

# Polymer-Based Materials for Space Radiation Shielding

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Space exploration requires the use of suitable materials to protect astronauts and spacecraft components (e.g. onboard electronics) from the hazardous effects of radiation, in particular, ionizing radiation, which is ubiquitous in the hostile space environment. In this scenario, polymer-based materials and composites play a crucial role in achieving effective radiation shielding while providing low-weight and tailored mechanical properties to different types of spacecraft elements.

space radiation shielding

polymer-based materials

space exploration

irradiation tests

## 1. Introduction

The growing interest in outer space exploration draws attention to the importance of protecting astronauts and facilities from exposure to hazardous radiation. Space radiation, comprised of high-energy particles, possesses the potential to cause ionization of atoms and molecular damage, affecting both biological tissues and spacecraft components [1][2]. In this context, the use of effective shielding materials is essential to prevent and mitigate deleterious effects on human health and on the systems that ensure a successful outcome of the mission [3].

Ionizing space radiation includes solar particle events (SPEs) and galactic cosmic radiation (GCR) [4]. GCR comprises highly energetic protons, alpha particles, electrons, and high atomic number ( $Z > 2$ ) particles. In particular, the GCR spectrum consists of approximately 87% hydrogen ions (protons) and 12% helium ions (alpha particles), with the remaining 1–2% of high  $Z$  and energy (HZE) nuclei with charges from  $Z = 3$  (lithium) to  $Z = 28$  (nickel) [5]. Transition metals such as iron ( $Z = 26$ ) are particularly difficult to shield after ionization, thus posing a risk from a biological point of view. Electrons and positrons from GCR are considered a minor biological risk during space missions since they can be shielded more easily. GCR ions pose a significant health threat to astronauts during interplanetary travels, as their energies can penetrate several centimeters of biological tissue and spacecraft materials. SPEs are produced by impulsive flares or by coronal mass ejections (CMEs). These fluxes involve electrons, protons, and other heavy-charged particles such as iron. The nature of SPEs is sporadic and unpredictable, typically associated with intense solar activity. SPEs generate energetic protons with fluences exceeding  $10^9$  protons/cm $^2$  [5]. Primarily composed of low linear energy transfer (LET) protons with energies up to 1 GeV/n, these can be adequately shielded by the protective structures of spacecraft. SPE dose rates vary during an event, ranging from 0 to 100 mGy/h inside a space vehicle and from zero to 500 mGy/h for astronauts during extravehicular activities (EVAs) outside of LEO. The frequency of SPEs is linked to sunspot activity, with the highest number of events occurring during periods of strong equatorial sunspot activity. Exploration missions

beyond low earth orbit (LEO) that involve interplanetary travel may expose crew members to multiple SPEs, as demonstrated by the five events that occurred during the recent transit of the Mars Science Laboratory (MSL) spacecraft from Earth to Mars [6]. Moreover, the interaction of high-energy SPE protons and heavy-charged GCR particles with spacecraft structures causes onboard radiation hazards. In addition to the primary particles that can affect spacecraft, secondary particles are generated through nuclear fission reactions. This secondary radiation, including protons, alpha particles, beta particles, gamma rays, X-rays, neutrons, and heavy-charged particles, can penetrate spacecraft shielding and contribute significantly to the overall mission dose and has the potential to critically damage human tissues [5]. NASA has categorized the human health risks from space radiation into four groups: carcinogenesis, degenerative tissue risk (such as cardiovascular disease), acute and late risks to the central nervous system (CNS), and acute radiation syndromes [7]. Concerning adverse effects on spacecraft materials, they can involve the development of defects in the structure and chemical and mechanical degradation, including surface erosion and embrittlement [8]. Therefore, the engineering of suitable, high-performance radiation-shielding materials is crucial to preserve the integrity of spacecraft and the health of astronauts.

Typically, radiation shielding exploits elements with the highest charge-to-mass ratio, which are shown to be effective against HZE particles [9]. Although aluminum is commonly used in spacecraft, its exposure to GCR can lead to the production of highly penetrating secondary radiation, including neutrons and ions, which can cause electronic failures and adverse biological effects. Hydrogen, with a high charge-to-mass ratio and the absence of neutrons in its nucleus, proves effective in slowing down GCR through direct ionization [10]. Additional considerations could be taken into account. According to Bethe's classical theory, it can be demonstrated that, for minimizing the mass of the shielding material, elements with low atomic numbers (low Z) are the most effective on a per-unit-mass basis. Conversely, if the goal is to reduce the thickness of the shielding material, elements with high atomic numbers (high Z) are most effective on a per-unit-thickness basis. A material characterized by high Z acts as a better absorber of electrons and bremsstrahlung compared to a low Z material, even if the production of bremsstrahlung is higher in materials with high atomic numbers. Nevertheless, a high Z material is less effective in proton shielding. Considering these effects, structures that incorporate both low Z and high Z materials could be promising to achieve effective radiation shielding [11].

Polymer-based materials (PBMs) have emerged as effective candidates for achieving protection against radiation while providing low-weight and tailored mechanical, thermal, and electrical properties to spacecraft components. The incorporation of suitable fillers into the polymers enables improved radiation-shielding properties. The addition of hydrogen-containing nanoparticles, as well as the incorporation of light metals, can enhance protection from GCR and SPEs [9]. Neutrons are produced as secondary particles through the interactions of GCR and SPEs with matter. Chemical elements with significant thermal neutron absorptions, such as boron, lithium, and gadolinium, can be exploited as radiation-shielding fillers [12]. Gadolinium nanoparticles, possessing the highest neutron absorption cross-section among all elements, and boron, with a substantial neutron absorption cross-section, emerge as excellent candidates for neutron shielding. Nevertheless, the use of low-Z boron compounds should be preferred to those based on gadolinium in order to avoid the generation of undesired secondary radiation, which has detrimental effects on structural materials and parasitic effects on electronic components. The neutron absorption cross-section for the isotope  $^{10}\text{B}$  is 3835 barns, and enriching boron compounds with  $^{10}\text{B}$  could

enhance protection against neutrons [9]. Compounds like boron carbide ( $B_4C$ ) and hexagonal boron nitride (hBN) in nanomaterial form, particularly nano- $B_4C$  and nano-hBN dispersed in polymer matrix, have demonstrated enhanced thermal neutron attenuation [12]. The positive effect of using nanosized fillers can be related to their surface-to-volume ratio, which increases the interactions with radiation, enhancing the shielding effectiveness [13] [14] [15] [16]. Boron and its low-Z compounds, like  $B_4C$  and hBN, prove suitable for space neutron-shielding applications, while heavier elements are less convenient due to their high atomic weight, leading to fragmentation and the generation of secondary radiation.

## 2. Experimental Studies

### 2.1. Polyethylene-Based Materials

Polyethylene (PE) is a versatile material successfully employed in different fields due to its ease of processing, chemical inertness, and low moisture absorption [17]. The mechanical and physical behavior of PE is strictly dependent on its crystal structure and molecular weight [18] [19]. The PE properties are particularly valued for industrial storage, electronics, and in the aerospace sector due to its ability to shield against radiation [20]. PE, composed of ethylene monomers, offers effective radiation shielding due to its high hydrogen content, and this aptitude can be enhanced by embedding suitable fillers into the polymer.

PE lacks the necessary strength and thermal stability for structural use. In this regard, multifunctional fillers, such as carbon nanoparticles, have been employed to enhance the mechanical and functional properties of PE and, at the same time, improve protection from space radiation [21] [22].

Zhang et al. proposed the use of a composite material made of ultrahigh-molecular-weight polyethylene fiber (UPEF), boron nitride (BN), and polyurethane (PU) for effective neutron radiation shielding [23]. Neutron radiation, composed of uncharged particles, has harmful effects on human tissues, leading to diseases like cancer and cardiovascular issues [24]. Traditional neutron-shielding materials like concrete and metal have limitations, especially in aerospace applications, needing the development of new materials. In this work, UPEF, known for its mechanical properties, is combined with boron, which absorbs thermal neutrons effectively. The composite, made of UPEF, boron modified with tannic acid (TA), and PU, showed promising neutron-shielding effectiveness. In particular, the dispersion of fillers in the matrix is crucial for efficient shielding, and the modification of boron with TA improved the dispersion. The results from mechanical testing indicated high tensile strength, suggesting the potential use of the UPEF/BN/PU composite as a structural material. Following the Beer–Lambert law, the attenuation of neutrons passing through the material is determined by the equation:

$$\frac{I}{I_0} = e^{-\mu x} \quad (1)$$

where  $\chi$  is the thickness of the UPEF/BN/PU composite and  $\mu$  is the linear attenuation coefficient that can be expressed as follows:

$$\mu = \frac{1}{\chi} \ln \frac{I_0}{I} \quad (2)$$

the mass attenuation coefficient ( $\mu/\rho$ ) was calculated as follows:

$$\frac{\mu}{\rho} = \frac{1}{\rho \chi} \ln \left( \frac{I_0}{I} \right) \quad (3)$$

where  $\rho$  is the density of the sample. The results unveiled that the neutron radiation intensity decreases by approximately 25%, 63%, and 85% when passing through UPEF/BN/PU-0 with thicknesses of 0.8, 1.6, and 3.2 mm, respectively. Considering samples without BN, the neutron attenuation results from the high hydrogen content in UPEF. The findings align with theoretical predictions that emphasize the effective neutron-shielding properties of materials rich in hydrogen. For the UPEF/BN/PU samples loaded with BN at 7 wt%, the neutron-shielding capability improves, as indicated by the decreasing of the  $I/I_0$  value. This improvement is attributed to the ability of boron to absorb neutrons through nuclear reactions with the boron nucleus in BN. Neutrons are sequentially moderated by hydrogen and absorbed by boron. However, above 7 wt% of BN loadings, the efficiency of neutron shielding decreases. This suggests that continuously adding BN fillers may not enhance neutron-shielding efficiency and could potentially affect the mechanical properties of the composites. Moreover, the thickness of the UPEF/BN/PU composite significantly influences neutron-shielding performance. For BN content below 7 wt%,  $I/I_0$  for UPEF/BN/PU with a thickness of 1.6 mm is approximately 25–30% lower than that of UPEF/BN/PU with a thickness of 0.8 mm. With increasing BN content, the difference in the  $I/I_0$  value between UPEF/BN/PU composites with different thicknesses decreases.

Neutron exposure experiments were conducted by Herrman et al. on high-density polyethylene (HDPE)-based composites [25]. Boron carbide (BC) and boron nitride (BN) with particle sizes less than 10  $\mu\text{m}$  were chosen as fillers and added to injection-molding-grade HDPE. Irradiation tests were performed using a 1-Curie Americium-Beryllium neutron source. A dose rate of 0.6 mSv/h/GBq at a distance of 1 m was applied for 15 min, with the source positioned 50 cm away from the detector, and counts were recorded at 10 s intervals. The neutron exposure tests were conducted using bare indium foil and bare indium foil/sample pairings. Bare indium foil was used as a reference due to its high neutron absorption cross-section. The indium foil/sample pairings included bare indium foils with 1%, 5%, and 30% BN samples. The neutron exposure tests aimed to determine the mass absorption cross-section ( $\mu/\rho$ ) for thermal neutrons and the effectiveness of shielding. The results suggested that higher BN content leads to lower initial radiation detected, and mass absorption (shield effectiveness) increased with lower initial activity. Atomic force microscopy (AFM) studies revealed that HDPE-BN blends were reasonably uniform at low BN concentrations, while higher percentages reduced uniformity, potentially due to the lubricating

effect of BN. Compressive strength was observed to decrease initially with BN addition, but higher amounts of BN induced an increase in the strength. The presence of boron nitride in the sample was found to influence mass absorption, confirming its role in shaping the shielding properties of the material. Based on these findings, the HDPE/BN composites can be considered for potential use in aerospace due to their advantageous mechanical and radiation-shielding properties.

Zaccardi et al. fabricated multifunctional nanocomposites using medium-density polyethylene (MDPE) loaded with multiwalled carbon nanotubes (MWCNTs), graphene nanoplatelets (GNPs), and hybrid MWCNT/GNP fillers [22]. Electrical properties, chemical structure, thermal behavior, wettability, and morphology were investigated before and after proton irradiation. In particular, the samples were irradiated for 294 s, with an energy of 64 MeV and a current of 1 nA, resulting in a total dose of 50 Gy. According to the U.S. Center for Disease Control and Prevention's information on acute radiation syndrome, a dose of 50 Gy is known to induce the fatal collapse of the human cardiovascular and central nervous systems. This dosage exceeds the acceptable exposure limits for astronauts [26]. The experiments were conducted at the Crocker Nuclear Laboratory of the University of California (Davis, CA, USA). FTIR analyses revealed a decrease in crystallinity ( $X_c$ ) after irradiation, more pronounced in the GNP-filled nanocomposites. Thermal analysis using differential scanning calorimetry (DSC) confirmed the decrease in crystallinity and unveiled thermal stability after irradiation. Contact angle measurements indicated a decrease in hydrophobicity after proton exposure, whereas morphological analysis by SEM highlighted surface erosions after irradiation. The results indicated that the MDPE/MWCNT 5 wt% nanocomposite maintains thermal stability, a hydrophobic behavior, and negligible changes in crystallinity, making it a promising shielding material in high-ionizing-radiation environments, such as space.

A multilayer composite material was developed by alternately stacking layers of high-density polyethylene/hexagonal boron nitride (HDPE/hBN) and low-density polyethylene (LDPE) [27]. The neutron-shielding ability of these PE/hBN composites was evaluated after irradiation experiments using neutrons with a wavelength ( $\lambda$ ) of 0.53 nm and a spread  $\Delta\lambda/\lambda = 16\%$ . The composites were fabricated by a two-step hot-pressing process, where HDPE/hBN and LDPE layers were individually hot-pressed into slices and then stacked alternately and hot-pressed to form multilayer composite films. This strategy aimed to align hBN along the in-plane direction for improved performance. The neutron-shielding effectiveness was evaluated using neutron transmission factor ( $I/I_0$ ), linear attenuation coefficient ( $\mu$ ), and mass attenuation coefficient ( $\mu/\rho$ ). The results indicate that the neutron radiation intensity decreases by ~50% when passing through PE films, and this can be justified by the high hydrogen content in PE. The incorporation of hBN into the PE matrix enhances the neutron-shielding performance, as proven by a decrease in the  $I/I_0$  value at increasing hBN loadings. This result can be ascribed to the synergistic attenuation effect of hydrogen and boron atoms. The optimal  $I/I_0$  value is achieved at 4.16% for the multilayer composite with a 30 wt% hBN content, indicating that ~95.84% of neutron radiation is shielded when passing through the composite. Comparatively, at filler loadings below 15 wt%, multilayer composites exhibit similar shielding ability to random composites, possibly due to incomplete coverage of hBN. Considering filler loadings above 20 wt%, the multilayer composites showed superior shielding ability compared to random composites. At 30 wt% filler content, the  $I/I_0$  for multilayer PE/hBN decreases to 4.16%, much lower than the random PE/hBN value of

14.95%. Overall, the performance of the PE/hBN multilayer sample suggests its potential application in neutron shielding and thermal management in fields such as aerospace.

Composite materials made of high-density polyethylene (HDPE) filled with  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{PbO}$  were fabricated and tested under  $\gamma$ -radiation [28]. A 60 KBq source of  $^{226}\text{Ra}$  was used to obtain the  $\gamma$ -rays beam at different energies: 0.295, 0.352, 0.609, 1.12, and 1.747 MeV. The following parameters were used to compare the radiation-shielding effectiveness of the composites: linear attenuation coefficient ( $\mu$ ), transmission factor (TF), mean free path (MFP), half-value layer (HVL), and radiation protection efficiency (RPE). These parameters are expressed as follows:

$$\text{TF} = \frac{I}{I_0} \quad (4)$$

$$\text{MFP} = \frac{I}{\mu} \quad (5)$$

$$\text{HVL} = \frac{\ln 2}{\mu} \quad (6)$$

$$\text{RPE} = \left(1 - e^{-\mu t}\right) \times 100 \quad (7)$$

The following materials were prepared and tested: pure HDPE, HDPE + 30%  $\text{Al}_2\text{O}_3$ , HDPE + 30%  $\text{Fe}_2\text{O}_3$ , HDPE + 10%  $\text{PbO}$ , HDPE + 30%  $\text{PbO}$ , and HDPE + 50%  $\text{PbO}$ . The values of  $\mu$  decrease at increasing radiation energies. A noticeable decrease in  $\mu$  was observed for radiation energies below 0.609 MeV, and this can be ascribed to the dominance of the photoelectric effects in the material. Above 0.609 MeV, the dominance of Compton scattering takes place. The results showed that the samples containing  $\text{PbO}$  have superior attenuation capacity and efficiency compared to those loaded with  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Among the composites, the one loaded with 50%  $\text{PbO}$  achieved the best results, demonstrating the highest value of  $\mu$  and the smallest values of MFP, HVL, and TF for all the tested radiation energies. Hence, these composites can be considered effective radiation-shielding materials to be potentially applied in fields requiring high  $\gamma$ -ray attenuation, such as space.

## 2.2. Polyimide-Based Materials

Polyimides (Pis) are a class of high-performing polymers showing outstanding thermal stability, chemical and radiation resistance, and suitable mechanical and dielectric properties [29][30][31][32]. Pis can be considered neutron moderators since their structure includes carbon, hydrogen, nitrogen, and oxygen, which mitigate the generation of secondary particles after collision with neutrons. The radiation-shielding effectiveness of Pis has been successfully enhanced by the incorporation of nanomaterials, such as bismuth oxide and boron nitride.

Pavlenko et al. fabricated polyimide-based composites filled with bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and tested their radiation-shielding behavior under  $\gamma$ -ray exposure [33]. The  $\text{Bi}_2\text{O}_3$  particles were modified with polymethylphenylsiloxane (PMPS) to achieve a uniform distribution in the composites. The irradiation tests were performed at 400 keV and 662 keV, using radionuclides  $^{192}\text{Ir}$  (400 keV) and  $^{137}\text{Cs}$  (662 keV) as sources. The results demonstrated that the incorporation of  $\text{Bi}_2\text{O}_3$  significantly improved the thermal stability of the composites. Moreover, the modified  $\text{Bi}_2\text{O}_3$  particles showed hydrophobic behavior, enhancing their distribution in the non-polar PI matrix. Composites produced by hot-pressing exhibited higher density and microhardness compared to those produced by cold-pressing, indicating a more uniform distribution of fillers. The radiation-shielding properties of the composites were assessed experimentally and theoretically, unveiling a high-radiation-protective behavior. In particular, the results showed that the mass attenuation coefficient ( $\mu_m$ ) increases linearly with the  $\text{Bi}_2\text{O}_3$  loading (0–60 wt%). Overall, the incorporation of PMPS-modified  $\text{Bi}_2\text{O}_3$  into the PI matrix and the hot-pressing method proved effective for fabricating attractive materials for space technology and radiation protection.

Baykara et al. developed composite materials with shielding properties against both neutrons and  $\gamma$ -rays. A thermoplastic polyimide was used as a matrix and filled with gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) and hexagonal boron nitride (hBN) nanoparticles [34]. The neutron-shielding properties of hBN/ $\text{Gd}_2\text{O}_3$ /PI samples with different filler loadings were assessed after irradiation with a  $^{239}\text{Pu}$ -Be neutron source. Neutron transmission factors were determined experimentally by measuring the ratio of incident ( $I_0$ ) and transmitted ( $I$ ) neutron fluxes. The macroscopic cross-section ( $\Sigma$ ) and mass attenuation coefficient ( $\mu/p$ ) were computed based on the count rate (cps) for neutrons and the gamma dose rate ( $\mu\text{R}/\text{h}$ ) for gamma radiation measured during the experiments. The source used for experiments generates both neutron and gamma radiation, and suitable measurements were conducted to distinguish and evaluate the shielding efficiencies of the nanocomposites against each type of radiation. The results unveiled that samples exhibited an exponential decrease in neutron flux attenuation, with fluctuations observed as the thickness increased. The fluctuations were attributed to the interaction of neutrons with nanoparticles within the shielding materials. The nanocomposite with 11 wt% hBN showed the highest neutron-shielding performance. Considering samples at high loadings of  $\text{Gd}_2\text{O}_3$ , the neutron transmissions exhibited fluctuations dependent on the thickness of the shield material. To validate the results, neutron permeability experiments for the nanocomposite with 11 wt% hBN/3 wt%  $\text{Gd}_2\text{O}_3$ /PI were repeated at different thicknesses. In this case, results demonstrated consistency in neutron-shielding efficiency between the initial and repeated experiments. The gamma shielding ability of the nanocomposites was also thoroughly investigated. The experiments involved measuring gamma dose rates resulting from the interaction between the neutron source and the neutron-shielding material. The nanocomposites showed an exponentially decreasing behavior in gamma transmission, with transmission percentages superior to that of neat polyimide. Further analysis involved the calculation of macroscopic cross-section and mass attenuation coefficient values for both neutron and gamma

rays. The macroscopic cross-section values for nanocomposites ranged between 0.1898 and 0.4052  $\text{cm}^{-1}$ , exhibiting a significant improvement compared to neat polyimide (0.1316  $\text{cm}^{-1}$ ). In summary, the findings of this experimental study demonstrated the multifunctional properties of the nanocomposites, with high efficacy in attenuating both neutron and gamma radiation due to the interplay between hBN and  $\text{Gd}_2\text{O}_3$ . The results indicate that these nanocomposites are promising materials for applications requiring effective protection against radiation sources in fields such as aerospace.

Polyimide-hexagonal boron nitride (PI-hBN) nanocomposites were fabricated using direct forming technology (DF) to enhance their tribological and radiation-shielding properties [35]. The process involved the incorporation of hexagonal boron nitride (hBN) nanoparticles at concentrations of 2 wt% and 5 wt% into a polyimide matrix. The ball milling technique was employed to minimize nanoparticle agglomeration and ensure the uniform distribution of hBN within the PI matrix. The neutron-shielding effectiveness of the samples was examined using an americium ( $^{241}\text{Am}$ )-beryllium ( $^9\text{Be}$ ) neutron source. The assessment of neutron shielding involved the examination of the linear absorption coefficient ( $\mu$ ) and mass absorption coefficient ( $\mu/\rho$ ). In particular,  $\mu$  was used to quantify the extent of incident radiation attenuation, normalized by thickness, whereas  $\mu/\rho$  expresses the attenuated radiation normalized by both density and thickness, as indicated by Equation (3). Quantitative measurements of neutron transmission through the nanocomposites were performed, and the results highlighted a significant decrease in neutron flux as a function of the hBN content. The 2 wt% and 5 wt% hBN-loaded PI nanocomposites exhibited significantly lower neutron transmission compared to the neat PI matrix. In particular, the linear and mass absorption coefficients exhibited substantial improvement, increasing by 1.9 and 2.2 times for 2 wt% and 5 wt% hBN-loaded PI, respectively, in comparison to the neat PI.

Cherkashina et al. focused on the impact of electron irradiation on the structural and property changes in polyimide materials [36]. Composite samples based on PI track membranes and nanodispersed lead (70 wt%) were fabricated. The impact of fast electrons with energies ranging from 1 to 5 MeV was evaluated on the neat PI and on the PI composite. The irradiation employed a one-sided mode, preceded by thermal treatment of the samples in a vacuum oven at 180 °C for 3 h. To assess the absorbed dose distribution and effective electron range, tests were conducted by incrementally increasing sample thickness. Samples of 25  $\mu\text{m}$  thickness were tightly stacked, and a detector was placed behind them. The effective electron range was determined by the total film thickness at which the detector ceased detecting radiation. All samples received a total dose of 10 MGy. The effective range of electrons detected in PI and PI composite is directly proportional to initial electron energy and increases with energy. Enhanced radiation-shielding characteristics of the composite, compared to PI, are attributed to the structure of composites. Contact between the track membrane and metallic lead results in a contact potential difference, creating an electric field preventing electron transition. The near-contact layer of the composite enriches with electrons, increasing conductivity. For high-energy electrons, the increased electron density in the near-contact layer leads to a higher probability of scattering at larger angles, causing ionization and radiation losses. This results in a significant reduction in electron flux in the PI composite. Overall, results showed that the penetration depth of electrons into PI is greater than in the composite. The tensile strength of both materials decreases slightly after irradiation, and the electrical properties of the composite remain largely unaffected. The

findings of this experimental study suggested the potential use of the PI/lead composite in space, offering protection against cosmic radiation.

Ultraviolet (UV)-shielding materials based on a highly fluorinated polyimide (FPI) filled with allomelanin nanoparticles (AMNPs) were developed by Li et al. [37]. The presence of fluorinated groups in FPI increases porosity and decreases density, expanding the propagation path of UV and enhancing UV-shielding performance. The results demonstrate improved mechanical and UV-shielding properties with the synergistic absorption of UV by FPI and AMNPs. In this study, curcumin was used to evaluate the UV-shielding performance of the composites through UV-vis measurements. Curcumin was chosen due to its high instability under UV irradiation, leading to the decomposition of the  $\alpha$ -carbon in its structure into aldehydes, further oxidizing into acids [38]. In the blank control group, the absorbance of curcumin dropped to zero after 50 min of irradiation. This correlated with a color change from dark yellow to colorless, confirming complete degradation. In contrast, curcumin covered by a pure FPI film only experienced partial degradation, with a residual rate reaching 72.2%, accompanied by a slight solution fade. When curcumin was shielded by FPI + 0.1% AMNPs, FPI + 0.3% AMNPs, FPI + 0.5% AMNPs, FPI + 0.7% AMNPs, and FPI + 1% AMNPs films, the concentration of the curcumin solution decreased less with an increase in AMNPs content. Simultaneously, the color change in the curcumin solution was not gradually evident, consistent with the initial solution.

### 2.3. Polydimethylsiloxane-Based Materials

PDMS shows advantageous properties such as flexibility, suitable thermal stability, chemical inertness, and low cost [39][40][41][42]. These properties have been extensively exploited for the development of membranes, enclosures, microfluidic structures, and sensors [43][44][45][46][47]. Low-Z fillers have been successfully embedded in PDMS-based matrices, obtaining promising radiation-shielding materials that can be potentially exploited in the space environment.

PDMS nanocomposites filled with tungsten oxide ( $WO_3$ ) and barium oxide ( $BaO$ ) were exposed to  $^{137}Cs$ ,  $^{241}Am$ , and  $^{60}Co$  with energies ranging from 0.059 to 1.333 MeV [48]. The following samples were fabricated: 100 wt% PDMS (S-1), 60 wt% PDMS + 40 wt%  $WO_3$  (S-2), 60 wt% PDMS + 40 wt%  $BaO$  (S-3), double layers of S-2 and S-3 (S-4), and double layers of S-3 and S-2 (S-5). The results showed that at the lowest energy level (0.059 MeV), the sample S-3 exhibited the highest  $\mu$  ( $5.66\text{ cm}^{-1}$ ), followed by S-4 ( $4.07\text{ cm}^{-1}$ ), while S-1 (neat PDMS) had the smallest  $\mu$  ( $0.29\text{ cm}^{-1}$ ). The addition of  $WO_3$  and  $BaO$  consistently improved the  $\mu$  values, indicating enhanced radiation attenuation for the composites. The transmission factor (TF) values obtained for the samples confirmed that the addition of  $WO_3$  and  $BaO$  contributed to increased radiation attenuation, particularly at lower energies. However, as energy increases, the differences in TF between samples decrease. The double-layered samples (S-5 and S-6) showed better TF, especially at low energies, compared to single-layered samples. The half-value layer (HVL), representing the material thickness required to reduce radiation intensity by 50%, was calculated. The results showed that S-1 (neat PDMS) had the highest HVL, confirming poorer shielding performance compared to samples containing  $WO_3$  and  $BaO$ . Sample S-2, loaded with 40 wt%  $WO_3$ , demonstrated better radiation attenuation efficiency. Samples containing higher percentages of  $WO_3$  and  $BaO$  showed lower MFP values,

indicating improved shielding efficiency. In summary, these flexible composites exhibited suitable performance against  $\gamma$ -ray radiation that could be potentially exploited in different fields, such as aerospace.

Cheraghi et al. fabricated PDMS-matrix nanocomposites filled with bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and multiwalled carbon nanotubes (MWCNTs) and tested their shielding properties against high-energy electron beam for potential application in space [49]. Samples of pure PDMS and nanocomposites filled with 30 wt% of  $\text{Bi}_2\text{O}_3$  and 3 wt% of MWCNTs were prepared and tested under electron beam energies of 9, 12, 16, and 20 MeV in attenuation mode. These values were selected according to the electron beam energies reported for outer space. The shielding behavior of the samples was compared with that of aluminum, which was considered as the reference material. During the irradiation tests, each sample received a 100 cGy dose at a rate of 1000 cGy/min. The percentage of electron attenuation efficiency (AE%), equivalent to the RPE factor mentioned in Section 2.1, was calculated as follows:

$$\text{AE}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (8)$$

where  $C_0$  and  $C$  are the intensities of the original and transmitted electrons measured using an ionizing chamber. The results unveiled that PDMS/BiO and PDMS/CNT/BiO nanocomposites have better shielding properties than aluminum, pure PDMS, and PDMS/CNT samples for all areal densities.

For all the samples, the electron attenuation efficiency showed a similar trend for all energies, with AE% values that increase at increasing areal densities. PDMS/CNT/BiO samples showed the highest weight advantages and AE% values at any electron beam energies. The difference between the attenuation values of PDMS/CNT/BiO and aluminum decreases for higher areal densities. Considering the density values of 0.5, 1, and 1.5 g/cm<sup>2</sup>, the PDMS/CNT/BiO sample showed better shielding capabilities than aluminum. Therefore, these PDMS-based materials can be potentially applied in space as shielding materials instead of aluminum, which has disadvantages such as heavy weight and generation of secondary electrons.

Borjanovic et al. fabricated PDMS-matrix nanocomposites filled with single-walled carbon nanotubes (SWCNTs), detonation nanodiamond (DND), and zinc oxide (ZnO) and tested their radiation-shielding behavior under proton exposure [50]. Irradiation experiments were performed using a 2 MeV proton beam and low fluence conditions with currents ranging from 30 to 100 nA. The samples were irradiated in the fluence range of  $10^{13}$  to  $10^{15}$  protons/cm<sup>2</sup> in four regions (D1-D4) with different conditions. In particular, the fluence associated with regions 1 (D1) and 2 (D2) is  $5.7 \times 10^{13}$  protons/cm<sup>2</sup>. In region 1, a beam current of 30 nA was used, while in region 2, a beam current of 50 nA was applied. The total charge for both regions 1 and 2 was kept constant at 5.6  $\mu\text{C}$ . For region 3 (D3), a fluence of  $5.7 \times 10^{14}$  protons/cm<sup>2</sup> was achieved with an 80 nA beam current, resulting in a total charge of 56  $\mu\text{C}$ . In region 4 (D4), a fluence of  $1 \times 10^{15}$  protons/cm<sup>2</sup> was provided using a 100 nA beam current, with a total charge of 100  $\mu\text{C}$ . The proton irradiation was conducted at room temperature. The study emphasized the influence of particle size on

ionizing radiation protection, with smaller particles showing enhanced stability in high irradiation environments. Raman and FTIR-ATR spectra revealed that PDMS-DND nanocomposites with 40 nm DND aggregates were more stable under high proton fluences compared to pure PDMS or other nanocomposites. The introduction of ZnO nanoparticles into the PDMS matrix (PDMS-ZnO) showed even better high-energy ionizing radiation resistance than the DND-filled materials. The multifunctionality of ZnO, including energy absorption and dissipation, contributed to its effectiveness in protecting the nanocomposite under high fluences. Moreover, results indicated that PDMS-SWCNT nanocomposites provided protection similar to other nanofillers under low proton fluences, while their effectiveness decreased at higher fluences (D3, D4). In conclusion, the nanocomposites with smaller filler sizes and those with ZnO exhibited the best shielding performance against high-energy proton irradiation, making them suitable candidates for applications in high-radiation environments.

## 2.4. Other PBMs

Prabhu et al. developed epoxy-based materials filled with micro and nano-tantalum oxide ( $Ta_2O_5$ ) particles and demonstrated their effectiveness in  $\gamma$ -ray shielding [16]. A diglycidyl ether of bisphenol A (DGEBA) epoxy resin was used as a matrix. The study determined  $\mu/p$  values for composites loaded with 10%, 20%, and 30 wt% of filler and irradiated using energy values of 0.356, 0.511, 0.662, 1.173, 1.275, and 1.332 MeV. Samples with the highest filler content (30 wt%) showed the best shielding ability. Considering the same filler content and energy level, the  $\mu/p$  values of the nanocomposites are higher than those detected for the micro-composites. In particular, samples containing nano- $Ta_2O_5$  with lower filler content provided shielding performance comparable to that of high-loaded micro-composite systems. This can be justified by the high number of nanoparticles, with shorter interparticle distances than those of microparticles for the same volume fraction of fillers. This involves fewer void paths for photons from  $\gamma$ -rays, resulting in greater photon attenuation. The results unveiled that nano- $Ta_2O_5$  epoxy composites have higher thermal stability, flame retardance, and tensile properties compared to micro-composites at the same loading. Overall, these nanocomposites can be considered promising materials for effective  $\gamma$ -ray shielding in space.

A DGEBA epoxy resin was also used by Adeli et al. to fabricate neutron-shielding composites [51]. Boron carbide was used as filler, and the effect of the particle size (20 and 150  $\mu m$ ) and loading amount (1, 3, 5 wt%) on the shielding effectiveness was investigated. The results confirmed a shielding enhancement using smaller boron carbide particles. Other composites were prepared by adding tungsten oxide ( $WO_3$ ) and aluminum trihydrate (ATH) into the polymer matrix. The presence of  $WO_3$  provides protection against gamma rays, whereas ATH improves the heat resistance of the material. Moreover, ATH could also contribute to gamma-ray attenuation due to its higher atomic number than carbon and hydrogen in the epoxy matrix. Composites filled with  $WO_3$  and ATH showed an enhancement of more than 60% in neutron shielding compared to those filled only with boron carbide. Overall, these findings can be exploited for designing efficacious space shields.

Bel et al. tested composites based on poly(methyl methacrylate) (PMMA) reinforced with colemanite (CMT) as shielding materials for gamma rays and neutrons [52]. Samples with different CMT loadings (5, 15, 30, and 40 wt%) were irradiated using  $^{137}Cs$  and  $^{239}Pu$ -Be as gamma-ray and neutron sources, respectively. At higher filler

contents, enhancements in the shielding effectiveness were found. Considering the gamma-ray irradiation tests, the addition of CMT at 40 wt% into the matrix led to an increase in terms of  $\mu$  values from 0.098 to 0.138, which corresponds to 11.1% enhancement in shielding performance for the composite with respect to the neat PMMA. The results from neutron exposure experiments also confirm the best shielding effectiveness for the composites loaded with 40 wt% of CMT. This effect can be ascribed to the increase in terms of boron and hydrogen that are in the filler, thus allowing an increase in neutron attenuation. The PMMA/CMT composites were proposed as potential shields for satellites and space shuttles after further tests to be carried out on the International Space Station (ISS).

Composite materials based on poly-ether-ether-ketone (PEEK) and tungsten were fabricated for potential use as gamma-ray shields [53]. Samples were prepared by fused deposition modeling (FDM) 3D printing. The functional properties and shielding effectiveness of samples containing 50, 60, and 70 wt% of tungsten were investigated and compared with those of neat PEEK.  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  were used as gamma-ray radiation sources.  $\mu$  value of the neat PEEK exposed to  $^{137}\text{Cs}$  source was found to be  $0.0728 \text{ cm}^{-1}$ . An increase in the  $\mu$  value by 54.81%, 64.45%, and 68.70% was observed for samples filled with 50, 60, and 70 wt% of tungsten, respectively. After exposure to a high-energy  $^{60}\text{Co}$  source, the  $\mu$  value of the samples reinforced with 50, 60, and 70 wt% of filler increased by 48.84%, 57.91%, and 62.91%, respectively, with respect to the pure polymer. The fabrication of multilayered hetero-structures based on PEEK/tungsten and PEEK/boron carbide was proposed for a contemporary shielding of neutrons and secondary gamma-ray radiations. The effective application of these composites in space could be evaluated, taking into account the advantages offered in terms of weight and costs. Polyether-polyurethane (PUR)-based composites filled with hexagonal boron nitride and amorphous boron were tested as neutron-shielding materials [54]. In particular, PUR composites loaded with 21% amorphous boron and boron nitride were fabricated. They showed suitable flexibility despite the high filler content and unveiled shielding effectiveness toward neutrons. These shielding properties and the possibility of using PUR matrix partly derived from renewable resources are factors that can be advantageously exploited in space applications.

Shemelya et al. fabricated 3D-printed polycarbonate (PC) composites filled with tungsten oxide for X-ray shielding [55]. Low loadings of filler were used to obtain a composite with suitable mechanical strength and reduced weight. After irradiation tests, an increase in X-ray attenuation ( $\sim 10\%$ ) was observed for the composite with respect to pure PC. At low X-ray energies (40 keV to 70 keV), a tungsten volume loading of 0.3% results in an attenuation factor of 96 to 98 (rad/rad). The increase in terms of mass is  $\sim 5\%$ , thus relatively low. Moreover, no significant changes in elongation to break or impact resistance were detected. Based on the results of this study, PC-based composites could be applied in space as shielding materials with suitable mechanical properties and low weight.

**Table 1** summarizes the different PBM systems developed for space radiation shielding. The comparison is based on the type of polymer and filler that were used and on the shielded radiation.

**Table 1.** Comparison of PBMs for space radiation shielding.

Polymer	Filler	Type of Shielded Radiation	Ref.
MDPE	Multiwalled carbon nanotubes, graphene nanoparticles	Protons	[22]
UHMWPE fibers, PU	Boron nitride	Neutrons	[23]
HDPE	Boron nitride, boron carbide	Neutrons	[25]
HDPE, LDPE	Hexagonal boron nitride	Neutrons	[27]
HDPE	Aluminum oxide, iron oxide, lead oxide	Gamma rays	[28]
PI	Bismuth oxide	Gamma rays	[33]
PI	Gadolinium oxide, hexagonal boron nitride	Gamma rays, neutrons	[34]
PI	Hexagonal boron nitride	Neutrons	[35]
PI	Lead	Electrons	[36]
FPI	Allomelanin nanoparticles	Ultraviolet	[37]
PDMS	Tungsten oxide, barium oxide	Gamma rays	[48]
PDMS	Bismuth oxide, multiwalled carbon nanotubes	Electrons	[49]
PDMS	Single-walled carbon nanotubes, detonation nanodiamond, zinc oxide	Protons	[50]
PDMS	Tungsten oxide, carbon nanotube sponge (sandwich configuration)	Gamma rays	[56]
DGEBA resin	Tantalum oxide	Gamma rays	[16]
DGEBA resin	Boron carbide, tungsten oxide, aluminum trihydrate	Neutrons	[51]
PMMA	Colemanite	Gamma rays, neutrons	[52]
PEEK	Tungsten	Gamma rays	[53]
PUR	Hexagonal boron nitride, amorphous boron	Neutrons	[54]
PC	Tungsten oxide	X-rays	[55]

**Abbreviations** MDPE: medium-density polyethylene; UHMWPE: ultrahigh-molecular-weight polyethylene; PU: polyurethane; HDPE: high-density polyethylene; LDPE: low-density polyethylene; PI: polyimide; FPI: fluorinated polyimide; PDMS: polydimethylsiloxane; DGEBA: diglycidyl ether of bisphenol A; PMMA: poly(methyl methacrylate); PEEK: polyetheretherketone; PUR: polyether-polyurethane; PC: polycarbonate.

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