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Development of reflective filaments based on polycarbonate with the addition of PTFE and TiO_2 for 3D printing of finely segmented plastic scintillators

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Reflective filaments were developed based on polycarbonate with the addition of 10-20 wt.% finely dispersed polytetrafluoroethylene (PTFE) powder and 5-15 wt.% titanium dioxide (TiO_2) pigment. The manufactured materials can be used to obtain reflectors by 3D printing for use in scintillation technology, in particular as part of finely segmented plastic scintillators. The produced reflective layers have a reflection coefficient of up to 90% and a transmission coefficient of about 0.2% at the wavelength of the maximum emission of polystyrene-based plastic scintillator. Technical approaches to the production of scintillation elements with a reflector using additive technologies are also considered.

Keywords: reflector, scintillation element, 3D printing, plastic scintillator, organic scintillator, composite material

Розробка світловідбиваючих філаментів на основі полікарбонату з додаванням PTFE та TiO_2 для 3D-друку сцинтиляційних елементів. *Т. Сібілєва, А. Бояринцев, А. Креч, М.Сібілєв, С. Міненко, Н. Караваєва, Л. Зосімова та колаборація 3DET*

Розроблено світловідбиваючі філаменти на основі полікарбонату з додаванням дрібнодисперсного порошку політетрафторетилену у кількості 10-20 мас%, пігменту діоксиду титану у кількості 5-15 мас%. Виготовлені матеріали можуть бути застосовані з метою отримання методом 3D-друку світловідбивачів для використання у сцинтиляційній техніці, зокрема у складі багатоелементних пластмасових сцинтиляторів. Виготовлені світловідбиваючі шари мають коефіцієнт відбиття до 90% та коефіцієнт пропускання близько 0,2% на довжині хвилі максимуму випромінювання сцинтиляційного полістиролу. Також розглянуто технічні підходи щодо виготовлення сцинтиляційних елементів з відбивачем при використанні адитивних технологій.

1. Introduction

Plastic scintillators are traditionally manufactured using cast polymerization [1], injection molding [2] or extrusion [3, 4] techniques. Afterward, they are shaped to fit the detector geometry through processes like machining or drilling. 3D printing enables new automated processes that simplify the production of finely segmented scintillators by allowing simultaneous printing of scintillation and reflective materials using two extruders.

Previously, we developed reflective filaments based on various polymer binders with the addition of titanium dioxide (TiO_2) for 3D printing of reflectors using Fused Deposition Modeling (FDM) technology, which can be used to create scintillation elements, in particular as part of finely segmented detectors [5]. The highest reflectivity was observed in filaments made from polystyrene (PS) and polymethyl methacrylate (PMMA). However, the PS-based filament was unsuitable for printing alongside the scintillation material, also made of polystyrene, as the materials mixed during printing. PMMA-based filament made it possible to print scintillation matrices of optically-isolated polystyrene scintillator using FDM technology, the light yield was found to be quite uniform among the different cubes of the matrix and the optical crosstalk was found to be less than 2% for the 3D printed matrix layer, acceptable for applications that require a combined particle tracking and calorimetry.

Our further research into improving the geometric tolerances and transparency of the 3D printed scintillator led to the development of a new 3D printing technology, which combines FDM and injection molding technology, and was named Fused Injection Modeling (FIM) [6]. In this case, the reflector is printed in the form of a matrix of empty cells using FDM technology, and the cells are then filled by injecting melted scintillation filament using a specially designed nozzle. However, the PMMA-based filament proved unsuitable for 3D printing with FIM technology due to its low heat resistance. Therefore, in order to print the first 3D-segmented detector, the commercial filament based on polycarbonate (PC) and polytetrafluoroethylene (PTFE) with high printing temperature was used. Although this filament was not designed as a light-reflecting material, we demonstrated its suitability for such applications. Nevertheless, despite this, its use in scintillation techniques is limited because it has a high level of transmittance (with a layer thickness of 1,5 mm, the printed layers have a transmittance of 13 to 18% depending on print orientation), which leads to an increase in crosstalk. This work aims to develop reflective filaments with high printing temperature, high reflectivity, and low transmittance, suitable for making finely segmented detectors used in high-energy physics experiments like MINERvA [7], MINOS [8], NOvA [9] and T2K [10, 11].

2. Experimental procedure

The reflective filaments were obtained using a Noztek ProHT desktop extruder [12]. PC granules were mixed with a dioctyl phthalate (DOP) plasticizer, and the mixture was stirred for 5 minutes. Then TiO_2 and/or PTFE powders were added and mixed for another 20 minutes. The resulting mixture was loaded into the extruder and filaments with a diameter of 1.75±0.1 mm were extruded at a temperature of 255-270 °C.

As starting components to produce the reflective filaments were used polycarbonate resin CALIBRE 303-22 by TRINSEO [13], titanium dioxide R-706 by Ti-Pure [14], PTFE powder by Ireneusz Katarzyński Selkat [15].

The Creatbot F430 [16] 3D printer with two extruders was used for printing of samples. 1 mm thick reflector samples were printed using the obtained filaments. Printing was carried out at a temperature of 265 °C. Samples of the same thickness, which were printed with commercial PC+PTFE Nanovia filament [17] and our manufactured analogue, as well as PC+TiO_2 and PMMA+TiO_2 filaments obtained in our previous work [5] were used as comparison samples. The area of all samples was 20*20 mm.

To perform the measurements of light transmittance T and optical reflection R in the range from 200 to 800 nm, was used a Shimadzu-2450 spectrophotometer with the integrating sphere.

The measurements of relative light output were performed by exposing scintillator samples to a ^{137}Cs γ source. The measurement was performed by directly coupling scintillator samples to 3-inch PMTs (Hamamatsu R1307) using optical grease. The samples were irradiated by placing the source 10 mm away from the sample by help of cardboard spacer. The whole setup was then placed in a light tight black box covered with black blankets in order to prevent light coming from outside. A 150 seconds exposure time was used for data acquisition. The Compton edge was extracted from each measured spectra and used for comparison.

3. Results and discussion

The reflection and transmission coefficients of the obtained samples at a wavelength of 420 nm are indicated in Tab. 1. The results of reflection measurements of 1 mm thick 3D-printed samples as well as pressed samples of raw TiO_2 and PTFE powders are given on Fig. 1. The results of transmission measurements of 1 mm thick 3D-printed samples are given on Fig. 2.

The reflective material for 3D printing is a diffuse reflector consisting of a polymer base with a uniformly distributed white pigment. For such a system, the difference between the refractive indices of a polymer base and pig-

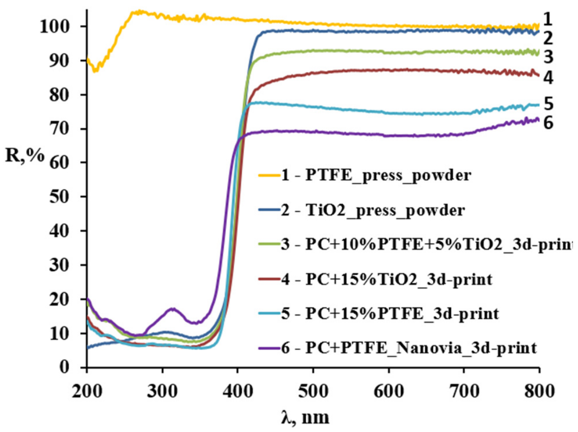

Fig. 1. Reflectance spectra of samples based on polycarbonate with the addition of PTFE and TiO_2 with a thickness of 1 mm

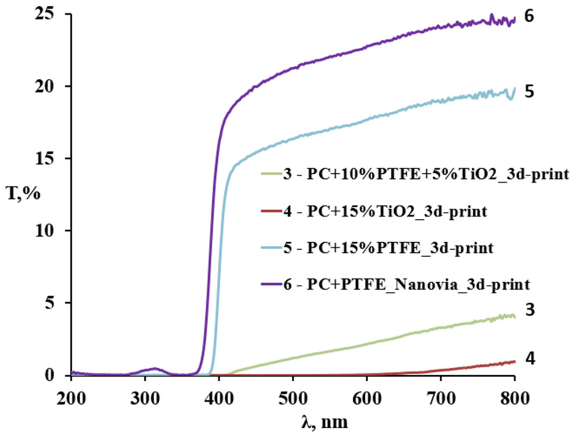

Fig. 2. Transmittance spectra of samples based on polycarbonate with the addition of PTFE and TiO_2 with a thickness of 1 mm.

Table 1. Reflection and transmission coefficients of samples 1 mm thick based on PC with the addition of PTFE and TiO_2 powders at a wavelength of 420 nm

No. on the graphs	Composition of the reflector	R, % (λ=420 nm)	T, % (λ=420 nm)
1	PTFE pressed powder	101,81	-
2	TiO_2 pressed powder	92,92	-
3	PC + 10% PTFE + 5% TiO_2 3d-printed	89.11	0.21
4	PC + 15% TiO_2 3d-printed	79.98	0.00
5	PC + 15% PTFE 3d-printed	77,44	14.37
6	PC + PTFE Nanovia 3d-printed	68.69	18.67
-	PC+15% PTFE + 5% TiO_2	87,56	0.66
	PC + 20% PTFE + 5% TiO_2	89.98	1.02
	PC + 10% PTFE + 10% TiO_2	83.94	0.18
	PC + 10% PTFE + 15% TiO_2	81.09	0.11

ments is important, as well as the granulometric composition of pigments. As is known, the greater the difference between the refractive indices of the filler and the binding medium, the higher the scattering and, accordingly, the lower the transmittance [18].

Thus, the high transmittance of the combination of PC+PTFE materials is due to the small difference between the refractive indices of polycarbonate (n=1.58) and PTFE (n=1.35). Accordingly, to reduce transmission, it is necessary to create a system with the largest difference in refractive indices.

From the presented data in Tab. 1, Fig. 1 and Fig. 2, it can be seen that 1 mm thick samples with the simultaneous addition of PTFE and TiO_2 with a total powder content of 15 wt.% have a higher reflectivity (90% - sample 3) compared to samples containing either only PTFE (77% - sample 5) or only TiO_2 (80% - sample 4). In addition, it is worth noting that the sample printed with the filament produced in this work and containing only PTFE in the amount of 15 wt.% has 9 wt.% better reflectivity compared to the sample printed with the commercial Nanovia filament. This may be due to the higher content of PTFE powder in the filament because the content of PTFE in the Nanovia filament is unknown. In addition, the reflection may depend on the type of PTFE powder used, namely on the particle size composition of the powder and the shape of particles in it. During filament development, we found that using PTFE powder with a particle size of 40-100 µm in the PC matrix resulted in samples with poorer reflectivity and a yellow tint compared to using powder with a particle size of <6 μm. At a thickness of 1 mm, the samples printed with the developed filaments have a transmittance of 0.1-1.0%, and the sample printed with the commercial Nanovia filament has a transmittance of 18.7%.

In this three-component system, PC provides the necessary printing temperature and mechanical strength, TiO_2 provides low transmittance, PTFE promotes homogenization and improves reflection. Thus, the resulting reflective filament has all the necessary specified characteristics, namely high reflectivity, low transmittance and high printing temperature for use as a reflector for 3D printing of multielement scintillators.

When the filament contains 5 wt.% TiO_2 and PTFE is increased from 10 wt.%% to 20 wt.%%, reflectivity improves, but transmission also rises. When the PTFE content in the filament is 10 wt.%% and the amount of TiO_2 is increased from 5 wt.% to 15 wt.%, a decrease in reflectivity is observed, but at the same time, transmission decreases.

Also it is worth noting that with an increase in the content of powders, the extrusion of the filament becomes more difficult. We adopted a maximum total powder concentration of 25 wt.%, which still allows printing smooth samples. When the content of powders increases, conglomerates of powders not completely mixed with the PC matrix are observed in the middle of the filament. Presumably, by improving mixing using an extruder with a longer screw, several heating zones, or using two screw extruders, it would be possible to obtain uniform filaments with higher concentrations of powders. But it is also worth noting that when the content of powders increases, flexibility and strength of the filament decreases, which complicates the 3D printing process.

Addition of the DOP plasticizer to PC polymer granules allows to evenly applying pigment to their surface. The optimal amount of DOP was determined experimentally and is 1-4 wt.%. An increase in DOP concentration of more than 4 wt.% leads to the complication of extrusion due to the fact that the polymer granules stick together during heating. Reducing the DOP concentration to less than 1 wt.% does not ensure uniform application of TiO_2 and PTFE on the surface of PC granules due to the fact that not all pigment particles are fixed on them and remain in the mixing device.

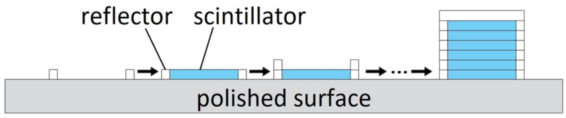

Fig. 3. Schematic representation of the creation of a scintillation element by two extruders using the FDM printing technology: blue shows the layers formed by scintillation filament based on polystyrene; white shows the layers formed by the polycarbonate-based reflective filament.

For the printing of a scintillation element, a scintillation filament was made with the addition of 5 wt.% diphenyl as a plasticizer, as described in our previous work [19], but it differs in that commercial polystyrene (PS) granules were used as the raw material. This made it possible to simplify the filament manufacturing process by adding fluorescent additives directly at the filament extrusion stage instead of adding them at the polymerization stage. The manufacturing process was as follows: PS granules were poured into a mixing device, DOP plasticizer was added in the amount of 0.2 wt.% and mixed for 5 minutes. Then *para*-terphenyl in the amount of 2 wt.%, 2,2-p-phenylene-bis(5-phenyloxazole) (POPOP) in the amount of up to 0.05 wt.%, diphenyl in the amount of 5 wt.% were added and stirred for another 20 minutes. The resulting mixture was loaded into the extruder and the scintillation filament with a diameter of 1.75±0.05 mm was obtained at a temperature of 230 °C.

The resulting scintillation filament had a minimum bending diameter of 55 mm, which allows the printing of scintillation elements using FDM technology without cracking the filament in the material supply system in the printer. For comparison, the filament made from polystyrene-based plastic scintillator without plasticizers, obtained by cast polymerization, had a minimum bending diameter of 120 mm [19], which led to cracking of the filament during the printing process.

Schematically, the 3D printing process of the scintillation element is shown in Fig. 3, the main idea is that the PC-based reflective material with a printing temperature of 260-270 °C when creating each successive layer acts as a frame that holds the layers of polystyrene-based scintillation material with printing temperature of 220-240 °C.

To form contact with the photodetector, the surface of the scintillation material was formed during 3D printing on a polished glass surface with a roughness class of no lower than 12. At the same time, the surface formation temperature should be about 110 °C, i.e. higher than the glass transition temperature of polystyrene. Instead of glass, it is possible to use another polished surface, which should have no adhesion to polystyrene and the coefficient of linear thermal expansion should be less than that of polystyrene. This allows to printing of scintillation elements of a given geometric shape without additional post-processing.

To study the light yield, a sample was printed using the obtained scintillation filament and the reflective filament with the addition of 10 wt.% PTFE and 5 wt.% TiO_2. The scintillator size was 10x10x10 mm, the reflector was 0.4 mm thick on all sides, except for the output window for contact with the PMT. The same sample, but with a 1 mm thick reflector made of Nanovia filament, was used as a comparison sample.

The results of measuring the relative light output are shown in Fig. 4. The light output obtained from a reflector with the addition of both PTFE and TiO_2 was 110% compared to the sample with a reflector obtained with Nanovia filament. This also allowed us to print a thinner reflector, which could potentially boost the overall scintillation efficiency in multi-element scintillators.

We will continue our research by manufacturing using FIM 3d-printing a highly granular scintillator with the developed filaments and studying its scintillation efficiency.

4. Conclusions

Reflective filaments were successfully developed based on polycarbonate with the addition of finely dispersed PTFE powder (10-20 wt.%) and titanium dioxide pigment (5-15 wt.%). Adding TiO_2 and PTFE together increases the reflectance by 11% and 13% compared to if we added only TiO_2 or only PTFE respectively.

The method of manufacturing scintillation filament using polystyrene granules with the addition of *para*-terphenyl in the amount of 2 wt.%, POPOP in the amount of 0.05 wt.%, diphenyl in the amount of 5 wt.% and DOP in the amount of 0.2 wt.% is presented, which allows avoiding the stage of polymerization in the mass. At the same time, the minimum bending radius of the filament is 55 mm, which successfully allows for the 3D printing of plastic scintillators.

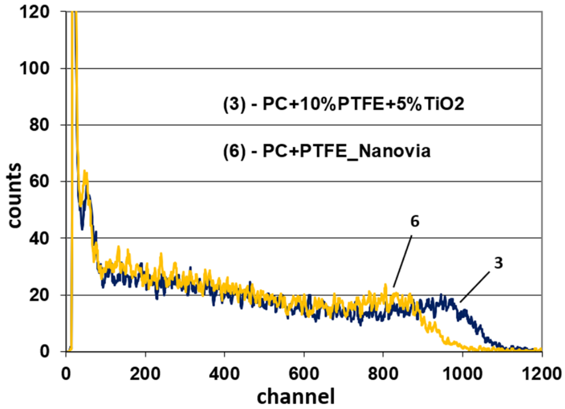

Fig. 4. Pulse height spectra of polystyrene-based plastic scintillator cubes in different reflectors exposed to a ^{137}Cs source: (3) in a reflector printed with PC-based filament with the addition of 10 wt.% PTFE and 5 wt.% TiO_2; (5) in a reflector printed with PC+PTFE filament by Nanovia.

Simultaneous 3D printing with scintillating and light-reflecting filaments allows to obtain scintillating elements based on polystyrene with a reflector and a surface ready for connection to a photodetector without additional post-processing, all within one production cycle. It is shown that due to the difference in extrusion temperatures of scintillation and light-reflecting filaments, it is possible to manufacture a rigid frame from light-reflective filament to fill the central part with scintillation filament. The surface for connection to the photodetector is formed by 3D printing on a glass, metal, or other polished surface with a roughness class of at least 12.

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