3D Printing of Scintillating Materials

Y. Mishnayot,1 M. Layani,2 I. Cooperstein,2 S. Magdassi,2 and G. Ron1,∗

1Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem, Israel 91904
2Casali Center, Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904

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We demonstrate, for the first time, the applicability of 3D printing technique to the manufacture of scintillation detectors. We report of a formulation, usable in stereolithographic printing, that exhibits scintillation efficiency on the order of 30% of that of commercial polystyrene based scintillators We discuss the applicability of these techniques and propose future enhancements that will allow tailoring the printed scintillation detectors to various application.

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I. INTRODUCTION

Scintillating materials are commonly used in charged particle detectors as detector elements due to their ease of manufacture, relatively low cost, and good timing resolution. The most common type of scintillator is the plastic scintillator, in which wavelength shifting dopants are embedded in a polystyrene matrix. A charged particle, traversing the polystyrene base excited some of the polymer molecules, causing them to emit UV light upon recombination. Typically, 2,5-diphenyloxazole (PPO) is used as a first step to down-convert the UV light to longer wavelength, peaking at 350nm. Due to the short absorption length of the polymer base in the UV range, a second wavelength shifting dopant, typically 1,4-di-(5-phenyl-2-oxazolyl)benzene (POPOP), with an emission wavelength peak at 410 nm is used to further shift the emitted light to the visible range, while keeping the wavelength short enough to be effectively detected by the detection element (usually a photocathode).

Scintillators are nowadays typically made by either casting of a resin+hardener combination, or by extrusion of a molten scintillator. These cast or extruded scintillator bars are then machined to the required geometry using standard machining techniques (note that the low melting/softening point of scintillators and to the requirements of a clean surface for light collection places severe constraints on the requirements from the machine shop, i.e., low temperature machining and extreme cleanliness with the additional need to polish the scintillator parts after machining). We note that while cast scintillators are more versatile in their possible designs, they suffer from long production times (up to 2 weeks for polymerization) and are also not amenable to complex geometries due to the requirement of producing a complicated mold.

We approach the problem of scintillator manufacturing differently. Rather than taking a top-down approach (i.e. machining a solid block into a preferred shape subtractive manufacturing), we take a bottom-up approach, using newly developed 3D printing techniques to directly print the required form (additive manufacturing), also allowing the creation of scintillator designs that cannot be achieved using a standard approach (e.g., hollow, gas filled, scintillators, or scintillator designs with features with are too small to be machined, both directly onto the scintillator or as a mold).

Three dimensional printing has evolved into a paradigm shifting technology in recent years. The ability to replicate and design, at home, structures down to the 10s of microns scale at less than 10 K$ is at hand. Several technologies have emerged, including laser sintering, Fused Deposition Modeling (FDM via extrusion), and photopolymerization. FDM 3D printing is performed by the extrusion of a plastic filament through a thin nozzle, constructing a geometry layer by layer. Photopolymerization (PP) approaches use UV light to selectively polymerize a liquid, either inside a resin bath, or in a sprayed layer, similar to the method used in inkjet printers.

II. EXPERIMENT

In order to test the applicability of additive manufacturing techniques to the manufacture of scintillators we designed a formulations, which is UV-polymerizable, based on an acrylic monomer, and doped with different fractions of scintillating and wavelength shifting materials. We roughly follow the recipes provided by [3] since they have been shown to achieve efficiencies on the order of several 10s of percent.

Ink preparation: The curable formulation was composed of 99.5 wt% SR9035 (Sartomer, Arkema) as the monomer and 0.5 wt% Lucirin TPO (BASF) as the photoinitiator. The formulation was stirred for 30 minutes in a water bath at 60 °C. To this formulation the following scintillator components were added at various concentrations (see Tab. 1). 2,5-Diphenyloxazole. (PPO, Sigma-Aldrich), 1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP, Sigma-Aldrich), and Naphtalene (Sigma-Aldrich). The final formulation was stirred for 1 hour in a water bath at 60 °C.

The compounds were polymerized into the required shape (a cylinder 6.3mm in height and 20mm diameter) using an Asiga Pico Plus 39 printer (Asiga, Australia). 2 different layer thicknesses were tested, 25 µm, and 127 µm, in order to test...
the effect of the interface between printed layers on the light collection efficiency. The printed output was compared to reference samples of clear PMMA (plexiglas) and EJ-204 scintillator (Eljen Ltd.) of the same dimensions. Fig. 1 is a photograph of the output of one of our printed samples containing the scintillating compounds.

All samples were tested in a light tight box using both background cosmic radiation and a 15.1 KBq $^{90}$Sr source. The samples were matched to a photomultiplier (Hamamatsu R647) operated at 1 kV, through a 100mm Perspex light guide. Light output was readout from the PMT into a CAEN charge integrating digitizer (V1720) and histograms were recorded to a PC. A typical histogram from the EJ-204 sample and our best sample is shown in Fig. 2.

In addition, several prints were made of scintillators with more complex geometries, in order to show that such geometries may be printed using our formulated materials. Since this geometries are almost impossible to machine, a comparison to a standard sample was not made. In particular, a geometry relevant for the Frozen Spin Active Target [4] at the Crystal Ball detector at MAMI [5] was printed, consisting of a thin walled, hollow cylinder, capped with a mesh to allow for the flow of super-fluid helium, and including external grooves for coupling to wave length shifting fibers. Fig. 3 shows the printed design, note the mesh and the threaded top of the cylinder, which is almost impossible to create in a scintillator using standard production techniques.

![FIG. 1: (Color online) A picture of the printed output of one of our representative samples.](image1)

![FIG. 2: (Color online) Typical spectrum from a reference sample (EJ-204), our printed sample, and the background measurement. The printed sample achieved ~ 30% efficiency compared to commercial scintillator material, proving the viability of this technique.](image2)

![FIG. 3: (Color online) Two views of the Active Target prototype (see text), note the external grooves, meshed cap, and threaded area. € 1 coin included for scale.](image3)

### III. RESULTS

Several different formulations were tested, with varying concentrations of the activator (Naphthalene) and the wavelength shifters. Table I summarizes the results of the different formulations, compared to a reference sample (EJ-204). The table clearly shows that efficiencies on the order of 30% are easily achievable using 3D printing, demonstrating the viability of such techniques. It should be noted that acrylic based scintillator are known to be less efficient that aromatic scintillators (such as our reference sample) and we attribute part of the efficiency loss to this difference, the other part being attributed to both optical quality of the printed sample and possible degradation of the active materials in the printed sample during the UV polymerization phase. Fig. 4 summarizes the efficiency achieved for the various samples listed in Tab. I.

Additionally, we have seen evidence of degradation with time of the scintillation efficiency. We attribute this degradation to the sublimation of the Naphthalene activator at high concentrations. In the future modifications of the formulation we use will investigate the replacement of the base polymer by a different polymer, or replacement of the Naphthalene activator by a different, less volatile compound (for example, 1,1,3-Trimethyl-3-phenylindane (TMPI), proposed in [3]).
| Number | Layer thickness (µm) | Naphthalene content (%) | PPO content (%) | POPOP content (%) | Efficiency (%) | Comments          |
|--------|----------------------|-------------------------|-----------------|------------------|----------------|------------------|
| 1      | 127                  | -                       | 1               | 0.05             | 0.6            | -                |
| 2      | 127                  | 3                       | 1               | 0.05             | 1.2            | -                |
| 3      | 127                  | 3                       | 1               | 0.05             | 1.5            | -                |
| 4      | 25                   | 3                       | 1               | 0.05             | 2.4            | -                |
| 5      | 25                   | 15                      | 1.5             | 0.08             | 28             | -                |
| 6      | 127                  | 15                      | 1.5             | 0.08             | 27             | -                |
| 7      | -                    | -                       | -               | -                | 0              | Clear Sample     |
| 8      | -                    | -                       | -               | -                | 100            | EJ-204 Scintillator |

TABLE I: Results of the comparison between the different formulations tested.

![Efficiency graph](image)

**FIG. 4**: Efficiency measured for the different samples listed in Tab. I compared to a commercial scintillator (sample 8).

**IV. CONCLUSIONS**

We have shown, for the first time, that additive manufacturing techniques are a viable alternative for scintillator manufacturing. In particular, such techniques are well suited for the production of small, complex, designs, which are hard to produce using either extrusion or machining techniques. While our current system uses a standard scintillating compound, designed for the detection of charged particles, a logical extension of our method is the inclusion of additional dopants, such as, for example, high-Z materials, or Gd, which can enhance detection capabilities for neutral particles such as photons and neutrons respectively. This doping can be achieved by the simple technique of mixing particles of the required dopants with our formulation prior to printing. An additional possible extension is the introduction of methods which are capable of printing multiple compounds simultaneously, or varying the concentration of dopants in a continuous manner (such as InkJet based printers). These further improvements will allow, for example, for the manufacturing of scintillation detectors with embedded wavelength shifting fibers, removing the for need coupling using optical grease.

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