Bis(pinacolato)diboron as an additive for the detection of thermal neutrons in plastic scintillators

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Abstract

A readily available and inexpensive boron compound was tested as an additive for the detection of thermal neutrons in plastic scintillators. Bis(pinacolato)diboron (B_2Pin_2) was determined to be a compatible boron source (8.51 wt% boron, 1.70 wt% ^{10}B) in poly(vinyltoluene) based matrices. Plastic scintillator blends of 1-20 wt% 2,5-diphenyloxazole (PPO), 0.1 wt% 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) and 1-15 wt% B_2Pin_2 were prepared that provided optical clarity, good mechanical properties, and the capability of thermal neutron detection. Independent of B_2Pin_2 concentration, strong ^{10}B neutron capture signals around 90 keV_{ee} were observed at essentially constant light output. Increasing PPO concentration allowed for the use of pulse shape discrimination (PSD) in both fast and thermal neutron detection. High PPO concentrations appear to cause additional alpha quenching that affected the ^{10}B neutron capture signal. Aging effects after storage in air for several months were observed, which led to degradation of performance and in some samples of mechanical stability.

1. Introduction

Detection of neutrons plays an important role in the identification of illicit trafficking of special nuclear materials. With increasing demand, the current state-of-the-art neutron detectors deployed, which are based on 3He gas proportional counters surrounded by thermalizing materials, have become significantly more expensive. Therefore, alternatives with lower cost and

similar efficiency as well as comparable signal to background ratio are sought [1,2]. Recent advances in ^3He alternatives have used plastic or liquid scintillator compounds that contain high neutron cross-section isotopes such as ^6Li , ^{10}B , and $^{155}\text{Gd}/^{157}\text{Gd}$ isotopes [3, 4]. Our group is focusing on the incorporation of boron containing organic compounds because of the significant natural abundance (~20%) of ^{10}B , its high thermal neutron reaction cross section and easy availability in highly enriched isotopic concentrations. Previous work incorporating boron in the chemical form of carboranes into plastic matrices achieved promising results [e.g. 5,6,7] and has been used in some commercial products (e.g. Eljen Technology EJ-254). However, the price of the neutron sensitive scintillator product is still dominated by carborane prices and would need to be lowered to allow widespread deployment in large portal type monitor applications. Additionally, the signal to background ratios achieved are not yet competitive to ^3He based detectors motivating further research on boron containing scintillator systems.

The neutron induced reaction on ^{10}B has a thermal cross section of 3837 barns (^3He is 5333 barns) and results in light charged ions (alpha and ^7Li) as the products that carry significant kinetic energy to be easily detected.

However, organic scintillators suffer in light ion detection from a type of pulse height defect, named alpha quenching, that reduces the number of emitted scintillation photons to a small fraction of the quantity emitted in detection of gamma photons of the same energy. It has been observed that the addition of higher concentrations of additives (fluorescing or neutron sensitive) can lower the overall light output of a scintillator and/or worsen the alpha quenching effect. The combination of light output and alpha quenching determines the overall performance of a scintillator in how well one can separate the neutron reaction signal from gamma backgrounds and electronic noise.

Molecular Weight: 253.94

Elemental Analysis: C, 56.76; H, 9.53; B, 8.51; O, 25.20

Figure 1: Molecular weight and elemental composition (%) of bis(pinacolato)diboron (B_2Pin_2)

Bis(pinacolato)diboron (B_2Pin_2) (Fig. 1) was first used in organic reactions by Miyaura et al to create an intermediate for Suzuki coupling [9]. The conversion of arylhalides to arylboronates using an inexpensive and readily available borylating reagent such as B_2Pin_2 has been extensively used in the pharmaceutical and organic electronics industries [10, 11]. Our group uses B_2Pin_2 to create high boron content benzene and pyrene derivatives for use as scintillator additives [12]. Before we were able to synthesize the gram quantities necessary for tests with radiation of our new compounds, we ran the series of tests described here with the commercially available precursor B_2Pin_2 (\$0.5/g).

2. Preparation of plastic scintillator samples

All chemicals used for this study were purchased from commercial vendors unless otherwise noted. Vinyl toluene (VT) was purified by removing the inhibitor 4-tert-butylcatechol (TBC) using a plug mixture of basic alumina with a small amount of potassium carbonate. The purified VT was stored in a freezer under nitrogen. Azobisisobutyronitrile (AIBN) radical initiator was recrystallized twice from methanol and stored in a freezer under nitrogen. B_2Pin_2 (Matrix Scientific cat. # 004889) was dried in a Buchi glass oven (model #B-585) at 40 °C for 24 h and stored in a nitrogen filled glovebox. Each scintillator sample was prepared by adding the specific amounts of dopants, AIBN, and vinyl toluene (20 g total) to a 120 ml (51 mm dia. x 102 mm) glass bottle, followed by a gentle bubbling of argon gas to displace and remove oxygen. The presence of oxygen inhibits polymerization, causes significant light emission quenching, and sample discoloration. The glass bottles were tightly capped and put into a Fischer Scientific Isotemp vacuum oven (model #280A). The atmosphere inside the vacuum oven was exchanged from air to argon via a few cycles of evacuation followed by argon refill. The sample

polymerization was performed in argon atmosphere over four days at 80°C and 12 hours at 90°C. After polymerization was complete, the glass bottles were broken to provide the raw scintillating polymer “puck”. As a first step rough edges were clipped and an even surface produced via machining or hand sanding with medium grid sand paper. Further sanding was performed using finer grit and polishing compounds until finally a buffing wheel achieved a polished surface sufficient for coupling to a photo-detector.

3. Experimental Procedure

To begin testing, the samples were wrapped tightly with white Teflon tape on all sides except the prepared polished face. This exposed face was then coupled to a photodetector (Hamamatsu PMT assembly, H2431-50) with a thin layer of optical grade silicone grease. The coupled assembly was wrapped in a layer of aluminum foil and sealed to a light-tight condition with black electrical tape. After an optimal voltage (-2.9 kV bias in all measurements) for viewing relevant features in the output spectra was determined, the PMT was connected to a data acquisition (DAQ) system and biased using standard NIM electronics. The DAQ system includes a 250 Msample/sec waveform digitizer built in-house, and is controlled by a MIDAS software interface [13]. In this approach the voltage pulse as it is recorded from the PMT anode is digitized and stored. The stored pulse is integrated over 2 different integration times where the full integration time period (“Pulse Area”) is proportional to the deposited energy in the sample which is converted to scintillation photons. The integral over a delayed time period (“Delayed Area”) can be used to describe the pulse shape. The ratio of “Delayed Area” and “Pulse Area” is the “Delayed Area Fraction” and is used later to display and quantify pulse shape discrimination.

Samples were first exposed to a ^{137}Cs source (1 μCi , gamma emission of 662 keV) in order to quantify general light output properties. Examining the position of the Compton Edge (C.E.) feature (at 477 keV) in this output spectra allowed us to calibrate each sample individually and establish an individual sample energy scale (in keV_{ee}). By comparing each sample's C.E. location to a commercial control sample's C.E. location on an absolute scale, we determined a relative light yield output.

Next, the samples were exposed to a $^{244}\text{Cm}/^{13}\text{C}$ source (160 mCi alpha activity; sealed with neutron and gamma emission) in two different shielding configurations, which produce different mixed neutron and gamma fields. First a “lead castle” setup was used to shield the detector and samples from the gamma flux and transmits a ‘fast’ neutron spectrum at the detector location, which allowed us to test fast neutron response as well as test and quantify the samples n/γ PSD capabilities. Next the sample and source were placed in a similar castle built out of poly(ethylene) bricks that would alter the neutron spectrum producing a more thermalized flux. This allowed us to test low energy neutron response and identify the ^{10}B neutron reaction occurring in the sample. Finally, the detector was wrapped in a cadmium shield within the poly(ethylene) cave. Due to the high cadmium thermal neutron capture cross section, this exposure of our samples eliminated the thermal neutron flux and allowed us to collect gamma background spectra that could be subtracted from the non-cadmium shielded spectra, exposing more clearly the samples’ response to thermal neutrons. The Cd-shield background subtraction was not performed on the spectra from which we extracted a figure-of-merit (FOM) for pulse shape discrimination.

Once enough statistics were obtained, the collected waveforms were analyzed using the ROOT data analysis framework, to develop relevant output spectra for extracting light output and pulse shape response information [14].

4. Results

Plastic scintillators generally consist of an inexpensive polymer matrix that absorbs incoming radiation. The matrix becomes “excited” and transfers this energy to fluorescent dopants within the sample that then emit photons in a spectral region matching the photodetector’s response function. In order to provide thermal neutron sensitivity, another dopant containing ^{10}B is added to the formulation; B_2Pin_2 in this case. The compatibility of these dopants is essential in creating optically clear, mechanically stable and efficient plastic scintillator samples capable of discriminating neutron signals from a gamma field. We chose the commonly used PPO and POPOP as primary and secondary dopants respectively in order to be able to allow direct comparison with previous literature reports. The initial set of samples (**Table 1**) was intended to test the solubility limit of B_2Pin_2 in PVT, holding the fluorescent dopant concentrations constant.

As B₂Pin₂ has a smaller boron content per molecule than carboranes, the achievable boron concentrations are lower than in commercially available products which advertise up to 5% natural boron content. For comparison, a typical ³He proportional counter with 10 atm gas pressure corresponds to a cross section weighted ¹⁰B content in polymers of app. 0.6 wt%. The increase in B₂Pin₂ concentration from 2 to 15 wt% did not result in significant physical change or a decrease in optical clarity (Figure 6, top). However, some slight nucleation could be seen in the 15 wt% sample and when increased to 20 wt% B₂Pin₂ (~1.7 wt% B), this sample showed significant nucleation which did not allow further machining and testing. Higher dopant concentration usually leads to softening of the polymer matrix, however, this was not noticeable until total dopant concentration was above 15%. Light yield and thermal neutron ¹⁰B capture results are detailed below in Figures 2-3.

Table 1: Optimizing boron additive in PVT

Sample*	Matrix	Primary dopant		Wavelength shifter		B ₂ Pin ₂ content	Nat-B content	¹⁰ B content
		Name	wt%	Name	wt%	wt%	wt%	wt%
1	PVT	PPO	1	POPOP	0.1	-	-	-
2	PVT	PPO	1	POPOP	0.1	2	0.17	0.03
3	PVT	PPO	1	POPOP	0.1	5	0.43	0.09
4	PVT	PPO	1	POPOP	0.1	10	0.85	0.17
5	PVT	PPO	1	POPOP	0.1	11.75	1	0.2
6	PVT	PPO	1	POPOP	0.1	15	1.28	0.25
7	PVT	PPO	1	POPOP	0.1	20	1.7	0.34

*Total mass of each sample is app. 20.0g

^{137}Cs Compton Edge Comparison

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154 Figure 2: Number of counts vs uncalibrated pulse area in scintillating PVT based samples as
155 measured through exposure to a ^{137}Cs γ -source using the same PMT bias value.

156

157 The B_2Pin_2 concentration appears to have little effect on light output when added at the 10 wt%
158 level as shown in Figure 2; most samples produce a Compton Edge (numerically characterized as
159 the halfway point between Compton edge maximum and zero) at 92-94% that of a commercial
160 control sample (Saint Gobain BC-408; 10,000 photons/1 MeV e^-). There is a more significant
161 decrease at 15 wt% which is suspected to be due to the approaching solubility limit of B_2Pin_2 . It
162 should be noted that in the few cases where we repeated samples of the same composition, our
163 measured light yields varied of order ± 2 -3 %-points. Therefore, we would characterize sample
164 variation in the range of 92-94% as essentially constant.

Figure 3: Number of counts versus calibrated pulse area (keV_{ee}) for ^{10}B thermal neutron reaction spectra with gamma response subtracted via cadmium shielded measurement. The keV_{ee} sample scale adjusts all samples to the ^{137}Cs Compton edge position of each sample (light yield adjustment) to make changes in alpha quenching apparent.

Thermal neutrons in the $^{244}\text{Cm}/^{13}\text{C}$ “Poly Cave” setup were captured by the naturally occurring ^{10}B isotope within B_2Pin_2 . As described earlier, although the reaction produces light ions with kinetic energies in the MeV range, the signal registered in the detector samples was, due to alpha quenching, around $90 \text{ keV}_{\text{ee}}$, only slightly varying with B_2Pin_2 concentration. In order to extract the neutron capture peaks clearly, the cadmium shielded spectra were subtracted from the “poly cave” capture spectra as shown in Figure 3. The results here reported on the position (keV_{ee}) of the ^{10}B neutron capture peak are similar to previously reported values on boron loaded plastic scintillators using carboranes [5,7]. As mentioned above, raising the B_2Pin_2 concentration appears to produce an essentially constant light output and alpha quenching. This indicates a good match of the neutron sensitive dopant to the plastic matrix in terms of scintillation relevant properties.

184

185 Table 2: Plastic compositions with over-doped PPO and 1% “boron” additive

Sample*	Matrix	Primary dopant		Wavelength shifter		B ₂ Pin ₂	DVB
		Name	wt%	Name	wt%	wt% *	wt%
1	PVT	PPO	10	POPOP	0.1	11.75	-
2	PVT	PPO	15	POPOP	0.1	11.75	0.1
3	PVT	PPO	20	POPOP	0.1	11.75	0.1
4	PVT	PPO	25	POPOP	0.1	11.75	0.1

186 *11.75% B₂Pin₂ is equivalent to 1% boron content.

187 A second set of samples was prepared and tested with the intent of achieving PSD in our samples
188 using the scintillating fluor over-doping method originally developed by Brooks et al. [15] which
189 in recent years inspired further work in several laboratories [16,17,18]. The compositions used in
190 this sample set are provided in Table 2. The 11.75 wt% B₂Pin₂ concentration is equivalent to 1
191 wt% natural boron content, and was chosen to be below the solubility limit of the B₂Pin₂/PVT
192 system. The plastic samples were polished and prepared as described earlier and their detector
193 response properties analyzed with the same radioactive source configurations. In our tests
194 significant PSD was not quantifiable until the sample contains at least 10% PPO. Meaningful
195 separation between neutrons and gammas in our energy range of interest (of order 100 keV_{ee})
196 was not seen until higher concentrations (~20%). The B₂Pin₂ content, combined with the high
197 amount of PPO necessary to achieve PSD, acts as “impurities” in the polymerization process
198 likely leading to lower polymer molecular weight and thus diminished mechanical properties. In
199 order to address this concern, divinylbenzene (DVB), a crosslinking agent, was introduced into
200 the sample solution prior to polymerization. With the crosslinking agent added, the plastic
201 sample containing 20 wt% PPO 0.1 wt% POPOP and 11.75 wt% B₂Pin₂ was at a “hardness”
202 level that could be cut and prepared for our standard detector test. The Compton Edge of the
203 ¹³⁷Cs spectrum was 98% light output of our commercial plastic scintillator (Saint Gobain
204 Crystals, BC-408). However, the PPO over-doping method appeared to worsen the alpha
205 quenching significantly and the ¹⁰B thermal neutron capture peak was located at app. 60 keV_{ee}.
206 The resulting spectrum from the thermalized ²⁴⁴Cm/¹³C neutron source is detailed in Figure 4 and
207 various PSD figures of merit (FoM) numbers using the fast neutron spectrum are shown in
208 Figure 5. The measured FoM at 100 keV_{ee} of 1.04 compares well to the published value of 0.9 at
209 120 keV_{ee} for the commercial Eljen Technology EJ-299-33, which presumably uses the PPO
210 over-doping method [19].

211

212 Figure 4: Full PSD (Full Pulse Area over Delayed Area Fraction) spectrum of PVT sample
 213 containing 11.75 wt% of B_2Pin_2 , 20 wt% PPO, 0.1 wt% POPOP as measured in the $^{244}Cm/^{13}C$
 214 “poly cave” setup. In addition to the thermal neutron capture peak a band between the fast
 215 neutron and gamma bands becomes tentatively visible which contains also thermal neutron
 216 capture events, however, here the excited state of the 7Li reaction product is populated and both an
 217 alpha and a 480 keV gamma is recorded in coincidence.

218

219

220 Figure 5: PSD Figure of Merit values resulting from various energy cuts (spectrum shown from
221 200 keV_{ee} cut) using the same sample as in Fig. 4 in the “lead cave” setup and projecting the Full
222 PSD Spectrum after the energy cut onto the y-axis.

223

224 In order to assess the aging effects, we retested the scintillator samples 9 months later after
225 storage in ambient conditions without humidity control. There was some slight visual
226 yellowing/clouding of the B₂Pin₂ doped samples (e.g. Fig. 6, bottom) with average decrease of
227 approximately 20% in light yield. However, ¹⁰B thermal neutron reaction signals could still be
228 detected from in the samples containing PPO at the 1 wt% level. The over-doped PPO samples
229 while still displaying n/γ PSD, had turned opaque with negligible light output (~10% of BC-
230 408). The physical change in our sample is likely due to oxidation of residual radicals left from
231 the radical bulk polymerization method used in our production process. Future work will need to
232 be devoted to employ radical quenchers, antioxidants or thermal annealing procedures to achieve
233 the long (~years) lifetimes expected from plastic scintillator products.

Fig. 6: Plastic scintillator sample containing 1 wt% PPO, 0.1% POPOP and 11.75% B_2Pin_2 in PVT at the time of first testing (top) and after 9 months ambient storage (bottom).

5. Summary

The research described here demonstrates that B_2Pin_2 can be used as a low cost ^{10}B additive that is compatible with commonly used plastic scintillator formulations to achieve plastic scintillator detectors with thermal neutron sensitivity. B_2Pin_2 concentrations up to the solubility limit have little effect on sample light yield and alpha quenching, allowing detectors to be produced with on the order of 1 wt% natural boron content. Thermal neutrons are easily detected with the ^{10}B neutron capture peak occurring at ~ 90 keV_{ee} in the basic formulations, and at ~ 60 -65 keV_{ee} in formulations with PPO overdoping to achieve PSD. In the PSD samples, analysis allowed for separation of gamma and proton (or alpha) signals down to low energies providing an additional factor to distinguish the thermal neutron signal. Further work is necessary to suppress aging

effects through improvements in the scintillator formulation and/or production process. The measurements here were performed using B_2Pin_2 with natural boron isotopic distribution, but pathways of synthesizing boron containing organic additives from readily available ^{10}B enriched compounds are being investigated by our group.

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