume of Composite (cm$^2$/cc)</td>
<td>0.30</td>
<td>0.35</td>
<td>1.04</td>
<td>0.72</td>
</tr>
<tr>
<td>Transmission Decrease (%) (at 500nm)*</td>
<td>10</td>
<td>10</td>
<td>92</td>
<td>30</td>
</tr>
</tbody>
</table>

*transmission decrease is with respect to a pure PVT detector

The composite’s light output was also of interest in this study. If the light output is decreased significantly by the increased density of material interfaces, then the detection efficiency can suffer. Each of the 30 minute measurements with $^{137}$Cs were normalized with the Compton edge in the light output spectrum. The light output for each composite and the pure PVT was determined consistently at 50% counts of the Compton edge. The light output for the rods composite decreased 33% compared to that of the pure PVT (Figure 3-5(a)).

![Figure 3-5: Light output of (a) rod-PVT and (b) shards-PVT composite detectors.](image)
For the shards composite, the light output decreased by 7 and 21% for the 1 and 3wt% content shards, respectively. The larger decrease in light output of the rods compared to the shards composite can be explained by the relative light output for each material. The glass has a light output of 20-30% of anthracene compared to the PVT, which is 58% of anthracene [3], [58]. The composite with the higher glass weight content will have an overall lower light output. This result indicates that the final detected light output is more affected by the glass content than the shape and interfacial surface area. Based on established procedure the composite was wrapped with Teflon tape to ensure efficient light collection by minimizing light leaks [80].

In this chapter, the neutron intrinsic efficiency is defined as the ratio of the number of neutrons detected by capture on $^6$Li to the number of neutrons incident on the detector, when the neutron spectrum is the spontaneous fission spectrum of $^{252}$Cf. The neutron background (including room return) was determined from measurements made with the shadow cone. A previous study has shown that the measured neutron intrinsic efficiency of the 5cm x 5cm rods composite is 0.33±0.02% [69]. Monte Carlo simulations were performed on a cylindrical detector with an aspect ratio of 1. If the detector diameter is increased from 5cm to 12.7cm while the lithium content is fixed to 7wt% (2.8vol%), then the intrinsic efficiency would increase over an order magnitude [2]. The simulation of the neutron intrinsic efficiency yielded a value of 6.96%. Driven by the simulations the rods detector was then scaled up to 12.7cm diameter and 12.7cm length cylinder and tested with a neutron and gamma source. Figure 3-6 shows the PSD plot of the 12.7cm rods composite. A well-defined neutron region can be seen above the gamma band.
Figure 3-6: PSD plot of 12.7cm x 12.7cm Rods composite using a $^{252}$Cf neutron source.

This region of high tail/total integral value is expected from the scintillation in the cerium activated lithium silicate glass rods when neutrons are present due to the longer decay time for light. This region is attributed to neutron capture in the lithium glass. The method used to determine the neutron region is described next and is consistent with methods in the literature for other capture based detectors [2], [48], [49], [52], [81]. A Gaussian function was fit in two dimensions (tail/total integral and light output) to establish a neutron region. A Tail/Total Integral range of 0.40-0.65 that was defined for the neutron capture region. This range corresponds to a 3σ upper and lower bound for the Gaussian fit. All events in this region were counted for both intrinsic efficiency and gamma rejection measurements. The measured neutron intrinsic efficiency of this composite was found to be 4.80±0.05% and the gamma rejection was around $10^{-4}$. The FOM was calculated to be 3.3 and the Equation 3-1 was used. The $n$ and $g$ represent the neutron and gamma responses. The larger FOM represents a greater separation between the two bands.
\[ FOM = \frac{\text{Centroid}_n - \text{Centroid}_g}{\text{FWHM}_n + \text{FWHM}_g} \] (3-1)

The 3wt% shards composite’s PSD plot is shown in Figure 3-7. Unlike the rod composite, a tail connecting the neutron island to the gamma band can be observed. This feature is a result of the shape and size of the glass shards. As the glass fillers decrease in size (from 1mm for the rods to 250µm for the shards), their surface area to volume ratio increases. The rods have a total surface area to volume ratio of 40.39 (cm²/cm³), while the shards ratio is 64.7 (cm²/cm³). The larger surface area to volume ratio corresponds to a higher probability of a neutron capture event occurring near the surface of the glass. The reaction emits two charged particles (\(^4\text{He}\) and \(^3\text{H}\)) which travel in opposite directions. The particles then deposit their energy in the materials they are traveling through. If this material were the PVT matrix, then the resulting light pulse would have a shorter decay time and smaller tail/total integral value compared to a light pulse in the glass. Therefore the shape of the neutron capture island is dependent on the surface area to volume ratio of the composite filler, with a larger ratio corresponding to the presence of the tail. The figure of merit for the shards composite is not calculated because of the presence of the neutron island’s tail and the inability to fit to a Gaussian function. The efficiency of the 3wt% shards composite is 0.097±0.036%, while that of the 1wt% shards detector is 0.091±0.017%. The gamma rejection for each shards composite was 10^{-6}. 
Figure 3-7: PSD plot of shards composite using a $^{252}$Cf neutron source.

### 3.3 Summary

Multiple Li-glass and PVT composite detectors with inherent PSD were successfully characterized both optically and with a neutron source. The optical transmission was assessed to ensure adequate light propagation within the composite. Since the shards detector had more interfacial surface area, the optical transmission was lowered considerably more when compared to the rods composite with similar glass content. This effect did not have an adverse effect on the light output however. The glass interfacial surface area mainly determines the magnitude of light scattering in the composite, while the light output is affected mostly by the glass content. The interfacial surface area to volume ratio for adequate PSD should be below 64.7 (cm$^2$/cm$^3$). The 12.7cm x 12.7cm rods composite has a gamma rejection of $10^{-4}$ and a neutron intrinsic efficiency of 4.80±0.054% which is approximately two orders of magnitude larger than previously fabricated 5cm x 5cm rods composite and in agreement with simulation [69]. The shards composite had a
neutron intrinsic efficiency of 0.097±0.036% and the gamma rejection was $10^{-6}$ for the 3wt% composite.

In summary, the results presented in this chapter indicate that interfacial glass surface area affects the light transmission through the detector, while the glass weight content affects the light output. Overall this chapter answers the question originally posed: how do the shape of the filler and the presence of internal interfaces affect the light output and efficiency of a polymer/glass composite detector? The PSD capabilities of the composite are dictated by the interfacial surface area per volume ratio as well. These findings have important implications for the maximum size that the detector can be fabricated. The larger the detector, the more light scattering of scintillation events occur before collection by the PMT. The light scattering from interfaces increases the path length meaning that if the matrix or glass filler is not completely transparent, then it will be absorbed before it can be collected.
Chapter 4

Triple-Pulse-Shape Discrimination Capable Composite

4.1 Introduction

This chapter describes the fabrication and characterization of a novel triple pulse shape discrimination (PSD) capable heterogeneous composite neutron detectors that utilizes fast neutron-sensitive scintillating polyvinyl toluene (PVT) and $^6$Li-glass. The objective of this chapter was twofold: 1) Assess the effect of PPO (primary dopant) loading on the mechanical properties of the PVT, and 2) fabricate a triple PSD-capable composite detector using PPO-doped PVT and $^6$Li-glass rods and shards. Thermal and mechanical characterization was utilized to study the glass transition temperature ($T_g$) of the PVT with the addition of dopants. A crosslinking agent (divinylbenzene, DVB) was introduced to control the mechanical properties while still exploiting the PSD capabilities of the high PPO content PVT. The composites were then fabricated using the crosslinked PVT as the fast neutron and gamma sensitive material and $^6$Li-glass as the thermal neutron sensitive material. The final fabricated composite samples have a glass weight content of 6% and dimensions of 2.5cm x 2.5cm. UV/Vis spectrometer was used to characterize the optical properties of the composite sample. A $^{252}$Cf source was used to test the PSD capabilities and intrinsic efficiency of the sample. The figure of merit for fast neutron, thermal neutron, and gamma rays was measured for detectors. A $^{60}$Co source was used to measure the gamma rejection of the sample. The question that Chapter 4 will answer is does doping the polymer matrix with fluors and crosslinking molecules help realize a structurally sound triple PSD detector? This question will be answered by completing the three following tasks: 1) synthesize and characterize pourable PSD capable crosslinked PVT, 2) fabricate triple PSD capable composite with PSD PVT in 1-3 and 0-
3 configurations, 3) characterize triple PSD detector with optical and nuclear techniques to determine detector performance.

### 4.2 On the Fabrication and Characterization of Heterogeneous Composite Neutron Detectors with Triple-Pulse-Shape-Discrimination Capability

As discussed in chapter 1, the development of innovative detectors sensitive to fast and thermal neutrons is important in the fields of nuclear nonproliferation and security, particularly for detection of special nuclear material (SNM). Different mechanisms exist for the detection of such fast and thermal neutrons. Fast neutron detection relies on neutron elastic scattering on protons, while thermal neutrons are usually detected via capture on $^3$He, $^6$Li or $^{10}$B [25]. In addition, the discrimination of neutrons from gamma rays is required and is achievable by distinguishing electronic from nuclear recoils [82]. These mechanisms are found in a variety of materials (liquids, polymers, and inorganic solids) that have been extensively studied and described in the literature [47], [49], [83], [84]. Our current research focuses on optically coupling these materials in heterogeneous composites to allow for combined sensitivity to fast neutrons, thermal neutrons, and gamma rays; such detectors have been referred to as *triple pulse shape discriminating* detectors. Multiple research groups have recently successfully fabricated triple PSD composite detectors with Cs$_2$LiYCl$_6$ (CLYC) embedded in a polymer matrix [53], [54]. The CLYC filler has the unique ability to detect and discriminate among all three of these events, while the polymer matrix can act to thermalize the incident neutrons as well as transport the emitted light. The drawback with CLYC is that it is expensive to fabricate and challenging to produce in large volumes [85]. Other heterogeneous triple PSD detectors have also been demonstrated, for example
by wrapping EJ299-33A (a PSD scintillating polymer) with EJ-426 (a $^6$LiF:ZnS(Ag) thermal neutron sheet), demonstrating good discrimination and gamma rejection [81]. This detector demonstrates that PSD capable polymers coupled with inorganic materials can result in high-performance, relatively simple to fabricate triple PSD detectors.

Zaitseva et al. were the first to show that PVT has the ability to discriminate between fast neutron and gammas when loaded with 30wt% PPO dye [48]. The discrimination arises from the increased spatial concentration of triplet state production in nuclear recoils when compared to electronic recoils and the subsequent triplet-triplet annihilation, which produces a longer scintillation pulse in neutron as compared to gamma interactions. However, it has been reported that PPO can act as a plasticizer in PS and PMMA, which results in mechanically soft polymers by reducing the glass transition temperature ($T_g$) [86], [87]. The $T_g$ is a step change in the heat capacity of the material, which indicates a shift from the polymers rubbery to glassy phase. To the best of our knowledge, the effects of PPO on the thermal and mechanical properties of PVT have not been studied to date. The first objective of this work is to unravel the effect of PPO content on these mechanical properties, especially how the crosslinking agent increases the robustness of the polymer. The second objective is to fabricate a novel triple PSD detector utilizing crosslinked PSD capable PVT and $^6$Li-glass rods and characterize its performance. By incorporating $^6$Li-glass, which acts as the material sensitive to thermal neutrons, into the PSD-capable PVT matrix, it is possible to create a triple PSD-capable heterogeneous composite scintillator. The fabrication process and composite geometry is similar to that reported in previous studies [2], [69].

The divinylbenzene (DVB), initiator (Luperox), 2,5-diphenyloxazole (PPO), 9,10-diphenylanthracene (DPA), and vinyl toluene monomer were all purchased from Sigma Aldrich. A TA instruments RSA-G2 dynamic mechanical analyzer (DMA) was used to characterize the
mechanical properties of the polymers. Samples were tested with a 20 mm three-point bending apparatus. A Perkin-Elmer Lambda 950 UV-Vis-NIR Spectrophotometer was used to explore the optical properties of the materials. The final triple PSD composite was coupled to a Hamamatsu R6231-100 photomultiplier tube (PMT) with optical grease while the matrix samples were coupled to a Hamamatsu H10580 PMT Module. A layer of PTFE and black Tedlar was used to surround the assembly to ensure all light collected by the PMT originated from the detector. A CAEN DT5533 was utilized to supply -1200 V to the PMT. The PMT signals were digitized with a CAEN DT5730 digitizer and data was stored in the ROOT format for analysis [70].

The PVT samples synthesis mirrored the method reported in Ref. [48] with the addition a crosslinking agent. The chemicals for the synthesis include the monomer (vinyl toluene), initiator (Luperox 231), crosslinker (DVB), primary dye (PPO), and wavelength shifter (DPA). All following steps were done in a glovebox purged with N₂ gas to minimize exposure to oxygen. First, the liquid chemicals were filtered through an aluminum oxide and silica gel column to remove dissolved oxygen and inhibitor. The DPA powder was washed in warm acetone for 30 minutes then collected with a vacuum filter and allowed to dry. The PPO powder was used without any washing and its content was varied from 0wt% to 30wt%. The powders with the appropriate weight contents were dissolved in the liquid chemicals and magnetically stirred for the 30 minutes. The solution was then placed in a silicone bath and allowed to cure at 55°C for 4 hours, 60°C for 4 days, 65°C for 2 days, 70°C for 4 days, and then 50°C for 5 hours. For each PPO content, samples were synthesized with and without the crosslinking agent DVB.

The PPO content that would lead to the best PSD performance, namely the highest figure of merit (FOM), is then used as a scintillator matrix. The glass rods were treated with a silane coupling agent (APTES) to promote adhesion with the surrounding matrix. The rods were then
assembled in the 3D-printed mold. The matrix resin process followed the same initial steps described above. Before the polymer solidifies, the liquid matrix was removed from the silicone bath and poured into the mold and the assembly is then placed in a vacuum oven to cure for one week. It was necessary to cure in the vacuum oven and not the silicone oil bath because the 3D-printed mold was slightly porous which could lead to oil leaking into the curing polymer. Once cured, the composite was removed from the mold, cut to a dimension of 3 cm x 3 cm, and polished to optical transparency. The final composite had a $^6$Li-glass weight content of 6%. The steps in the fabrication process are summarized in Figure 4-1.

![Figure 4-1: Facile process flow of triple PSD rods composite fabrication.](image)

Dynamic mechanical analysis (DMA) was used to probe the effect of the PPO and crosslinker on the mechanical properties. The DMA functions by applying a sinusoidal stress at 1 Hz on the sample and measuring the resulting strain at different temperatures. This technique can accurately measure the sample’s storage (stiffness) and loss modulus, which is then used to extract the glass transition temperature. A three-point bending apparatus is used to test the samples at a heating rate of 2°C/min. Tan(delta) is the ratio of the loss modulus by the storage modulus and is
calculated for all the samples without (a) and with (b) crosslinker. The glass transition temperature ($T_g$) is the temperature at which the polymer transitions from glassy to rubbery behavior. Around $T_g$, the storage modulus drops and Tan(delta) maximum peak occurs. Table 4-1 summarizes the glassy region storage moduli and $T_g$ values for all the samples with and without crosslinker. As the PPO weight content increases, the storage modulus and $T_g$ decrease, indicating the plasticizer effect of PPO. Figure 4-2 (a) shows a comparison between the storage moduli and Tan(delta) of 30wt% PPO-PVT with and without crosslinker. Without crosslinker, the samples would flow immediately above the glass transition temperature, discontinuing the measurement as shown in Figure 4-2 (a). With the addition of the crosslinker in Figure 2 (b), the curve continues above the glass transition temperature. For samples without crosslinker, the glassy region storage modulus ranges from $4 \times 10^9$ to $9 \times 10^9$. In the rubbery region, the storage modulus decreases by 3 orders of magnitude to around $1 \times 10^7$–$2 \times 10^7$, resulting in a soft polymer more susceptible to mechanical deformation and damage. When the crosslinker is added, the glassy region storage modulus increases by 25% for the pure PVT, -20% for the 15 and 20wt% PPO, and more than 800% for 30wt% PPO, indicating a higher mechanical robustness. The drop in $T_g$ results in a mechanically soft polymer which is difficult to machine and susceptible to physical deformation and damage. With the introduction of the crosslinking agent, the $T_g$ of the polymer increased for the 0, 5, and 30wt% PPO samples. It is important to note that for the 15 and 20wt% PPO samples, the crosslinker did not significantly increase the $T_g$. This indicates a tradeoff between the plasticizer effect of the PPO and the crosslinking by the DVB. The DVB weight content (5wt%) is held constant compared to the total weight of initial components. Thus, an increase in the PPO weight content results in a decrease in the weight content of the vinyl toluene base. This means that the fraction of crosslinker to vinyl toluene base increases as the weight content of the PPO increases.
For samples up to 15wt% PPO, the plasticizer effect dominates and results in a drop in \( T_g \) when compared to non-crosslinked samples. After 20wt% the crosslinking effect dominates, which leads to an increase in the \( T_g \) for 30wt% PPO sample with crosslinker.

![Figure 4-2: Comparison of storage modulus and Tan(delta) with and without crosslinking agent (CR).](image)

![Figure 4-1: Comparison of storage modulus and Tan(delta) with and without crosslinking agent (CR).](image)

<table>
<thead>
<tr>
<th>PPO wt%</th>
<th>Storage modulus (GPa)</th>
<th>( T_g ) Values (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No CR</td>
<td>With CR</td>
</tr>
<tr>
<td>0</td>
<td>3.89 ± 0.52</td>
<td>4.88 ± 0.97</td>
</tr>
<tr>
<td>5</td>
<td>5.42 ± 0.51</td>
<td>8.03 ± 0.34</td>
</tr>
<tr>
<td>15</td>
<td>6.10 ± 0.91</td>
<td>4.79 ± 0.42</td>
</tr>
<tr>
<td>20</td>
<td>5.94 ± 0.91</td>
<td>4.81 ± 1.04</td>
</tr>
<tr>
<td>30</td>
<td>0.47± 0.030</td>
<td>4.45 ± 0.23</td>
</tr>
</tbody>
</table>

It is important to study the effects of the PPO loading and crosslinking on the optical properties of the polymer matrix compared to the lithium glass. The wavelength of maximum emission of the glass is 395 nm; therefore, the absorption edge of the polymer must be shorter than or as close as possible to this wavelength. If the absorbance edge for the PPO doped PVT is at longer wavelengths compared to the maximum glass emission, then the matrix will reabsorb the
emitted light, lowering the light output of the detector. Figure 4-3 shows the spectral absorption curve for PPO loaded PVT without and with crosslinker. There is no significant change of the absorbance with the addition of increased weight content of PPO or the presence of crosslinker. The wavelength of emission for the polymer matrix is another important optical property, which could have an effect on the detector efficiency. A spectrofluorophotometer was used to test the fluorescence of materials at different wavelengths. The emission peak did not change with the increasing PPO content or crosslinking agent.

![Figure 4-3: Absorbance comparison of varying PPO content without (a) and with (b) crosslinking agent (CR).](image)

As discussed previously, the PPO allows for triple-triplet annihilations to occur, resulting in a scintillation decay time for nuclear recoils that are longer than that in the case of electron recoils. As the weight content of the PPO increases, the rate of annihilation increases, which may result in improved PSD capabilities. The samples' PSD capabilities were tested using a $^{252}\text{Cf}$ source. Measurements associated with varying the PPO concentrations were conducted in a light-tight box with a Hamamatsu H10580 PMT module with 5 cm of lead between the detector and $^{252}\text{Cf}$ source. Lead was used to absorbed gammas emitted from the neutron source. Figure 4-4 shows the PSD plots for these measurements of all the samples tested without crosslinker. The top band is attributed to the fast neutron interactions (proton recoils) with the greater PSP and the
bottom band to the gamma events (electron recoils). As the PPO content increases, the separation between the bands becomes more prominent. The FOM is calculated as the distance between the centroids of the two PSP distributions over the difference between full-width at half-max of each distributions for the 400 – 1600 keVee energy range. The results indicate that increasing the PPO content increases the FOM, which is consistent with the results in Ref. [48]. With the addition of the crosslinking agent, the FOM increases for the 15 and 20wt% samples. Future research will focus on better understanding the mechanism behind the FOM increase.
Figure 4-4: Comparison of the FOM of PVT with varying PPO loading with and without crosslinking agent.

In order to ensure good transparency through the composite, the glass must be optically coupled to the surrounding polymer matrix. Without chemically treating the lithium glass there exists an air gap which adds more interfaces scattering the light, decreasing transmission. As
previously discussed, APTES was used to treat the glass surface to improve polymer adhesion to the glass surface. This is a result of the chemical structure and functionalization process of the APTES, which can be seen in Figure 4-5. The long amine terminated chain interpenetrates the polymer matrix increasing affinity through hydrogen bonding. After the APTES is dissolved in ethanol, hydroxyl groups form that covalently bond to the glass surface.

Figure 4-5: APTES structure and functionalization process on glass surface.

In order to characterize the functionalization of the glass surface, XPS is used. This is a surface sensitive (top 0 – 10 nm) technique which measures the elemental composition the material. Therefore by measuring certain elements, such as nitrogen, before and after the functionalization one can determine if the surface has been chemically altered. The peak corresponding to an amine functional group is found around a binding energy of 399 eV and
appears after APTES functionalization (See Figure 4-6) [88]. The peak around 531 eV corresponds to an oxygen molecule bonded to an organic carbon, which can be attributed to native carbon that naturally exits. The peak near 284 eV indicates the presence of C-C bonds while the two peaks at 150 and 103 eV are associated with SiO$_2$. Additionally a fluorine peak at 688 eV can be seen in the bare glass curve, which could have been due to impurities on the surface. Overall the XPS spectra indicates the clear presence of APTES functionalization.

![XPS spectra of bare and treated glass showing presence of an amine functional group.](image)

As discussed above the APTES chemically modifies the glass surface to promote better adhesion to the polymer matrix. Figure 4-7 shows an SEM image of APTES-treated glass embedded in the PVT matrix. This was obtained by freeze fracture of a glass rod in the cured
polymer matrix using liquid nitrogen. This technique ensures there is minimal plastic deformation during the fracture that could ruin the polymer glass interface. Figure 4-7 shows the cross-section of a glass rod without the silane coupling agent (a) and with the coupling agent (b). The other two images in Figure 4-7 are of the magnified interface without (c) and with the APTES treatment (d). There is no gap between the two components indicating successful adhesion for (b) and (d). If an air gap existed, light would be scattered due to the added interfaces, resulting in poor light propagation through the detector.

Figure 4-7: Freeze fractured cross-section of a glass rod embedded in a cured PVT matrix without (a) and with (b) functionalization along with a zoomed image of each (c & d)
As previously stated, the triple PSD rods composite was fabricated with the 30wt% PPO PVT matrix with crosslinking agent. The detector performance was characterized with a $^{252}$Cf neutron source. The data was collected for 2.5 hours and the source was placed 1.3 m from the detector. The measurements were performed twice, with a shadow cone placed between the source and detector for the second measurement. This ensures that only room scattered neutrons were detected by the composite and their contribution can be subtracted, as described by the method in Ref. [79]. Figure 4-8 (a) shows the resulting PSD plot. There are three distinct regions, which correspond to interactions of gamma rays, fast neutrons, and the thermal neutron capture. The thermal neutron capture region was isolated using a double Gaussian fit and all events occurring within 3$\sigma$ were identified as neutron capture events. This region was localized at PSP = 0.43 and around 533 keVee. A fiducial cut isolates the fast neutron band from the other events and is shown in Figure 4-8 (b). The FOM was calculated at 500 keVee for both the thermal neutrons/gammas and fast neutrons/gammas. The FOM for the fast neutron and gamma band was calculate to be $\sim$1, while the thermal neutron capture region and gamma band FOM was $\sim$3 for the full energy range. The capture efficiency was 0.09% and measured using a $^{252}$Cf source and a shadow cone. This values closely matched the simulated capture efficiency of 0.11% performed with Geant4.10.02 framework [89]. The gamma rejection with respect to neutron captures was measured to be $10^{-5}$ using the standard procedure outlined in reference [34].
In this part of the chapter we presented the first characterization of the effect of PPO on both the thermal and mechanical properties of PSD capable PVT. As the PPO content increases to 30 wt%, the glass transition temperature decreases to 25°C, leading to a mechanically soft polymer, which is not desirable as a matrix material. By introducing crosslinking agents (like DVB) during the polymer cure, the glass transition temperature increases around 15°C for the PVT, resulting in more robust matrix. The storage modulus of the PSD PVT is increased by 3 orders of magnitude with the addition of the crosslinking agent. Additionally, the crosslinking did not have any negative effect on the particle discrimination performance of the PSD PVT and seems to increase the FOM in some samples. The crosslinked PSD PVT was utilized in a novel triple PSD composite detector through coupling with $^6$Li-glass rods. The capture efficiency was measured at 0.09% and the gamma rejection with respect to neutron captures was measured to be $10^{-5}$. A FOM of ~1 for the fast neutrons/gammas and ~3 for the thermal neutrons/gammas was demonstrated as well. Future
research will focus on minimizing polymer clouding and testing different glass geometries to improve detection performance.

4.3 On the Novel Fabrication of 0-3 Heterogeneous Polyvinyl Toluene and Lithium Glass Composite Detector with Triple Pulse-Shape-Discrimination Capabilities

Recent novel composite detectors have been developed for the detection and non-proliferation of special nuclear materials (SNM) [54], [69], [80], [81], [90]. For SNM detection, it is important to have efficient pulse shape discrimination (PSD) between fast neutrons, thermal neutrons, and gammas. The detector’s PSD capabilities are a result of a mismatch in the decay times of the scintillation materials or intrinsic properties of the material itself. For example, if thermal neutron capture occurs in cerium-doped glass on $^6$Li, the resulting scintillation light pulse will have a decay time of around 50-70 ns [58]. While when high-energy photons, gammas, undergo proton recoil in the polymer, the resulting light pulse will have a decay time of ~3ns [3]. The fast neutron detection mechanism has been demonstrated in highly doped polyvinyl toluene and occurs when a neutron elastically scatters on hydrogen nuclei [48], [82]. Due to the slightly delayed nature of the triplet-triplet annihilation necessary for the fast neutron detection, the scintillation light pulse has a longer decay time than the gammas at ~10ns. Research has been focused on coupling two of these mechanisms together [47], [49], [83], [84], however not much has been performed on coupling all three together into a triple PSD detector.

This chapter expands on our previous research by introducing a triple PSD shards-based glass geometry, which has as higher efficiency and lower gamma rejection as simulated by GEANT4 [2]. Additionally, this glass geometry requires less processing than glass rods, resulting in a faster fabrication process. In this paper an inexpensive triple PSD neutron detector has been
fabricated with fast neutron sensitive polyvinyl toluene and lithium glass shards. The optical and nuclear properties were characterized to measure the effect of the light scattering on transmission along with the figure of merit, gamma rejection, and intrinsic efficiency of the detector.

The matrix components; divinylbenzene (DVB), initiator (Luperox 231), 2,5-diphenyloxazole (PPO), 1,4-bis-(o-methylstyril)-benzene (bis-MSB), and vinyl toluene were all purchased from Sigma Aldrich. The silane coupling agent (3-aminopropyl)triethoxysilane (APTES) was also purchased from Sigma Aldrich. The bulk GS20 was purchased from Scintacor, Inc.. The maximum emission wavelengths of the composite and its components were measured using a Shimadzu RF-1501 Spectrofluorophotometer. A Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer was used to measure the transmission and absorption spectra as a function of wavelength of the components and final composite. A NanoSEM 630 Field Emission Scanning Electron Microscope (FESEM) was used to image the interface between the glass shard embedded in the PVT. A Physical Electronics VersaProbe II X-Ray Photoelectron Spectrometer (XPS) was used to characterize the surface chemistry of the glass shards before and after functionalization. To test the detection capabilities, the composites were prepared using the same steps as previously discussed in Chapter 2, page 38 and 39.

The composite fabrication process begins with crushing the bulk GS20 piece to obtain shards using a vibratory ball mill. Sieves with 60 and 35 mesh sizes were used to sieve the shards to a size distribution around 500 µm. The shards size was selected to minimize the partial energy deposition based on our previous work [90]. To eliminate fine powder on the shards surface, they were cleaned with deionized water followed by ethanol. The shards were then placed in a 5wt% APTES solution in ethanol to functionalize their surface. The next step of the fabrication process focused on the polymerization of the PSD capable PVT matrix. The general polymer synthesis was
based on a paper published by Zeitseva et al., with some modifications [48]. In order to ensure minimal moisture and oxygen uptake, which causes cloudiness in the polymer, the chemicals filtration and most of the polymer synthesis steps were conducted in a nitrogen filled glovebox. The vinyl toluene (VT) and crosslinker (DVB) were filtered using column chromatography, while the initiator, PPO, and bis-MSB were used as received. All the components loadings in weight % (wt%), were with respect to the vinyl toluene monomer. The initiator, at 0.01wt% loading and the crosslinker, at 5wt% loading, were dissolved in the vinyl toluene monomer for 30 minutes. PPO % and bis-MSB at 20wt% and 0.1wt% respectively were dissolved for 1 hour in the vinyl toluene solution. The solution was then poured into a glass mold and placed in a silicone oil bath. The polymer was magnetically stirred at 55°C for 6 hours to partially cure it. The viscous solution was then transferred to a vibrational mixer container and the chemically modified Li-glass shards were added. The lithium glass loading was 7wt% with respect to the total weight of the composite. The polymer and glass shards were mixed at 600 rpm for 100 sec at 30 kPa then 1000 rpm for 200 sec at 3 kPa. The mixing step was performed under vacuum to degas the solution and remove any bubbles. After mixing, the solution was placed in an oven at 60°C for 15 minutes for partial curing. The mixing-curing cycle was repeated until the shards remained suspended in the PVT solution. The mixture was then poured into a glass mold and sealed. The composite was cured at 60°C for 4 days, 65°C for 2 days, 70°C for 4 days, then 55°C for 5 hours in the glovebox. Once fully cured, the composite was cut to dimensions of 3.5cm x 3.5cm and polished to optical transparency (See Figure 4-9).
Figure 4-9: Fabricated triple PSD shards detector in ambient (a) and UV (b) light.

The optical properties of the individual components and the composite were tested with different techniques. The UV/Vis spectrometer measured the transmission of the composite and its components. The spectrofluorophotometer measured the emission at different wavelengths at a specific wavelength of excitation. When a neutron is captured in the glass on lithium it emits a triton and alpha particle that deposit energy as they travel through the glass. This creates scintillation light in the glass which is eventually detected by the attached PMT. Since the glass shards are surrounded by the matrix, there must be adequate propagation of scintillation light originating from the shards and traveling through the matrix. Figure 4-10 shows the emission of the shards Li-glass, matrix, and shards composite. The Li-glass has a wavelength of maximum emission around 385 nm, while the PVT matrix and shard composite both have emission peaks at 423. The transmission of the polymer matrix is at a maximum of 88% from 420 to 600 and drops to ~10% around 405 nm. The glass emission curve and the matrix transmission overlap, while
above 420nm there is a portion of the emission curve in the matrix’s high transmission region. It is worth noting that the matrix and composite emission spectra are almost identical. There is a slight deviation around 400 nm but this is within the error of the machine. This indicates that the matrix is the dominate contributor to the overall fluorescence of the composite because of the wavelength shifted reemission of the absorbed lithium glass light.

Figure 4-10: Emission spectrum of the shards composite compared to the matrix and Li-Glass showing composite fluorescence is dominated by the polyvinyl toluene matrix.

Another important optical property for light propagation through the composite is the components’ relative refractive index. Any light that travels from one medium to another loses intensity due to Fresnel reflection. The loss increases with the increase in the difference between the refractive indices of the two media [91]. The detector needs to allow any created light to propagate through the detector until it reaches the photomultiplier tube. At a wavelength of 400 nm (where the difference in refractive indices is greatest, ~2%), the reflectance of light from the PVT and lithium
glass interface was calculated to be approximately ~0.0004% using Equation (4-1) with PVT as $n_1 = 1.56$, and lithium glass as $n_2 = 1.62$. In order for a composite to be optically transparent, the refractive indices need to be identical to minimize loss due to Fresnel reflectance [92].

$$R = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2$$ (4-1)

While the reflectance loss is only 0.0004% at the interfaces, the small shard size and high surface area to volume ratio results in many interfaces in the composite. In order to quantify the effect of the interfaces on the light transmission, the composite was characterized and compared to a sample of pure matrix without any glass shards. Figure 4-11 shows the UV/Vis transmission curve for the shards composite and PVT matrix. At longer wavelengths (500 to 600 nm) the transmission decreases 44% to 35% for the composite compared to the matrix. For wavelengths at the absorption edge (415 to 450) the transmission of the composite compared to the matrix decreases 62% to 44%.
The intrinsic efficiency is defined as the number of detected neutrons compared to the original number of neutrons incident on the detector. For this study, the intrinsic efficiency measurement was performed using a $^{252}$Cf source with and without a lead/borated polymer shadow-cone, which ensures only room-scattered neutrons reach the detector. The efficiency was measured to be 0.111% ± 0.002% which is in agreement with the value simulated with the Geant4.10.02 framework and found to be 0.119% ± 0.003% [89].

The gamma rejection measurement was performed with a 95.25 uCi $^{60}$Co source at a distance such that the dose rate at the detector’s surface was 12 mR/h, following the standard as stated by Kouzes et al. [34]. This rate was consistent with the other tested detectors in previous chapters. The capture region was defined using a 3σ sigma cut in energy and PSP dimensions and the gamma rejection was calculated to be $9.3 \times 10^{-7} \pm 1.2 \times 10^{-7}$ (See Figure 4-12). The shard
composite’s gamma rejection is lower than the previously reported triple PSD detector which was constructed using Li-glass rods [93]. This result supports the original simulation of composite detectors using different glass geometries where the composite with glass spheres had a lower gamma rejection than the glass rods composite [2]. The gamma rejection for the recoil region is $\sim 5.8 \times 10^{-2} \pm 9.1 \times 10^{-6}$. Future studies will work on improving this number by increasing the PSD properties of the composite matrix. The FOM were calculated using the equation below based on the centroid and distance between each peak. The FOM calculations was carried out in the energy range of 400-1600 keVee to ensure all neutron capture events were included. For the fast neutron to gamma recoil, the calculated FOM was 0.96. Additionally the FOM for the thermal neutron to gamma recoil was 3.94 and the fast compared to the thermal neutron was 2.55.

![PSD plot of triple PSD shards detector showing thermal neutrons, fast neutrons, and gamma features.](image)

4.4 Summary

This chapter answers the question originally posed in Chapter 1 of this dissertation: Does doping the polymer matrix with fluors and crosslinking molecules help realize a structurally sound triple PSD detector? We demonstrated the feasibility of triple pulse shape discrimination composite neutron detectors by synthesizing PSD capable PVT and combined with silane treated-
lithium glass shards. The fabricated detector was sensitive to a wide of particles thermal neutrons, fast neutrons, and gammas. The composite was characterized with a variety of techniques to determine the optical properties and detection performance using neutron ($^{252}$Cf) and gamma ($^{60}$Co) sources. UV/Vis spectroscopy revealed that light emission from the lithium glass is absorbed and reemitted by the PVT matrix between 400 and 475 nm, which is the range of maximum quantum efficiency of the PMT [30]. The intrinsic efficiency was measured at 0.111% ± 0.002%, which is in agreement with the simulated efficiency of 0.119% ± 0.003%. The detector had good gamma rejection in the thermal neutron capture region at $9.3\times10^{-7} \pm 1.2\times10^{-7}$. The gamma rejection for the fast neutron region was $5.8\times10^{-2} \pm 9.1\times10^{-6}$, and future work will focus on improving this value by increasing the separation between the fast neutron and gamma recoil band. This could be achieved by loading the PVT with a higher weight content of PPO and DVB for a structurally sound matrix.
Chapter 5

Optical Light Transport Simulations

5.1 Introduction

In the previous chapters, it was established that filler geometry and interfacial surface area play a role in the overall performance of the composite. The original motivation for utilizing different filler geometries was from GEANT4 (GEometry ANd Tracking 4) modeling software which simulated particles traveling through matter. This platform is mainly used for nuclear radiation experiments, high energy physics, astrophysics, medical physics, and space science [94]. GEANT4 uses Monte Carlo sampling to model the probability of different simulation outcomes. The user can control multiple aspects of the simulation such as experimental geometry, tracking, detector response, run management, and visualization. This allows for a wide range of customization to tailor the simulations to as close to the actual experiment as possible. Additionally, GEANT4 has several different packages that can be included to further adjust the physics which can be simulated such as optical photon transport. In the original study, the optical photon package was not included and therefore optical transport was not simulated in the composite neutron study [2]. In this study another optical simulation software is utilized.

TracePro from the LAMBDA Research Corporation is a powerful optical modeling software. It utilizes Monte Carlo ray tracing combined with a solid modeling engine to simulate light transport through materials. The user interfaces allow for modification and creation of composites with complex geometries. The material properties that can be simulated include absorption, scattering, specular reflection and transmission, fluorescence, and index of refraction. Additionally the light rays can be visualized and tracked as they travel through the composite,
which provides more insight into highly scattering media. It is also worth noting that TracePro does not have the ability to model nuclear radiation, but this is not within the scope of this dissertation since we are focused on optical photon propagation. Therefore this software helps achieve the goal of answering the initially posed question: \textit{how does the interfacial surface area effect the light transport through a composite detector?} The next sections of this chapter will explain the modeling, validation, and analysis of composite with different interfacial surface area.

### 5.2 Composite Design and Modeling

The overall goal for this chapter is to study the effect of interfacial surface area on light transport through composite detectors. In order to address this goal, a model with tailorable shard parameters, such as glass volume content, interfacial surface area, and composite thickness must be constructed to accurately simulate the transmission of light through the composites. Additionally the light transport software must be validated with experimental light transmission to ensure consistent simulations. Within the model, there are several assumptions that could affect the simulation output:

1. Approximation of shard shape as ellipsoids
2. Perfect contact between glass particle and polymer matrix (i.e. no air gap)
3. Perfect material (i.e. no impurities or inclusions)
4. No diffuse reflection at all composite interfaces
5. No bulk scattering (i.e. only scattering from Fresnel reflection)

This section focuses on the process flow developed to model the shards based composite with varying glass volume content and interfacial surface area. The first step for creating the composite is calculating the number of shards required to populate a volume with specific weight.
fractions and interfacial surface area. As discussed in chapter 3, the shards are estimated to be ellipsoid shaped with fixed semi axis ratios. The volume and surface area were calculated for ellipsoids with a range of a-axis lengths. The number of shards and interfacial surface area per unit volume were then calculated using the method in Appendix I, and are presented in Figure 5-1. The ellipsoid diameter, in Figure 5-1 graphs, refers to the full length of the a-axis.

Figure 5-1: Graphical representation of (a) the number of shards and (b) the interfacial surface area calculations for a range of ellipsoid diameters and weight contents.

Using the calculated number of shards for a given ellipsoid dimensions and weight content, a 3-dimensional model was created using Matlab R2017b software. Refer to Appendix II for the Matlab code. The code can be separated into 6 main steps:

1. Set the composite’s boundaries, so that the ellipsoids can only populate within this volume, and set its dimensions and number of the ellipsoids.
2. Generate random orientations and locations for each ellipsoid.
3. Calculate the distances between all the points and evaluate if any of the ellipsoids overlap. If the distance between two points is less than the ellipsoid diameter, then one of the points will be rejected and replaced with another randomly generated point. This step repeats until there are no
point violating the minimum distance. It is worth noting that this method does not take into account
the orientation of the ellipsoids and assumes their excluded volume to test for overlap. This
assumption is acceptable for lower weight contents and small aspect ratio shards and is thus
appropriately implemented in this dissertation. If one was to simulate a higher content or high
aspect ratio fillers, then the code would need to be modified to take into account particle
orientation.

4. Create one particles at a time by using the ellipsoid function at the generated points with
the randomly generated orientation to create the glass particle. This is repeated until all the
ellipsoids are generated.

5. Plot the surfaces of all the particles in a figure for visualization. Figure 5-2 is a Matlab
generated visualization of 720μm ellipsoids with 3.5 wt% in a cylindrical volume.

6. Generate the composite’s structure into a file readable by TracePro.
Step #6 is carried out in two (2) parts. It starts by converting the surfaces of each particle to a file type that is readable by a CAD (computer-aided design) software. Then the surface mesh is converted into solid bodies. TracePro only has a few types of files that it is possible to read, which are SAT, STP, and STL. First, a function called “surf2stl” written by Bill McDonald is implemented to convert the surface mesh CAD file to an STL file [95]. The surface mesh STL file is then converted into a SAT file that enables saving the ellipsoids as solid and not just mesh surfaces. Depending on the amount of shards and size of the composite volume the run time of STL to SAT conversion ranges from 5 to 30 minutes.

This paragraph outlines how the surface mesh generated by the MatLab script is converted to a solid body that is in a file type which can be read by TracePro. A software called MeshLab is
used to repair any defects that might be present in the STL file. Duplicate vertices and faces are removed and the close vertices are merged to heal the mesh. If needed, the file size can be reduced using the “Simplification: Quadratic Edge Collapse Decimation” option. This coarsens the mesh allowing for the shards to be saved with fewer number of surfaces. However, this coarsening might affect the shape and thus surface area of the ellipsoid. Figure 5-3 shows how the shape of the ellipsoids change when this technique is implemented. The 720 μm shards are shown before (a) and after (b) this reduction. Regardless if this reduction is performed, the next step is to normalize the face normal to ensure all the surfaces are facing the same direction. Once this process is complete the assembly is saved as another STL file.

![Figure 5-3: 720μm shards before (a) and after (b) implementation of “Simplification: Quadratic Edge Collapse Decimation” in MeshLab](image)

At this point, the mesh surfaces are healed and now ready to convert to solid bodies. The file is opened in a new program called FreeCAD. This software has the ability to convert the mesh surfaces to solids along with saving the file as a STEP format. This format has the ability to save the assembly as solids. First, the bodies must be separated into multiple solid parts using the “split mesh” function in FreeCAD. Then, shapes are created using the “create shape from mesh”
function. The final step is to make a solid body from the shape with “convert to solid” option. After all these steps are performed, the ellipsoid solid assembly is saved as a STEP file. The last software needed to finish converting the file is SolidWorks. The STEP file is then opened in SolidWorks and resaved as a SAT file. The assembly can finally be read in TracePro and used in the simulation.

5.3 Material Property Check

Before the composite’s optical properties are simulated and validated, it is important to check the output of each material to ensure the model runs properly. The model inputs are absorbance, emission, excitation, and refractive index of the materials composing the composite. These properties were measured using UV/Vis spectrometer and spectrofluorophotometer, as detailed in Chapter 2. Figure 5-4 shows the graphs of the measured absorption (a), index of refraction (b), and emission and excitation (c) for PVT and Li-glass. It is also worth noting that the absorption curves must be corrected for reflectance, explaining the close to 0 absorption for PVT in the visible light range.
Figure 5-4: Graphs showing absorption (a), index of refraction (b), and emission and excitation (c) used as inputs for the PVT and Li-glass.

An integrating sphere was built into the model with dimensions matching the one used experimentally for UV-Vis measurements. This sphere allows for all the transmitted light to be collected even if it is scattered from within the composite. The process is outlined in the TracePro Integrating Sphere Tutorial [96]. Figure 5-5 shows the model schematic with the sample highlighted in black, the detection surface on the lower part of the sphere in green and the integrating sphere in grey. The light source is shown in red on the left side of the figure. The model’s output is transmission and it was compared to the experimentally measured values to validate the model.
Figure 5-5: Schematic of the model of the UV-Vis test with the integrating sphere (grey), the sample (black), and the light source in red on the left side.

The simulated transmission is calculated using the same method as the experimental setup. The light intensity is collected without the sample in the beam path as the reference. Then the sample is placed in the beam path and the ratio of the intensities are calculated and multiplied by 100 to obtain the transmission percentage. Figure 5-6 shows the transmission check for the PVT used in the simulation. Three types of PVT were simulated: (a) 30wt% PPO PSD PVT, (b) pure PVT (Pure PVT and 30wt% PPO-PVT synthesized in-house as detailed in Chapter 4), and (c) Eljen EJ-290 PVT (kit in Chapter 3).
Figure 5-6: Transmission check for (a) PSD PVT, (b) pure PVT, and (c) Eljen PVT with the simulated and experimental curves.

The range of wavelength was chosen to be from 350 to 500 to include the absorption edge of the PVT and glass. This range is also where the PMT has the highest efficiency for the collected light. The dashed curves in Figure 5-6 represent the simulated transmission and the solid curves are the experimental transmission values. Overall the trend for the simulated curves are in agreement with the experimental curves. The transmission values obtained from TracePro are around 5 to 10% higher than the measured values. This can be attributed to the simulation assumptions that (1) the materials are free of defects and inclusions, which are present in the actual
samples, and (2) the surfaces of all samples are perfectly flat and do not have any scratches or clouding. Figure 5-7 shows the simulated and experimental transmission of the Li-glass. As with the PVT samples, the trend is consistent between the two curves and the simulation overestimates the transmission by around 5%.

![Figure 5-7: Comparison of the experimental and simulated transmission of the Li-glass](image)

The check of the individual materials transmission demonstrates that the model is working properly. While the model does have a slightly higher transmission, this is to be expected since the materials are assumed to be free of bulk and surface defects which would be present in actual samples. The next step for modeling the light transport is to combine the material properties and the generated ellipsoids into one composite. The transmission through the composite is then simulated and compared to experimental values to validate the model.

### 5.4 Light Transport Model Validation

In order to successfully validate the simulated composite, a model must be built in the TracePro software. First, the generated solid ellipsoids are opened and scaled to the correct size.
The default global length scale for the program is in millimeters. If the thickness of the composite varies then the ellipsoid assembly can be duplicated to reach the desired length. It is worth noting that the thicker the composite, i.e. more duplicates of the assembly, the more time consuming the simulation will be. Figure 5-8 shows a composite with 250μm ellipsoid at 3wt% and a thickness of 35mm built in TracePro. The grey cylinder is the PVT matrix and the black ellipsoids are the Li-glass shards.

![Composite model](image)

Figure 5-8: TracePro model of the composite neutron detector, with the ellipsoids highlighted in black and the PVT matrix in grey

Next the same integrating sphere used to check the material transmission individually was utilized for the composite validation. A 500μm 7wt%, 250μm 1wt%, and 250μm 3wt% composites were generated and implemented into the model. The material properties were assigned to the appropriate parts of the composite. The dimensions were matched to the physical composites fabricated in Chapters 3 and 4. The transmission was calculated using the same method as
described in the previous section in the same wavelength range. Figure 5-9 shows a comparison between measured and simulated transmission of the 7wt% GS20-PVT composite with 500μm shards and 1 and 3wt% GS20-PVT composites with 250μm shards.

![Graphs showing comparison between measured and simulated transmission](image)

**Figure 5-9: Validation of the TracePro simulations for 7wt% Li-glass/PVT composite with 500μm shards and 1 and 3wt% Li-glass/PVT composites with 250μm shards**

The simulated transmission trends for all the composites are similar to the experimental measurements. Small deviations can be seen from 420 nm to 500 nm for the 500μm 7wt% composite. This could be due to the assumptions of defect-free composite with perfect interfaces in the model. Impurities or temperature changes could result in delamination of the polymer from the glass surface which introduces an air gap. Air has an index of refraction around 1, therefore the reflectance at the interfaces would lower the transmission through the composites. Additionally, the ellipsoid surfaces are assumed to be perfectly flat in the simulations, when in reality this is not the case. The glass surfaces are not polished and their roughness increases the interfacial surface area, which in turn increases the light scattering and reduces the transmission. While the simulation does not perfectly match the experimental results, it still accurately and consistently models light transport through a variety of different glass weight content and sizes.
The model’s validation allows expanding its use to simulate light transport through other composites with a spheres or ellipsoids of different sizes and a range of particles contents.

### 5.5 Model Analysis

The main goal of this chapter is to understand how the light scattering from polymer/glass interfaces, the particles size, and content affect the light transport through composites. Therefore this section will seek to construct and analyze models with a variety of interfacial surface areas. The transmission of the light was simulated and calculated as previously detailed, then used as a way to estimate the detector performance. If the light transmission is not sufficient to reach the PMT, the detector efficiency suffers. The first analysis performed to study the effect of glass weight content on the light transmission. Figure 5-10 shows the plot of the transmission as a function of glass content, while the ellipsoid diameter is held at 500 µm and the composite volume is kept constant. This is done for a single wavelength (440nm), but can be tailored to multiple wavelength as well. The plot shows an inverse relationship between the glass shard content and the transmission of the light through the detector. This is due to the increased scattering when more glass shards are incorporated into the composite. The plot demonstrates how the model can be used to predict the light transmission through a composite for a range of weight contents.
Figure 5-10: Graph showing inverse relationship between glass content and light transmission of 500µm ellipsoids at 440 nm

The model can also be used to study how the interfacial surface area effects light transmission. This is done by keeping the weight content of the glass constant and varying the ellipsoid diameter. The smaller the ellipsoid the larger the interfacial surface area is as demonstrated in Figure 5-1. The detector thickness is also held constant at 35 millimeters for each composite simulated. Additionally the wavelength of interest is the same as the previous analysis, 440nm. Figure 5-11 shows the relationship between the interfacial surface area per unit volume of the composite and the light transmission. As the surface area increases the light transmission decreases in a roughly linear trend. This trend might not be valid for higher interfacial surface area, however due to the long time required to simulate 7wt% it is omitted from the study.
Another aspect of composite design that this model can simulate is the effect of thickness on the light transmission. For large area detectors, where the light transverse long distances, this is an important aspect to consider. Single phase detectors only require knowledge of the attenuation length of the material to accurately predict the maximum thickness the light can travel. This is not the only factor taken into account for composite detectors, since the light will be scattered. For this study the weight content, ellipsoid diameter, and wavelength of interest are kept constant at 7wt%, 500µm, 440nm. Figure 5-12 shows the graph depicting the relationship between composite thickness and transmission. With this model it is possible to explore the effect of different composite parameters on light transmission without the need of physically fabricating the composite.
Another advantage of using this model is that it can be easily tailored to other glass filler shapes. For example, in the original paper that was discussed in the beginning of this chapter, the glass is simulated as spheres [2]. Using GEANT4, the neutron efficiency and amount of misidentified gammas were simulated for glass spheres with a range of dimensions. The values were taken from the paper and graphed to better show the relationship between neutron efficiency and misidentified gammas as a function of sphere diameter. Figure 5-13 shows graphical representation of the data presented in the paper. The optimized detector should have high neutron efficiency and a low percent of misidentified gammas. As the glass diameter increases the neutron efficiency increases however, the amount of misidentified gammas also increases. Therefore there is a tradeoff between these two detector properties. Now that the light transport simulation has been built, there is another metric to consider when choosing the optimum sphere diameter.
Using the same process as before, a sphere based composites are created and imported into TracePro. Only the MatLab code is altered to generate spheres instead of ellipsoids. The weight content is kept the same as in the paper at 7wt%. The thickness of the composite is not mentioned in the paper therefore it is chosen to be 35mm. The thickness allowed for comparison between the spheres and ellipsoids with equivalent interfacial surface area. Figure 5-14 shows a modified plot from the previous graph with the transmission instead of the neutron efficiency. There is a direct relationship between sphere diameter and light transmission. However the deviation is less than 10% transmission for the range of simulated sphere diameters. This means the light transport will not be drastically affected by the glass filler size for this detector thickness. There could be a more exaggerated scattering effect if there is an increase in detector thickness, which might be a future study.
Summary

This chapter answers the question posed in the beginning of this dissertation: *how does the interfacial surface area effect the light transport through a composite detector explored with optical modeling software?* The light transport for PVT and Li-glass composites was successfully simulated using the ray tracing software, TracePro. The glass filler generation process was shown to be relatively quick and easily tailored to create composite with a wide range of composite dimensions, glass weight content, filler diameters, and filler shapes. All of these factors alter the interfacial surface area. TracePro was proven to have the ability for accurate and consistent simulation of the material properties along with integration into complex composite designs. The increased glass weight content was shown to have an inverse effect on the light transport, while increasing the ellipsoid diameter was shown to have a direct effect. Meaning that overall the interfacial surface area has an inverse relationship with light transport. The composite thickness also has a large effect on the transmission of light with a trend similar to an exponential decay.
This chapter lays the groundwork for future development of composite neutron detectors from an optical light transport perspective.
Chapter 6

Conclusions and Future Work

6.1 Summary and Conclusions

Polymer and glass composites are promising candidates for the detection of neutrons emitted by special nuclear material. By coupling materials that have unique properties such as scintillation decay time, it is possible to have excellent discrimination between different particle types like neutrons and gammas. Additionally, composite detectors allow for the ability to tailor the detector capabilities, such as the ability to detect a wide range of neutron energies. This is accomplished by utilizing materials that have sensitivities to different neutron energies. For the dissertation, only a system of two materials is researched, but the potential exists to couple more materials together to realize a detector for many types of radiation. Previous research has shown the ability of composites to detect neutrons, however, it was mainly focused on development from a nuclear perspective.

This dissertation aimed to look at the challenge of composite neutron detector development and analysis from a material science and optical light transmission standpoint, which has been a crucial area of research that has been overlooked up to this point. For scintillation detectors, when two materials are couple together with mismatched index of refraction, the optical light propagation is adversely affected. The research in this dissertation addressed that challenge and provided solutions that were not previously considered. These solutions include glass surface functionalization and light transmission modeling to name a few. The groundwork laid with these studies could help optimize detector performance for composite detector by identifying optimal filler shape and geometry. The main scope focuses on composite fabrication and experimental
characterization of polyvinyl toluene and lithium glass to better understand their role in neutron detection. The studies performed in this dissertation seek to answer the three questions posed in the beginning:

1) *How do the shape of the filler and the presence of internal interfaces affect the light output and efficiency of a polymer/glass composite detector?*

2) *Does doping the polymer matrix with fluors and crosslinking molecules help realize a structurally sound triple PSD detector?*

3) *How does the interfacial surface area effect the light transport through a composite detector explored with optical modeling software?*

The initial composites were fabricated using commercially available material to demonstrate their feasibility. Several composites with different glass fillers (i.e. rods and shards) were characterized with optical and nuclear techniques. The polymerization was studied to ensure the accelerated curing time produced a stable and robust matrix. By increasing the temperature of the cure the amount of synthesis time was reduced to 30 hours form 14 days. It was also discovered that curing the polymer in a nitrogen-rich environment eliminated clouding most likely produced by oxygenation and the presence of moisture. Over the course of our measurements, the composite were relatively stable. The composites’ optical light propagation was studied using a UV/Vis spectrometer. It was found that the interfacial surface area has a greater impact on light transmission than the volume content of the glass. The composites’ light output was measured in the presence of a neutron source ($^{252}$Cf) and found to be more dependent on the glass volume content than the interfacial surface area. Additionally it was discovered via the PSD plots that the glass particle size and thus interfacial surface area has a significant effect on the figure of merit for composite detectors. Neutron capture is more likely to happen at the glass surface than in the
bulk resulting in a partial energy deposition and misidentification of neutrons as gammas. This study postulated that increasing the particle size could help mitigate the edge effect.

The next iteration of the PVT and Li-glass composite focused on fabrication and characterization of a triple pulse-shape-discrimination neutron detector. The matrix was functionalized to allow for detection of fast neutrons by increasing the weight content of the PPO dopant. Mechanical, thermal, optical, and nuclear properties of the loaded matrix was characterized using a variety of technique. It was found that as the weight content of the PPO increased the glass transition temperature and storage modulus decreases, creating a soft and deformable matrix at room temperature. This plasticizer effect was mitigated with the addition of a DVB crosslinker which increased the $T_g$ and storage modulus. The optical properties were also studied and found to not be impacted by increasing the dopant concentration. The figure of merit between the fast neutron and gamma band had a direct relationship with the amount of PPO. The max value obtained for the figure of merit was 1.01. A rods composite with 7wt% Li-glass was fabricated and tested using the in-house synthesized PSD capable PVT. The neutron efficiency and gamma rejection was measured for this composite using a $^{252}$Cf source. This part of the study successfully demonstrated a novel triple PSD capable composite.

The same matrix was utilized in the fabrication of a triple PSD 500μm glass shards composite. Glass functionalization was utilized to eliminate an air gap at the polymer matrix and glass shard interface by increasing adhesion between the two materials. The treatment was predicted to increase the light transmission through the composite thanks to the closer index of refraction match. A modified shard composite fabrication process was created to maximize the amount of shards suspended in the matrix after the cure. A 7wt% glass content was obtained by using the adapted process. Additionally a neutron source was used to measure the figure of merit,
neutron efficiency, and gamma rejection of the shards based triple PSD composite. When compared to the Li-glass rods, there was an order of magnitude reduction in the number of misidentified gammas and the Figure of Merit of the gammas and thermal neutrons was increased. Additionally the edge effect explored in Chapter 3, was mitigated with the shard size increase which can be seen in the minimal neutron capture tail in the PSD plot.

There are still challenges associated with the 0-3 shards composite detector. The fabrication process of the shards detector can be arduous since the pre-cure time must be determined by trial and error. The PVT could cure too fast resulting in a matrix with inadequate degassing and bubbles. On the other hand, the PVT could cure too slow meaning the shards would not remain dispersed and settle before the PVT is completely cured. Additionally there are several challenges associated with the detection performance using the 0-3 composite detector. In the study, it is determined that the smaller shard size results in better gamma rejection. However, the smaller size also decreases the FOM, due to the partial energy deposition during a thermal neutron capture event into the PVT matrix. The glass shard fillers also introduce more interfaces that scatter light within the composite. The decreased light transmission through the composite lowers the amount of light collected by the PMT, thus lowering the efficiency of the detector. Even with all the challenges discussed for the 0-3 shards composite it is still the best solution to address the needs of a solid-state detector for the identification of fast neutron, thermal neutrons, and gammas. The other configuration studied in this dissertation is the 1-3 glass rods composite. This detector configuration has respectable gamma rejection and FOM, along with better light transmission compared to the 0-3 composite, however the fabrication and cost limit its possible application. For example, the 1-3 rods composite requires additional materials and steps such as a 3-D printed mold and placement of individual rods. The glass rods must also be cut to the specified geometry, which adds another
processing step and increases fabrication cost. Overall the 0-3 shards composite exhibits an easier fabrication process, lower manufacturing cost, better gamma rejection, and poorer light transmission than the 1-3 composite.

The nuclear simulations and experiments both show that the gamma rejection is also affected by the different glass geometries. For the 1-3 triple PSD composite the gamma rejection is poorer than the 0-3 triple PSD composite due to the size and shape of the glass. The larger glass filler size and shape in the 1-3 triple PSD composite result in a farther travel distance of the gamma through the glass. This increases the probability of the gamma interacting with the glass, resulting in a light pulse with the same decay time as a neutron capture event. The light pulse of the gamma would then be misidentified as a thermal neutron capture leading to a higher gamma rejection. In the 0-3 triple PSD composite the shards are small enough in size and shape that the probability of gamma interaction in the glass is very low, resulting in a smaller gamma rejection. One the other hand, the 1-3 composite has a lower interfacial surface area than the 0-3 composite with the same glass weight content because of the larger size of the glass rods compared to the glass shards. Therefore the light transmission through the 1-3 composite would be better than the 0-3 composite. This tradeoff between gamma rejection and light transmission must be taken into consideration when designing a composite detector. For example, if the detector needed occupy a larger volume, one might consider the rods based detector because of the better light transmission properties. If the detector is required for the identification of thermal neutrons in a high gamma rate environment, then the shards detector would be the more suitable choice.

In order to better understand the relationship between the interfacial surface area and the light transport through the composite an optical model was created using TracePro software. The glass spheres were approximated as ellipsoids since the crushing procedure did not produce perfect
spheres. A process was developed to generate composites with solid ellipsoids which can be imported into the ray tracing software. The parameters of the composite included the size of the matrix, glass weight content, particle size, and particle shape. The individual materials properties were checked and the composite transmission was validated with several shards based detectors. The glass weight content and interfacial surface area were found to have an inverse relationship with the light transmission. The ellipsoid size had a direct relationship with the transmission. As the thickness of the composite was increased the transmission decreased with an exponential trend. This versatile simulation allows the user to accurately simulate the light transport for a wide range of composite designs. Also a tradeoff was established to relate the optical simulations to the nuclear detector performance. Glass sphere composites were generated with the same diameters and weight content as the GEANT simulation paper. There was found to be a tradeoff between the interfacial surface area and the misidentified gammas. As the interfacial surface area increased the number of misidentified gammas increases which is not desired. On the other hand the transmission increased with a decreasing interfacial surface area. While this tradeoff was not dramatic with the composite thickness or sphere diameter range that was simulated, it could be more exaggerated with thicker composites or higher interfacial surface areas.

6.2 Contribution of this Dissertation

There were several major conclusions and results obtained from the work throughout this dissertation. This section will focus on articulating the contributions and their possible impacts. The three main contributions all relate to the original questions and are listed below:

1) Discovered glass filler interfacial surface area impacts both light transmission and pulse shape discrimination
2) Learned that crosslinkers increase the structural stability for highly doped PVT to help realize a triple-pulse-shape discriminate composite

3) Developed accurate light scattering simulations that has the ability to model light transmission through composite neutron detectors

To the best of our knowledge this was the first project to experimentally study the effect of glass filler geometry on composite neutron detector performance. Past research mostly utilized simulations to guide their detector design. However it is important to have the experimental data to help validate simulations, which this aspect of the study provided. One of the challenges was creating a fabrication method to suspend the particles with a much higher density then the surrounding matrix. This was overcome by using a vibrational mixer and partially cured matrix. This technique can be scaled too much larger sizes since the shard and polymer solution can be poured. Additionally the effect of interfacial surface area on detector performance was quantified for the first time, specifically its impact on the figure of merit. There is most likely a threshold where the energy deposition within the bulk dominates the partial energy deposition at the surface. While the threshold has not been quantified, this study provides the first steps towards its identification.

The original composites consisted of commercial materials which limited the control over the material properties and detector performance. Therefore the next major contribution focused on synthesizing a PVT resin in-house to have better control over the components and understanding of the structure-property relationship. A pourable PSD capable resin was developed that allowed for detection of fast neutrons. The PSD PVT was based off of a polymer with similar components as Zaitseva et al. [48]. However this study expanded the characterization to encompass the material properties. The plasticizer effect on the thermal and mechanical properties was
quantified and a crosslinker was added to mitigate the negative effects. It is therefore possible to increase the PPO loading to higher concentrations than would have been previously possible. We successfully applied characterization of thermal and mechanical properties to help engineer a more robust polymer matrix. The other major contribution within this field is the fabrication and characterization of a first of its kind triple pulse-shape-discrimination capable composite. While other materials have this ability, like CLYC, this is the first time it has been demonstrated in a composite detector. Also, glass surface modification was implemented to reduce light loss due to scattering at the polymer and glass interfaces. The functionalization increases the affinity of the polymer matrix to the glass surface, which is the first time this technique has been used to fabricate composite detectors.

A flexible modeling process was developed to accurately simulate light transport through the composite. The effect of light scattering due to interfacial surface area can now be quantified for a variety of glass particle shapes, sizes, weight content, and composite thicknesses. There was found to be an inverse relationship between the interfacial surface area and light transport. Additionally, the higher the weight content of the glass fillers, the lower the light transmission. A tradeoff between the number of misidentified gammas and light transmission for a range of interfacial surface areas was established. To the best of our knowledge this was the first time optical modeling has been used to help design a composite neutron detector. The simulation also has the potential to accurately predict the transmission of light without the need of fabricating a physical composite. There is a tradeoff between light propagation and detection efficiency of thermal and fast neutrons. This would be very prevalent in larger composite detector since the light would be significantly attenuated before reaching the PMT. For example, if a large volume composite detector was required with a specific filler content, the filler size and shape could be
optimized using this model to maximize light transmission. The model could be used in conjunction with GEANT4 to maximize the neutron detection efficiency and minimize the gamma rejection.

6.3 Future Work

There are several aspects of this dissertation that can be explored in future studies. For example, a more direct study of the effect of interfacial surface area on neutron detector performance would be very beneficial. This would allow the researcher to identify a glass filler size threshold such that the neutron tail would be eliminated. Another aspect of the composite detector development that was not discussed in this dissertation is the long term effect of aging on the composite performance. Along the same line, the mechanisms of aging and mitigation of the deleterious effects is also an area of open study. Several studies have been performed and suggest that the combination of moisture uptake and temperature changes results in a condensation of water within the matrix [97], [98]. This results in a fogging of the polymer matrix, which reduces the light transmission and detection efficiency. Wrapping the composite was postulated to mitigate the aging with some success [99]. However if a single point defect in present in the wrapping then the aging will not be stopped or slowed. Therefore it is worth considering additives to prevent water condensation at the molecular level. Figure 6-1 shows the fogging effect in a freshly fabricated rods composite (a) that has been aged in ambient conditions for 1 year.
Another area of the research that is worth further consideration is increasing the glass transition temperature of the PSD capable polymer. With the addition of the crosslinker the glass transition temperature was increased 20°C above room temperature (25°C). This mean it is still below the maximum temperatures that some areas of the country are exposed to (50°C or more). Therefore one could possibly increase the glass transition temperature further by adding more crosslinker. One possible drawback of increasing the crosslinker content would be decreasing the monomer concentration, which would reduce the ability of the polymer to moderate the neutrons. The other option would be to decrease the PPO content, which would lower the sensitivity of the PVT to fast neutrons. It is also worth researching the reason why the FOM increase with the addition of the DVB, which could be a result of decreased spacing between polymer base and primary fluor. The efficiency of the energy transfer from the base to the primary fluor is dependent on the separation distance with an inverse 6th-power law. As discussed in section 2.2, this energy transfer mechanism is known as FRET. It is could be possible that the DVB crosslinker increases
the density of the PVT matrix, which results in a closer distance between the polymer and fluor, leading to a more efficient energy transfer. This efficient energy transfer could lead to an increased figure of merit, however further research into this hypothesis is required. Also the loss of light at the interfaces can be mitigated even further by using a refractive index matching coupling agent between the glass filler and polymer matrix [100]. By closely matching the refractive indices of the two materials, the amount of reflected light is reduced at the interface. The less light that is reflected, the more light is transmitted through the detector at each polymer/glass interface resulting in a more efficient detector. A possible option of index matching coupling agent for this system could be magnesium fluoride (MgF₂) [101]. Integration of optical and nuclear modeling will also further research in composite detectors. As discussed previously this is theoretically possible using GEANT4, however more time is required to fully simulate the shards composite than could be afforded at this time. The MatLab script could possibly be used to generate ellipsoids to be exported in a format that GEANT4 can read. If this is possible, then the user would be able to simulate an entire experiment with a neutron source and take into account the optical photon transport through the composite. This would streamline the simulation process and directly relate composite design to detector performance.
APPENDIX A: Interfacial Surface Area Calculations

Each glass rod used was 0.1 x 0.1 x 7.73 cm, resulting in a rod surface area of 3.11 cm$^2$. The surface area per rod was multiplied by the total number of rods (155) in order to get the total glass surface area of 482.05 cm$^2$. The total glass surface area was divided by the total volume of the detector in order to calculate the surface area per unit volume of composite. For the 12.7cm x 12.7 cm rods detector (with volume=1608.8 cm$^3$), the interfacial surface area per volume of composite is 0.30 cm$^2$/cc.

While the shards do not have consistent shapes, for the purpose of this analysis they were estimated to be ellipsoids (see Figure A-1). Ellipsoid’s surface area $S$ is

$$S = 4\pi \left(\frac{(ab)^{1.6}+(ac)^{1.6}+(bc)^{1.6}}{3}\right)^{1/1.6}, \quad (A-1)$$

where $a$, $b$, $c$ are the lengths of axes, while the volume $V$ is

$$V = \frac{4}{3}\pi abc. \quad (A-2)$$

The following case only shows calculations with 3wt% 250 µm (for the a-axis) shards for the sake of brevity. The same method can be applied for the 1wt% shards detector and 7wt% 500 µm shards.

ImageJ was used to measure the averages of all three axes ($a = 312\mu$m, $b = 198\mu$m, $c = 71\mu$m) from SEM images with an example shown in Figure A-1.
Figure A-1: SEM image of ellipsoid shaped glass shards.

Equations (A-3 and A-4) were created based on these averages to calculate surface area of the shard from one measured axis, in this case axis a.

\[ b = a / 1.58 \]  \hspace{1cm} (A-3)

\[ c = a / 4.39 \]  \hspace{1cm} (A-4)

Only histograms using this a-axis were created from measuring the shard size with ImageJ and Equations (3 and 4) shown in Figure. By using Mathematica the Log Gaussian (A-5) function was determined to have the best fit and the values are tabulated in Table A-1.

\[ y = \frac{1}{x\sigma\sqrt{2\pi}} e^{-\frac{(lnx-\mu)^2}{2\sigma^2}} \]  \hspace{1cm} (A-5)
Figure A-2: Histograms of shard size, surface area, and volume fit with a Log Gaussian function.
Table A-1: Table of pertinent values from the Log Gaussian fit

<table>
<thead>
<tr>
<th>Histogram Type</th>
<th>µ</th>
<th>σ</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>5.71</td>
<td>0.20</td>
<td>306.6 µm</td>
</tr>
<tr>
<td>Surface Area</td>
<td>11.45</td>
<td>0.40</td>
<td>1.07*10^5 µm^2</td>
</tr>
<tr>
<td>Volume</td>
<td>16.44</td>
<td>0.60</td>
<td>1.65*10^7 µm^3</td>
</tr>
</tbody>
</table>

The mean values from the Log Gaussian fit in Table A-1 were used to calculate the average surface area and volume of a glass shard. The dimensions of the detector (7cm x 3.8cm) were used to calculate the volume was 146 cm^3. The volume of glass per unit volume of composite (A-6) was calculated from the volume of glass in the detector and total volume of the detector. The m_{glass} was measured at 5.25g and the ρ_{glass} is 2.5g/cm^3 therefore the V_{glass} (per cm^3) was 0.0144cm^3.

\[ V_{glass} = \frac{m_{glass}}{\rho_{glass}} \frac{1}{146cm^3} \]  

(A-6)

Using the mean volume from Table A-1 and the calculated V_{glass}, the amount of shards was calculated to be 873 (per cm^3) (A-7).

\[ N_{shards} = \frac{V_{glass}}{1.65 \times 10^{-5} cm^3} \]  

(A-7)

Next the mean surface area from Table A-1 and number of glass shards (A-8) was used to calculate the interfacial surface area per unit volume of composite at 0.93 cm^2/cc.
\[ S_{glass} = N_{shards} \times 106771 \mu m^2 \] (A-8)

The same procedure was performed on the 1wt% shard composite and the interfacial surface area per unit volume of composite to be 0.31 cm\(^2\)/cc.

In order to calculate the surface area to volume ratio the total surface area and volume of the glass is needed. The rods total surface area is 482.05 cm\(^2\) and the total glass volume is 11.94 cm\(^3\). The ratio of the total surface area to the volume is 40.37 cm\(^2\)/cm\(^3\).

The same process is applied to the shards detector. The total surface area for a 3wt% shards detector of the detector is calculated from Equation (A-8) at 135.78 cm\(^2\). The total volume of the glass is extracted from Equation (A-6) at 2.102 cm\(^3\). The calculated total surface area to volume ratio for the shards composite is 64.7 (cm\(^2\)/cm\(^3\)).

A tabulation of all the relevant values previously discussed can be found below in Table A-2.

<table>
<thead>
<tr>
<th></th>
<th>Rods (6wt%)</th>
<th>Shards (1wt%)</th>
<th>Shards (3wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Dimensions (cm)</td>
<td>0.1x0.1x7.73</td>
<td>312x198x71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Glass Surface Area (cm(^2))</td>
<td>483.05</td>
<td>45.26</td>
<td>135.78</td>
</tr>
<tr>
<td>Total Glass Volume (cm(^3))</td>
<td>11.94</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Detector Dimensions (cm)</td>
<td>12.7x12.7</td>
<td>7x3.8</td>
<td></td>
</tr>
<tr>
<td>Interfacial Surface Area per Unit Volume of Composite (cm$^2$/cc)</td>
<td>0.30</td>
<td>0.31</td>
<td>0.93</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Total Surface Area to Volume Ratio (cm$^2$/cm$^3$)</td>
<td>40.37</td>
<td>64.7</td>
<td>64.7</td>
</tr>
</tbody>
</table>

To calculate the interfacial surface area within one standard deviation (67.5 percentile) the $\sigma$, $\mu$, and mean from Table A-1 was used from the size row. The values were calculated to have a lower bound of 251$\mu$m and an upper bound of 374$\mu$m. The lower and upper bound of the surface area for the 250$\mu$m shards were $7.17 \times 10^4\mu$m$^2$ and $1.6 \times 10^4\mu$m$^2$. The lower and upper bound of the volume for the 250$\mu$m shards were $9.06 \times 10^6\mu$m$^3$ and $3.01 \times 10^7\mu$m$^3$. The total glass volume was taken as constant and used to weight the interfacial surface area. These values were then used to calculate a new interfacial surface area weighted 16.25% for the upper and lower bound and 67.5% for the mean using the same method described above in equations A-6 – A-8. The new values are below in Table A-3 and slightly higher for the 250$\mu$m 1% and 3% in. For the 500$\mu$m 7wt% the value decreases slightly, which is most likely due to the shard size distribution.

Table A-3: Interfacial surface area per unit volume of the composite taking into account the shard size distribution

<table>
<thead>
<tr>
<th>Interfacial Surface Area per Unit Volume of Composite (cm$^2$/cc)</th>
<th>250$\mu$m (1wt%)</th>
<th>250$\mu$m (3wt%)</th>
<th>500$\mu$m (7wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>1.04</td>
<td>0.72</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX B: Ellipsoids Generation Code

clc, clear all, close all

Define Parameters

\[ r = 0.68; \quad \% \quad r = \text{radius} \]
\[ h = 0.68; \quad \% \quad h = \text{height} \]
\[ N = 495; \quad \% \quad N = \text{number of particles} \]

% Axis of Ellipse
xa = 0.072/2;
yb = xa/1.58;
zc = xa/4.39;

First Generation

% Generate an array of random numbers
pmatrix = zeros(3,N); % use random numbers

% Generate random orientations
for j=1:N
    Theta = pi*rand; % random numbers between 0 and pi
    Phi = 2*pi*rand; % random numbers between 0 and 2pi

    D(1,j) = cos(Theta)*sin(Phi);
    D(2,j) = sin(Theta)*sin(Phi);
    D(3,j) = cos(Phi); % function of theta and phi (spherical coordinates like \( z = R \cos(\phi), \) if \( R = 1 \), then \( z = \cos(\phi) \). \( x = \sin(\phi)\cos(\theta) \), ...)
end; clear j Theta Phi

% Generate random locations
for i=1:N
    pmatrix(1,i) = sqrt(rand)*(r);
    pmatrix(2,i) = rand*2*pi;
    pmatrix(3,i) = rand*(h);

    x = pmatrix(1,i)*cos(pmatrix(2,i));
    y = pmatrix(1,i)*sin(pmatrix(2,i));
    z = pmatrix(3,i);

    X(:,i) = [x,y,z];
end; clear i x y z
First Evaluation

distmatrix = squareform(pdist(X.', 'euclidean'));
[row, col] = find(distmatrix<xa); % Identify conflicts
pos = [row, col]; % Assemble into one matrix
del = []; % Initialize rows for deletion
for p = 1:length(pos)
    if pos(p,1) == pos(p,2) % Check if it is referring to the same point, i.e. (1,1), (2,2), ... 
        del=[del, p]; % Add to deletion list
    end
end
pos(del,:) = [];  % Delete redundant conflicts
conflicts = length(pos); % Check how many conflicts

Iterations for conflict resolution

iterations = 0; % Number of iterations run
while conflicts>0 % Check if conflicts are present
    for i = 1:length(pos)
        i = pos(i); % Define which point to regenerate
        pmatrix(1,i) = sqrt(rand)*(r);
        pmatrix(2,i) = rand*2*pi;
        pmatrix(3,i) = rand*(h);
        x = pmatrix(1,i)*cos(pmatrix(2,i));
        y = pmatrix(1,i)*sin(pmatrix(2,i));
        z = pmatrix(3,i);
        X(:,i) = [x, y, z];
    end
    distmatrix = squareform(pdist(X.', 'euclidean'));
    [row, col] = find(distmatrix<xa); % Identify conflicts
    pos = [row, col]; % Assemble into one matrix
    del = []; % Initialize rows for deletion
    for p = 1:length(pos)
        if pos(p,1) == pos(p,2) % Check if it is referring to the same point, i.e. (1,1), (2,2), ... 
            del=[del, p]; % Add to deletion list
        end
    end
    pos(del,:) = [];  % Delete redundant conflicts
    conflicts = length(pos); % Check how many conflicts
    iterations = iterations+1; % Add one iteration
end
iterations
clearvars -except N X D xa yb zc
Plotting

```matlab
iterations = 4

figure('visible','on')
hold on
f = waitbar(0,'Please Wait...');

zold = [0,0,1]; % axis of ellipse
x = [];
y = [];
z = [];

for i = 1:N
    [a, b, c] = ellipsoid(x(1,i),x(2,i),x(3,i),xa,yb,zc,10);
    %[a, b, c] = sphere;
    %a = a*xa;
    %b = b*xa;
    %c = c*xa;
    %S(i) = surf(a+X(1,i), b+X(2,i), c+X(3,i));
    S(i) = surf(a, b, c);
    rot(i,:) = vrrotvec(zold,D(:,i));
    rotate(S(i),rot(i,1:3),rot(i,4)*(180/pi),[X(1,i),X(2,i),X(3,i)]);
    x = [x;S(i).XData];
y = [y;S(i).YData];
z = [z;S(i).ZData];
    waitbar(i/N,f)
end

xlabel('cm')
ylabel('cm')
zlabel('cm')

close(f)
hold off
```
Export to STL

```
surf2stl('720Shards_3.5wtPercent_Unit_Figure.stl',x,y,z)
```

Warning: NARGCHK will be removed in a future release. Use NARGINCHK or NARGOUTCHK instead.
Wrote 108880 facets

*Published with MATLAB® R2016a*
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VITA

Albert Foster III is a Pennsylvania native and has lived there his entire life. He grew up in Camp Hill, PA, where he attended Cumberland Valley High School. Albert pursued a Bachelor of Science at Lock Haven University in Applied Physics. In addition, he also earned an Associates of Science degree in Nanotechnology along with minors in Mathematics and Chemistry. His research at LHU focused on surface modification of gold surfaces for biotechnology applications. In the summer of 2013, Albert had the opportunity to attend a research experience for undergraduates at the University of South Dakota, where he worked on merging nanotechnology with anti-counterfeiting applications. He graduated in 2014 and immediately began working under the tutelage of Dr. Zoubeida Ounaies. His graduate research at Pennsylvania State University consisted of fabricating and characterizing polymer and glass composite for neutron detection.