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Methacrylate based cross-linkers for improved thermomechanical properties and retention of radiation detection response in plastic scintillators

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ABSTRACT

Pulse shape discrimination (PSD) is an important method that can efficiently sort and separate neutron and gamma radiation signals. PSD is currently achieved in plastic scintillators by over-doping poly(vinyl toluene) (PVT) matrices with fluorescent molecules. Meaningful separation of the signals requires addition of >20 wt% 2,5-diphenyloxazole (PPO) fluor in PVT. At these concentrations PPO acts as a plasticizer, negatively affecting the physical properties of the final plastic such as hardness, machinability, and thermomechanical stability. This work addresses these issues by implementing a cost-effective solution using cross-linking chemistry via commercially available bisphenol A dimethacrylate (BPA-DM), and a synthesized fluorinated analogue. Both improve the physical properties of over-doped PPO based plastic scintillators without degrading the measured light yield or PSD and Figure of Merit (FoM). In addition, the fluorinated analogue appears to enhance the hydrophobicity of the surface of the plastic scintillators, which may improve the scintillators' resistance to water diffusion and subsequent radiation response degradation. The new formulations improve the feasibility of widely deploying long lifetime PSD capable plastic scintillators in large area coverage assemblies.

1. Introduction

Plastic scintillators are currently utilized as first line radiation detectors for special nuclear materials (SNM), due to their low cost, ease of manufacture and fast response time. Research is currently being performed on these detector materials and systems with various goals; such as making the plastic scintillators sensitive to thermal neutrons through neutron sensitive additives (e.g. ^{10}B, ^{6}Li), improving the photoelectric effect response of plastic scintillators through incorporation of high Z elements (e.g. Bi, Pb), and improving the radiation type classification capabilities (neutron/gamma discrimination) of different polymer/fluor formulations [1–7]. The most common technique used to address the latter is pulse shape discrimination (PSD). One current method of introducing PSD capabilities into plastic scintillators is based on incorporating >20 wt% fluorescent dopants, such as 2,5-diphenyloxazole (PPO) into poly(vinyl toluene) (PVT) matrices [8]. Although this formulation has been commercialized, the high concentrations of PPO required for meaningful PSD induce a plasticizing effect in the scintillators [9]. The resultant plastic scintillators are softer, difficult to machine and polish, and lack the thermal and structural integrity required for larger detector systems [10,11].[2] In addition to these issues, when deployed in certain environments, current plastic scintillators are susceptible to degradation due to weathering from ambient humidity and temperature fluctuations which can lead to fogging [11,12].

Research into improving the physical properties of PSD capable plastics includes developing new fluorescent dopants and using cross-linkers or alternative polymer matrices [3,5,13]. Common commercially available cross-linkers such as divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDMA) used with polystyrene (PS) or PVT, have

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[2] At the time when this manuscript was submitted, Eljen Technology is starting to introduce a new variant of its PSD capable plastic (EJ-299-33M), which tests very similarly to the scintillators prepared in this work.

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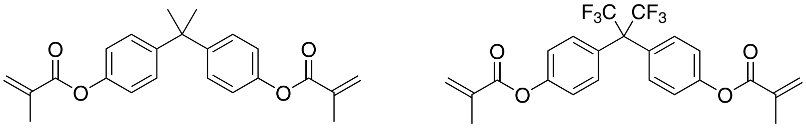

Fig. 1. Molecular structure of BPA-DM (left) and BPAF-DM (right).

been shown to enhance the thermomechanical properties of plastic scintillators to varying degrees, but these improvements appear to come at a cost of degrading the radiation response of the scintillator [14–16].

We report here on the use of cross-linkers that combine the aromaticity of DVB with the methacrylate functional groups of EGDMA. Retaining aromaticity was broadly expected to maintain radiation response due to the delocalized π-electrons, while the methacrylate groups provide the functionality to be co-polymerized into vinyl toluene matrices. A combination of these two properties was achieved with a commercially available cross-linker, bisphenol A dimethacrylate (BPA-DM) and its analogue, bisphenol AF dimethacrylate (BPAF-DM) (Fig. 1). BPAF-DM was designed to improve the hydrophobicity of the scintillator surface and bulk in an attempt to reduce water permeability, as previously observed in fluorinated polymers [17–20]. We have prepared BPAF-DM in minimal step and high yield reactions using inexpensive and benign starting materials thus demonstrating its scalable production (Pages S1–S4 of Supplemental Information). Both BPA-DM and BPAF-DM proved effective at maintaining or even improving light yield and PSD capabilities while simultaneously enhancing the thermomechanical properties of the plastic scintillators.

2. Experimental methods

2.1. Preparation of plastic scintillators

Additional details on the preparation and testing of plastic scintillators can be found in our previous publications [3,4]. Glass vials were silanized according to literature [21] with dichlorodimethylsilane (DCDM) (Sigma-Aldrich) and used as scintillator molds. The inhibitor was removed from vinyltoluene monomer (VT) (TCI America) via an alumina (basic) column plug with dry potassium carbonate (Sigma-Aldrich). Azobisisobutyronitrile (AIBN) (Sigma-Aldrich) was used as a radical initiator (after purification from two recrystallizations in methanol) and dissolved in VT monomer to prepare a 0.01 wt% (0.014 mol%) AIBN/VT stock solutions. BPA-DM (Sigma-Aldrich), PPO (Sigma-Aldrich), and 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP) (Sigma-Aldrich) were used as received. Varying amounts of PPO (20–30 wt%), cross-linkers (0–10 wt%), and 0.1 wt% of POPOP (used as a wavelength shifter in each prepared sample detailed in this work) were added to AIBN/VT stock solutions in silanized glass vials to produce 20 g samples which were then gently sparged with argon for ~30 min to displace oxygen. In our standard procedure, the vials were capped and placed in an argon filled vacuum oven (Fisher Scientific Isotemp 280 A) under a slight vacuum, and cured for four days at 80 °C, then 24 h at 90 °C before being allowed to slowly cool to room temperature. This polymerization period needed to be altered for samples modified with BPAF-DM as discussed later in Section 3.1. The glass vials were broken to extract the plastic pucks that were ~4.7 cm in diameter and ~1.25 cm thick. Samples were finished to a flat surface by machine and hand sanding before a final polishing on a buffer wheel.

2.2. Radiation and hardness characterization

Each finished sample was wrapped in PTFE tape, coupled to a Hamamatsu PMT (H2431-50) with light-tight covering, and exposed to different fields of ionizing radiation. The samples' response was measured with a DAQ system based on an in-house built, 250 Msample/s waveform digitizer, which was controlled by a MIDAS software interface [22]. The individual waveforms were saved and the ROOT data analysis framework [23] was utilized to analyze the collected data, and develop relevant output spectra.

The gamma response of each sample was measured using a ^{137}Cs (~1 μCi) source. The collected, integrated PMT anode pulse content spectra produced a visible Compton edge for each sample, which was used to calculate a sample specific light yield by comparing the position of the edge to one produced from a commercial scintillator (BC-408) machined to the same size as our samples. Samples were also exposed to a mixed neutron and gamma radiation field emanating from a ^{244}Cm/^{13}C (~60 mCi) source. Each samples' response was measured on a $\mathrm{keV_{ee}}$ (kilo-electron Volt, electron equivalent) scale, calibrated using the ^{137}Cs response spectrum. The quality of the PSD in each sample was quantified by a dimensionless Figure of Merit (FoM),

$$\mathrm{FoM} = \frac{\mathrm{Centroid}_n - \mathrm{Centroid}_g}{\mathrm{FWHM}_n + \mathrm{FWHM}_g}$$

through analysis of a delayed pulse content interval compared to total pulse content in the analyzed waveforms. With typical decay times of order ~8–10 ns, a delayed integration time window from 32–120 ns is compared to the total integrated pulse content in order to display PSD. The FoM metric was calculated for both 100–200 $\mathrm{keV_{ee}}$ and 400–600 $\mathrm{keV_{ee}}$ energy cut intervals.

Sample hardness was subjectively observed for machinability on a belt sander and polishing wheel during sample preparation by noting how each sample melted with the added friction. A Shore-D durometer (GxPro model# 560-10D) was used to quantify the hardness. The Shore-D values were obtained with the ASTM standards (ASTM D-2440) testing procedure, where 6 equidistant points were sampled on the face of the sample for ~1 s and then averaged.

2.3. Thermal characterization

Thermal stability was quantified via thermal gravimetric analysis (TGA) using a Q200 TA Instrument. To determine the decomposition temperature (T_d) of the plastics, portions were typically cut from the top edge of the plastic scintillator samples and ramped at 15 °C/min to 600 °C under an inert nitrogen atmosphere. Similar portions were cut from samples to use for differential scanning calorimetry (DSC) measurements to determine glass transition temperatures (T_g). DSC was performed on the Q2000 TA Instrument by heating from −5 °C to 150 °C at 10 °C/min. TGA and DSC analysis used Universal Thermal Analysis software. Portions were also taken from the interior of the scintillators, but no difference was observed.

2.4. Contact angle

Contact angle measurements were made on a Ramé-Hart Instrument Co. Standard Goniometer (Model No. 200-00) using 10 μl deionized water droplets. Analysis was performed on DropImage software.

2.5. Kinetics of polymerization

Admixing the different cross-linkers into the monomer significantly affected the rate of polymerization. These effects were quantified as compared to pure monomer via gravimetric measurements adapted from established methods in literature [23,24]. A stock solution of 0.01 wt% AIBN in VT monomer was used to dissolve 2 wt% of cross-linker.