

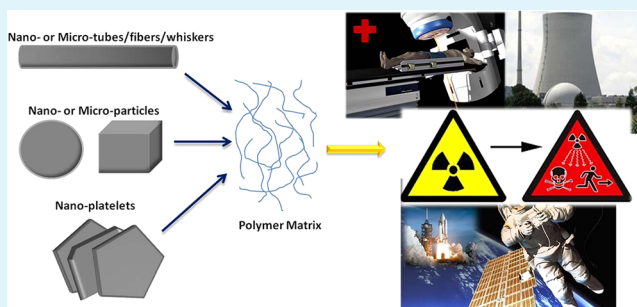
Polymer-Composite Materials for Radiation Protection

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ABSTRACT: Unwanted exposures to high-energy or ionizing radiation can be hazardous to health. Prolonged or accumulated radiation dosage from either particle-emissions such as alpha/beta, proton, electron, neutron emissions, or high-energy electromagnetic waves such as X-rays/ γ rays, may result in carcinogenesis, cell mutations, organ failure, etc. To avoid occupational hazards from these kinds of exposures, researchers have traditionally used heavy metals or their composites to attenuate the radiation. However, protective gear made of heavy metals are not only cumbersome but also are capable of producing more penetrative secondary radiations which requires additional shielding, increasing the cost and the weight factor. Consequently, significant research efforts have been focused toward designing efficient, lightweight, cost-effective, and flexible shielding materials for protection against radiation encountered in various industries (aerospace, hospitals, and nuclear reactors). In this regard, polymer composites have become attractive candidates for developing materials that can be designed to effectively attenuate photon or particle radiation. In this paper, we review the state-of-the-art of polymer composites reinforced with micro/nanomaterials, for their use as radiation shields.

KEYWORDS: reinforced polymers, polymer nanocomposites, radiation shielding, space radiation, particle shielding, X-ray protection, gamma-ray protection



1. INTRODUCTION

High-energy radiations such as alpha/ β particle emissions, X-ray or gamma ray electromagnetic radiation, or neutron particle emissions are often employed or encountered (as a byproduct) in a wide range of industries that includes nuclear power plants, healthcare industry, and aerospace. Unwanted exposure/s to any of these radiations may be hazardous to life. However, the implications of such exposures are related to a number of factors that include the type of radiation and the energy associated with it, the amount of dose administered (absorbed dose), exposure time, etc. Table 1 summarizes different types of radiation encountered in the spacecraft industries, hospitals, and nuclear reactors. Cosmic radiation imposes important safety concerns for space exploration missions. Several studies have speculated the radiation risks associated with exposure to both galactic cosmic rays (GCR) and solar particle events (SPE).^{1,2} The radiation-induced health risks include carcinogenesis, cardiac problems, cataracts, and other acute radiation syndromes.¹ Damage to neuronal system has been a potential concern related especially to the heavy ions present in the GCR.²

In medical radiation applications, radiotherapy is a common technique used to treat cancer patients. High-energy ionizing radiations (up to tens of MeV) are used to control tumor growth as part of cancer treatment. It is also used to treat nonmalignant conditions such as severe thyroid eye disease, abnormal growth of mucousal tissue (pterygium) or bone (heterotopic ossification), aggressive joint lesions such as

pigmented villonodular synovitis, etc. The tissues near the region of treatment often get exposed to the penetrative X-rays leading to harmful side effects to both internal and superficial organs. One such side-effect that occurs in patients treated for head and neck cancer is xerostomia—a condition that reduces saliva secretion, alters speech and taste, and induces other secondary nutritional deficiencies.³ X-rays with energies in keV range are often employed in interventional procedures (X-ray image-guided procedures), and in diagnostic radiology such as computed tomography (CT) examinations.

Neutrons are uncharged particles commonly used in nuclear reactors for producing nuclear energy. They readily pass through most materials and interact with the nuclei of the target atom. Many of the sources that emit X-rays and γ rays also tend to emit neutrons. Exposure to neutron radiation is particularly hazardous to body tissues since they are capable of generating a much denser ion path as they lose/deposit their energy within the target material (in this case, body tissues). Interactions with biological matter may also result in the production of other radiations such as γ rays, protons and alpha particles. Nuclear plant workers and aircraft crew are most susceptible to occupational exposure of neutrons.⁴ Hence, there is a significant demand for effective, durable radioprotective gear in applications related to potential health hazards from

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Table 1. Overview of the Different Sources of Radiation Used or Encountered in Three Representative Industries

industry	radiation sources	composition	typical energy range
aerospace ^{5,6}	(i) galactic cosmic rays (GCR) (ii) solar particle events (SPE) (iii) trapped particle belts	GCR consists of high-energy protons, alpha particles (helium nuclei), and heavy nuclei accounting for nearly 85%, 14%, and 1% of the total flux, respectively. SPE consists of transient burst of low- to medium-energy protons and alpha particles. Trapped radiation belts mainly consist of high-energy electrons and protons.	(i) 10 MeV to 10 GeV (ii) few MeV to 100s of MeV
medical radiology: diagnostic, interventional and radiotherapy ⁴	(i) X-rays & γ -rays (ii) protons & electrons	electromagnetic radiation – wide range of X-rays & γ rays. Particle radiation for therapeutic purposes	(iii) electrons: few MeV and protons: several 100s of MeV tens of keV to tens of MeV
nuclear reactors ⁴	(i) particle emissions (ii) γ -rays	neutrons, alpha and beta particles, and γ -rays	(i) 0 to 15 MeV for neutrons, 0 to 4 MeV for alpha and beta particles (ii) 10 keV to 3 MeV

different types of radiation. In this paper, we focus on radiations that have high energy and/or high charge (referred to as HZE, where Z stands for atomic number), or have charge-inducing capability when they traverse through a medium.

Numerous experimental investigations and theoretical studies have reported the use of a variety of shielding materials (e.g., concrete, polymer composites, heavy metals such as lead, composites of lead oxide/tungsten/tin, etc.) for attenuation or absorption of the undesired radiations.^{7–10} The shielding effectiveness of a given material largely depends on the type of radiation and the range of energies associated with the radiation.¹¹ Lead and other high Z materials have been employed to attenuate high-energy radiations such as X-rays and γ rays. However, high Z elements may not always be able to block all types of radiations, particularly the emissions of neutron particles in space or nuclear laboratories. Moreover, the radio-protective gear made from these materials are heavy and bulky, both of which often are unwanted features for most applications. For example, in mobile nuclear devices and manned spacecrafts, radioprotective materials that are light-weight and have less volume are preferred due to the space and maneuverability constraints imposed by the vehicles/devices.¹² There is an increasing demand to develop new shielding materials that can be customized according to specific application (or radiation type). In the past two decades, several studies have reported application of nano- and microcomposite materials to attenuate/absorb high energy radiation. Because of the large surface-area-to-volume ratio, the nanoparticles have been reported to show enhanced ability to absorb photons.¹³ Micro- or nanomaterials (also known as “fillers” in this context) dispersed in a polymer matrix can be used to design effective radiation shields. The attenuation is obtained by a combination of the filler/s and the structural material/s. Polymer-based composites are particularly interesting candidates as radiation-shielding materials for varied reasons. First, they offer geometric conformability and can be used as a structural material like metals or alloys commonly used in air-/space-craft industries. Second, they are lighter than their metal counterparts, and therefore utilize lesser fuel to get to high altitudes or orbits.¹⁴ Finally, they can be processed to achieve effective shielding for radiations associated with specific industry.

In this paper, the state-of-the-art polymer composites with micro- or nanomaterials used as radiation-shielding materials are reviewed. In section 2, an overview of the basic interactions between the incident radiation and the target (shielding material) are presented. In section 3, the polymer composites are broadly categorized based on the structure of the micro/nanomaterials used and a brief literature review is presented. The use of new polymer-based shielding materials and some pointers relevant for effective shielding are outlined in section 4.

2. RADIATION AND TARGET INTERACTIONS

In order to design or select an effective radioprotective material, it is important to consider the following: (i) the type of radiation (photons or particles) to be attenuated (or absorbed), and (ii) the type of interaction of the radiation with the target material. In this section, radiation-target interactions are categorized into 2 subsections according to the type of radiation: (i) high-energy photon–matter interactions, and (ii) particle–matter interactions. In each of these subsections, a brief overview of the basic mechanisms of interactions, and

subsequently the selection criteria for effective shielding, will be presented.

2.1. High-Energy Photon (X-rays and γ -rays)–Matter Interactions. There are three main mechanisms of photon interactions: (i) photon scattering (elastic or inelastic), (ii) photoelectric effect, and (iii) pair production.¹⁵ In this subsection, each of these processes is briefly described along with its effects from a radiation-attenuation point of view.

2.1.1. Photon Scattering. Elastic scattering (or Rayleigh scattering) is one of attenuation without absorption since no energy is permanently taken up by the irradiated material. Another type of photon scattering is the inelastic scattering (or Compton scattering) during which, the photon imparts some of its energy to the electron and gets scattered with reduced energy (increased wavelength). The electron recoils with the energy lost by the incident photon and the photon gets scattered with a new longer wavelength.

2.1.2. Photoelectric Effect. Similar to Compton scattering, the incident photon causes ejection of core electrons in the target atom. However, the photon completely disappears such that part of the energy is taken up in overcoming the binding energy of the electron and the rest becomes the kinetic energy of the ejected photoelectron. The ionized atom (of the irradiated material) may return back to the ground state by emission of characteristic radiation or by ejection of another electron (the Auger effect).

2.1.3. Pair Production. If a photon with energy equivalent to or greater than the mass of two electrons (i.e., $2 \times 511 \text{ keV} = 1.02 \text{ MeV}$) interact with a nucleus or an electron from the target then it disappears producing an electron-positron pair. The electron eventually gets absorbed by a positive ion and become part of a neutral atom while the positron interacts with another electron from the target, generating two annihilation photons of equal energy, of minimum value 511 keV each. These annihilation photons move in opposite directions and the rest of the energy (i.e., initial photon energy minus 1.02 MeV) is permanently absorbed by the target material.

2.1.4. Conclusion. For a given material, each of the above-mentioned effects plays a dominant role within a specific range of X-ray/gamma-ray energies. For example, the photoelectric effect has been observed to be most dominant for high Z materials at low energies (typically <500 keV). Therefore, high-Z materials are typically used to develop radiation shields, especially in medical applications such as interventional radiological procedures whereby X-rays with tube-voltages not more than 120 kV are employed. Protective garments made of high Z materials such as lead and composites of heavy metals^{16–18} have been developed for protection against radiation exposure during radiological examinations. However, conventional aprons are heavy and cause discomfort to the users, especially during prolonged procedures.¹⁹ Alternatively, a variety of polymer composites have been investigated because of their desirable properties such as lighter weight, workability, and ability to effectively attenuate radiation. Lightweight, “lead-equivalent” polymer composites are typically fabricated using high concentrations of high-Z fillers embedded in a conformable polymer matrix. The role of the high-Z filler/s is to effectively attenuate radiation while the polymer matrix reduces the overall weight of the composite when compared to conventional shielding materials.

2.2. Particle–Matter Interactions. When high-energy, high-Z particles (HZE particles) traverse a medium (or target), e.g., body of a spacecraft or a tissue, they lose their energy

through a number of interactions with the incident material. Of all the possible interactions, the two most important mechanisms from a radiation-shielding point-of-view are: (i) energy loss (due to radiation, ionization, or excitation of the target material) and (ii) nuclear fragmentation of projectile ions, target material or both.^{5,8}

2.2.1. Energy Loss. Energetic charged particles interact with matter by electrical forces and lose their kinetic energy (inelastic phenomenon) through ionization, excitation and radiative losses. Nonradiative energy loss occurs when charged particles (HZE or beta particles) collide/interact with the electrons of the target resulting in ionization or excitation of the target-atoms along the path traversed by the incident ions. Radiative type of energy loss occurs because of deceleration (slowing down of the charged particles) as they traverse through a medium. This secondary radiation, the intensity of which is directly proportional to the square of the Z of the target material and inversely related to the mass of the incident particles, is called bremsstrahlung. The ratio of the energy loss due to radiation and that lost through ionization and excitation is proportional to the energy of the particle and to the atomic number Z of the target material.

2.2.2. Nuclear Fragmentation. Another important interaction between incident particles and the target material is fragmentation of projectile ions, the target or both. Projectile ion fragmentation involves disintegration of the incident heavy ions into lighter charged particles and neutrons. In other words, nuclear fragmentation of the heavy ion projectile leads to the formation of smaller fragments with the same velocity as the incident ion (i.e., through elastic collision in which the kinetic energy is conserved) but with a lower ionizing power due to its lower atomic number. Target fragmentation, on the other hand, results in the production of secondary radiation. Breaking up the heavy ions present in the cosmic rays into smaller fragments (with lower ionizing power) while minimizing target fragmentation is the only practical solution for developing effective shielding materials.⁵

Neutrons are uncharged particles that do not interact with electrons but with the atomic nuclei of the target material. They lose energy through nuclear interaction resulting in liberation of secondary charged particles, fragmentation of target nucleus or retention of the incident neutron by the atomic nucleus of the target atoms.

2.2.3. Conclusion. The production of bremsstrahlung within the target material (i.e., a shielding material) because of radiative energy loss may pose additional health risks.^{20,21} For example, use of high Z material for shielding against GCR or SPE particles results in emission of highly penetrative γ rays that require additional shielding, adding to the total bulk of the material and to the cost. Therefore, to reduce energy loss due to radiation, low Z materials such as hydrogen are preferred for effective protection. Moreover, for outer space applications, any proposed shielding material must be composed of elements that maximize the probability of projectile fragmentation and minimize the fragmentation of the target material. In this regard, polymers rich in low Z materials, especially hydrogen or boron, have shown to be best-suited materials for radiation shielding. Recent studies^{8,22–24} have shown that elements with low atomic number tend to provide effective shielding against charged-particle radiations encountered in interstellar space (namely, the GCR and the SPE). Hydrogen being the smallest atomic diameter provides a large number of interaction points in the polymer for projectile fragmentation. Moreover, the

absence of elements heavier than carbon minimizes the production of target fragments and hence, the secondary radiations. Thus, a hydrogenous composite polymer–polyethylene (PE) has been chosen as a reference material for the accelerator-based radiation testing of multifunction composites currently being developed by NASA.

2.3. Radiation-Induced Effects in Polymers and Polymer Composites. In nuclear reactors, PE and borated PE (mixture of polyethylene and boron oxide) are widely used as neutron shielding materials. However, these polymers have poor mechanical and thermal stability and exhibit poor durability when exposed to continuous irradiation.^{12,25} The radiation-induced free-radical formation is responsible for the degradation of the material properties. Generally, upon photon/particle irradiation, the ionizing energy absorbed by the polymer backbone initiates a free radical process.²⁶ Subsequently, the polymer then undergoes chain scission (results in reduction of tensile strength and elongation) and cross-linking (increases tensile strength and but reduces elongation), both of which alter the material characteristics of the polymer. Reinforcement of polymer with micro- or nanomaterials has shown to improve radiation-resistance properties of the composite material.^{27,28} Seo et al.²⁹ observed radiation-induced interfacial bonding (polar–polar interaction) between epoxy (polymer) and graphite fiber (filler) in their composite material upon exposure to electron beam of 0.5 MeV. Polyimide (PI), commonly used on spacecraft structures, is highly susceptible to atomic oxygen (AO) in Low Earth orbit (LEO) resulting in severe degradation. Incorporation of polyhedral oligosilsesquioxane (POSS), comprised primarily of inorganic silicon–oxygen cage-like structures ranging from 0.5 to 3 nm in diameter, into PI significantly improved the oxidation resistance through the formation of a protective silica layer upon exposure of POSS-PI nanocomposite to high incident fluxes of AO in LEO.³⁰ In addition to the radiation resistance, several studies have shown that the composite material exhibit enhanced mechanical strength and higher thermal stability when compared to the polymer without filler/s.^{12,31–33} The enhancement in the material properties has been attributed to the properties of the filler material, uniform dispersion of the filler within the polymer matrix, the type of interaction between the filler and the polymer (interfacial effects), and the size effects of the filler.^{24,34} For example, the properties of carbon nanotubes (CNTs) - exceptionally high elastic-modulus and tensile strength (~1 TPa and tens or hundreds of GPa respectively) along with excellent thermal and electrical conductivity, and very high resistance to oxidation in air (>700 °C), have shown to improve the material properties of CNT-based polymer composites at relatively low loading of CNTs.^{25,34,35} Moreover, small-sized filler particles do not create large stress concentrations within the material and helps in retaining the ductility of the polymer.³⁴ Furthermore, both experimental and simulation studies reported that nanocrystalline materials showed enhanced radiation-resistance when compared to their polycrystalline counterparts. This property of nanomaterials has been attributed to the large volume-fraction of grain boundaries that may serve as effective sinks for defects produced upon irradiation of ions and proton beams.^{36–39} Recently, Bai et al.⁴⁰ proposed a “self-healing” mechanism especially near the nanograin boundaries through efficient annihilation of interstitial defects produced upon irradiation.⁴¹ Subsequently, one may hypothesize that incorporation of nanocrystalline materials into polymeric matrix may

impart their radiation-resistant behavior to the nanocomposite through “self-healing” mechanisms. Few studies have systematically investigated the enhanced resistance of the polymer/clay nanocomposites under exposure to high-energy radiation.^{42–46} Addition of a small weight percentage (wt %) of nanoclay into various polymers resulted in increased radiation resistance through effective grafting of the polymer molecules onto the nanolayered clay. Based on the advantages offered by the nanomaterials-based fillers, few studies have proposed the use of nanocomposites of a high-performance polymer - polybenzimidazole and carbon nanofibers or other nanomaterials for durable space applications.^{31,32} Carbon-based filler materials such as carbon micro/nanofibers and recently, nanotubes used as reinforcements in a variety of polymers (resins and plastics) exhibit high strength-to-weight ratio; rendering the carbon composites as suitable candidates in applications requiring mechanical strong, ultra lightweight materials.⁴⁷ Thus, depending on the type of filler and the application, effective and durable radiation shields can be designed using polymer composites.

3. DIFFERENT TYPES OF MICRO-/NANOMATERIALS USED FOR RADIATION SHIELDING

In this section, the polymer composites are broadly categorized based on the structure of the reinforcements used in the materials: tubular structures and micro/nanoparticles.

3.1. Polymer Reinforced with Micro- or Nano-whiskers/Fibers/Tubes. Graphite fiber composites have exceptionally high mechanical strength, and hence, they are used as replacements for metals with poor mechanical properties and high densities such as aluminum alloys. Gaier et al.²⁷ demonstrated the application of graphite microfiber-based epoxy resin composites for shielding against cosmic radiation. They studied the effect of the intercalation of bromine (Br₂) and iodine monobromide (IBr) on the graphite composites and proposed the use of the composites as electromagnetic interference-shields for power systems in spacecrafts. Br₂ and IBr were intercalated into woven fabrics of graphite microfibers which were then stacked up together with epoxy–resin in between two layers of the intercalated (or pristine in case of control samples) graphite clothes. They compared the shielding performance of all the composites against high energy photon radiation—X-rays and γ rays with 13 and 46.5 keV energies respectively. The results indicated that equal shielding effectiveness was achieved by 8 mm thick pristine graphite epoxy material, 1.8 mm of Br₂ intercalated graphite epoxy material and less than 1.4 mm thick IBr intercalated graphite epoxy. Thus, intercalated IBr composite significantly reduced the mass of the shield. In other words, they concluded that composites with a few heavy atoms within the light matrix acts as a more efficient shield against high energy photons than a uniform, electron-rich material. The composite materials were also tested for high-energy electron (100 keV to 1.16 MeV) absorption as a function of areal densities of all composites. Interestingly, they found that regardless of the material been used, the absorption was independent of atomic number of the material and limited by areal density (Figure 1). Moreover, intercalation increased the shielding effectiveness because of their higher mass density.

Few researchers have explored the possibility of using CNTs for improving radiation resistance and mechanical strength of hydrogenous polymers.^{25,28,48} Najafi and Shin⁴⁸ reported the high-energy radiation-induced (UV ozone and 20 keV electron

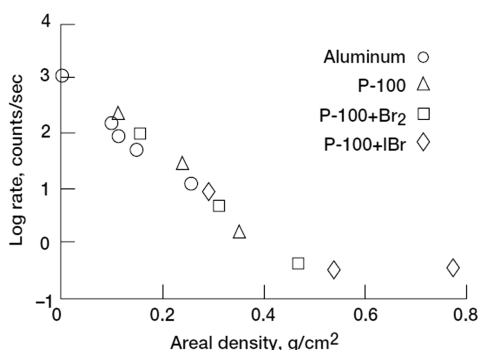


Figure 1. Energy absorption as a function of areal density. P-100 is a type of graphite microfiber.²⁷

beam) effects of CNT-based reinforcements in polymethylmethacrylate (PMMA) polymer matrix. They demonstrated that incorporation of CNTs in PMMA reduced the etch depth of their samples until the percolation threshold of CNT network (at 0.5 wt % of CNTs) within the polymer matrix was achieved, beyond which the etch depth attained saturation (Figure 2).

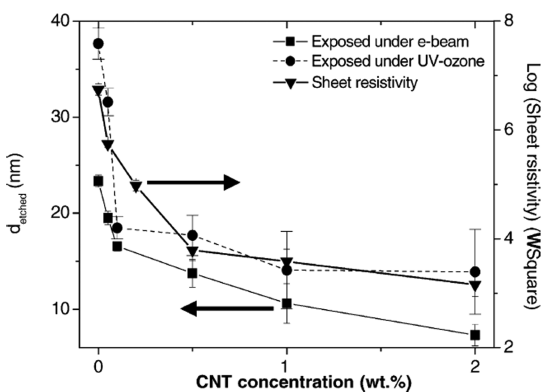


Figure 2. Etched depth (d_{etched}) vs CNT concentration upon 15 min of exposure under e-beam (closed squares) and UV ozone (closed circles) together with sheet resistivity (closed triangles) of the CNT-PMMA composite thin films.⁴⁸

The percolation threshold, confirmed from the sheet resistivity measurements, was observed to be the saturation point for the shielding behavior of the CNT network. The authors concluded that the addition of CNT fillers had a dramatic reinforcement effect on the radiation-induced degradation of PMMA and in successful dispersion of the radiation.

For space applications, the structural materials are required not only to be radiation-resistant, and mechanically strong but also to be able to withstand thermal cycling. Clayton et al.²⁵ studied the material properties of poly(4-methyl-1-pentene) (PMP) reinforced with 0.5 wt % loading of single-walled CNTs. They proposed the use of PMP, as an alternative to PE for use as a shielding material against GCR, because of its high performance material properties when compared to that of PE. The dynamic mechanical analysis (DMA) of the neat polymer (PMP) and the composite (PMP + 0.5 wt % SWCNTs) showed that the addition of the SWCNTs enhanced the viscoelastic properties of the composite; both the storage and the loss modulus were found to be higher than those of the neat polymer. Moreover, the DMA plots showed that the addition of SWCNTs increased the glass transition temperature of the composite and enhanced the relaxation intensity at the

amorphous region of the PMP, both of which indicated that the CNTs improved the crystalline character and mechanical properties of the PMP polymer.

Zhong et al.²³ (2009) reported the radiation shielding performance of ultrahigh molecular weight polyethylene (UHMWPE) fiber-reinforced nanoepoxy composite characterized by radiation tests at the NASA Space Radiation Laboratory. The authors reinforced epoxy matrix with reactive nanofibers of graphite to form a “nanoepoxy” composite and showed that the mechanical (strength, modulus, and toughness) and the thermal properties, and wetting and adhesion ability to UHMWPE fibers improved remarkably when compared to UHMWPE fabric alone. Upon testing the material composite against high-energy heavy ion (1 GeV/nucleon) such as the ones encountered in GCR flux, the authors found that the shielding effectiveness was not compromised by the addition of nanofibers into the epoxy/UHMWPE matrix (Figure 3).

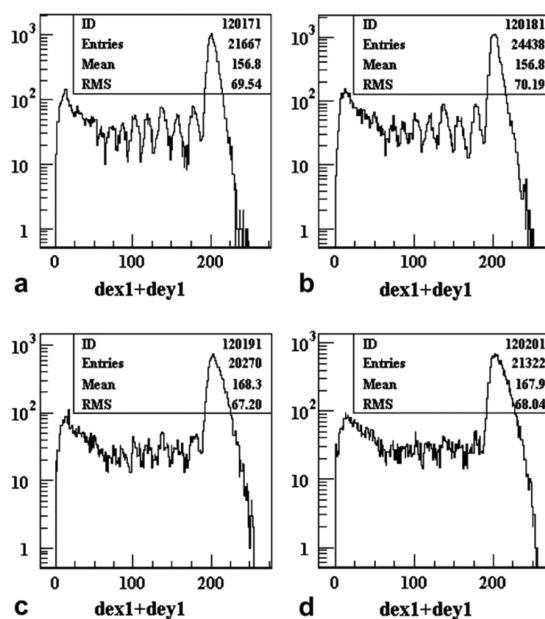


Figure 3. Energy loss spectra obtained from the following targets: (a) UHMWPE/nanoepoxy, (b) UHMWPE/pure epoxy, (c) hybrid fiber/nanoepoxy, where “hybrid fiber” is composed of UHMWPE and S-glass in 2:1 layer ratio and (d) hybrid fiber/pure epoxy. The silicon detectors “dex1” and “dey1” detected the average energy deposited downstream of the targets a, b, c, and d.²³

3.2. Polymer Reinforced with Micro- Or Nano-particles/Powder. Cement or concrete is commonly used in nuclear reactors for blocking neutron flux and γ rays produced as part of nuclear fission reactions. Gunduz et al.⁴⁹ developed several composite materials by impregnating polystyrene into pure concrete (composed of baryte aggregates and cement), concrete loaded with Vitrified Colemanite, VC, ($\text{Ca-B}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O}$) in powder form (88 μm in size) and in coarse form (0.833 to 5.613 mm), and concrete/iron-chunk composites loaded with and without VC. The boron-oxide content in the concrete/VC composites showed improved absorption against thermal neutrons when compared to pure concrete. The composites without the iron chunks blocked the thermal neutrons (secondary emissions produced from primary neutron blockage) efficiently but the γ rays were not blocked as

effectively. However, upon addition of iron chunks, the composite improved attenuation for γ rays. Finally, the incorporation of polystyrene into the concrete composites improved the shielding ability toward fast neutron flux.

PE has been commonly used for shielding purposes in spacecrafts, however, its structural integrity at high pressures and temperature has been concern. Ashton-Patton et al.⁵⁰ reported the use of low density PE (LDPE, bulk density: 924.5 kg m⁻³) reinforced with three different types of hollow glass microspheres (HGM) - soda lime borosilicate (bulk density: 170 kg m⁻³), borosilicate (bulk density: 150 kg m⁻³), and aluminosilicate (bulk density: 160 kg m⁻³), all tested against high compression pressures with the following load conditions: (A) 6.51 MPa and 110 ± 11 °C, (B) 3.9 MPa and 110 ± 11 °C, and (C) 3.9 MPa and 120 ± 11 °C. The borosilicate composite, with bulk density 150 kg m⁻³, showed the best resistance to breakage for all three conditions. The use of HGM improved the modulus with minimum weight gain. The authors proposed the use of these impact-resistant LDPE/HGM composites as high-energy radiation shields in space exploration studies. Harrison et al.²⁴ developed composites of high-density PE (HDPE) and boron nitride (BN), and evaluated the materials for mechanical and space-radiation shielding properties. Upon addition of 15 vol % neat or functionalized BN to HDPE, the tensile modulus of the composite improved from 588 to 735 and 856 MPa respectively. The authors compared the shielding effectiveness of 2 wt % BN composite with neat HDPE and aluminum (Al) against neutron-beam energies up to 600 MeV, and against 120 GeV protons. Under high-energy neutrons, both neat HDPE and HDPE/BN composites exhibited similar shielding efficiencies to that of Al (Figure 4). However, Al proved to be the better shielding material for high-energy protons.

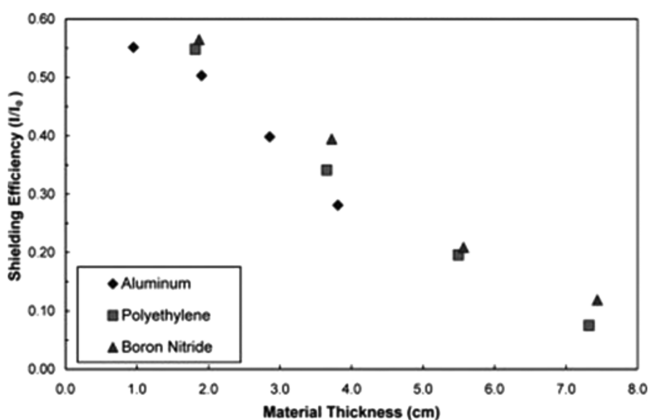


Figure 4. Comparison of attenuation results for Al, PE, and PE/BN composites. Reprinted with permission from ref 24. Copyright 2008 Wiley.

Silicone rubber is another family of polymers that have been used in spacecraft industry for its excellent electrical insulation properties, performance at wide range of temperatures, and good resistance to aging, chemicals, ozone and irradiation. Di et al.⁵¹ compared material properties and high-energy proton irradiation responses of the silicone rubber composites. They tested two composites: (i) silicone rubber reinforced with MQ (M: monofunctional silicon-oxygen units, Q: tetra-functional silicon-oxygen units) silicon resin (represented as M-SR), and (ii) silicone rubber modified with titanium dioxide nano-

particles (nano-TiO₂) based on the M-SR composite (represented as T-SR). Both the composites (M-SR and T-SR) were tested against a range of proton energies -30 to 200 keV. Analysis of the changes in the surface morphology, mass loss, and mechanical properties of the irradiated composites showed similar cross-linking and degradation effects in both T-SR and M-SR composites. However, the magnitude of degradation in T-SR was found to be lower than M-SR (Figure 5). For both the composites, the storage modulus increased

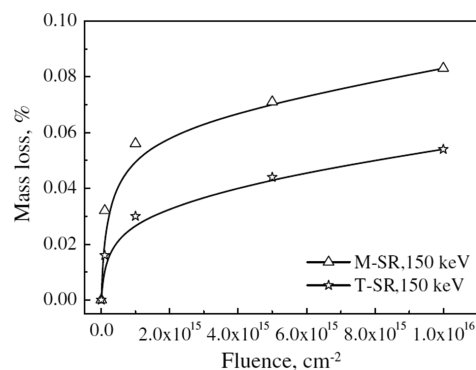


Figure 5. Mass loss ratio versus proton fluence for the M-SR and the T-SR composites. Reprinted with permission from ref 51. Copyright 2006 Elsevier.

upon proton irradiation (fluence = 1 × 10⁻¹⁴ cm⁻²) and then decreased for fluence greater than 1 × 10⁻¹⁴ cm⁻². The fluctuation of the modulus was attributed to the sudden increase followed by severe radiation-damage induced decrease in the cross-linking-density for fluence greater than 1 × 10⁻¹⁴ cm⁻². The authors concluded that the incorporation of nano-TiO₂ into the silicone rubber not only improved the mechanical properties of the rubber but also increased its resistance to proton radiation.

3.3. Polymer Reinforced with Clay Platelets. It has been well-established that clay minerals considerably enhance the mechanical, thermal, electrical, and barrier properties of standard polymers.^{43,52,53} Moreover, they significantly reduce flammability of the polymer composite in comparison to that of the pure polymer. The clay minerals are disk-shaped (platelet) and typically contain a layered structure of tetrahedral and octahedral sheets. Polymer-clay composites can be broadly categorized into three different types based on the mode of addition of the clay to the polymer matrix:⁵³ (i) phase-separated (microcomposite) (ii) Intercalated (nanocomposite), and (iii) Exfoliated (nanocomposite). In “phase-separated” polymer composites, the clay minerals (i.e., layered silicate) are dispersed in polymer matrix without penetration of the polymer between the layered structures of the clay. However, in both intercalated and exfoliated composites, the polymer penetrates between the interlayer spacing of the clay, resulting in increased interfacial area between the polymer and the filler layers. Both of these types lead to the formation of polymer-clay nanocomposites.

Several studies have investigated the physical and chemical performances of different types of polymer-clay nanocomposites showing remarkable improvements in mechanical properties, thermal stability, and corrosion resistance of the nanocomposites in comparison to the microcomposites and pure polymer.^{42,46} Polymer-clay nanocomposites, therefore, find a wide array of applications in the form of structural

materials, heat-resistant coatings, gas barriers, and electronic materials. In recent years, few groups have explored the radiation-resistant properties of polymer nanocomposites.^{42–46} Of the different types of clay minerals, montmorillonite (MMT) has been the most commonly used filler in polymers because of their high surface area and surface reactivity. MMT is a hydrous aluminosilicate clay mineral with an Al octahedral sheet sandwiched between two layers of silicon tetrahedron.⁵³ Each layered sheet is approximately 1 nm thick with the lateral dimensions on the order of 30 nm to several micrometers. Studies have shown that different types of MMT-based polymer nanocomposites have enhanced resistance toward high-energy radiation such as γ rays and HZE particles. Zhang et al.⁴² investigated the effects of γ radiation on nanocomposite based on triblock copolymer styrene–butadiene–styrene (SBS) intercalated into the layers of organophilic MMT (OMMT). They characterized the radiation-induced effects on SBS/OMMT nanocomposite using X-ray diffraction (XRD), DMA, electron spin resonance (ESR) spectra, and gel fraction measurements as a function of dosage. The XRD data showed that under a dosage of 75 kGy, the SBS/OMMT nanocomposite had higher intensity peaks (i.e., increased ordering of structure) than those irradiated with a dose of 150 kGy (Figure 6). On the basis of the XRD data, the authors concluded that

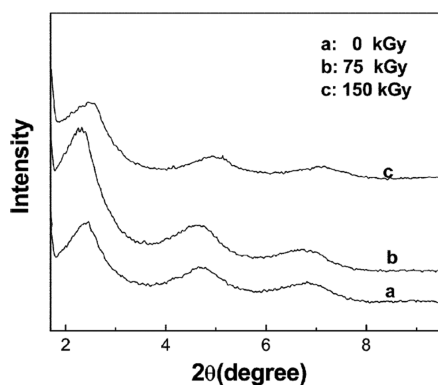


Figure 6. XRD curves for SBS/OMMT nanocomposite at different radiation doses. Reprinted with permission from ref 42. Copyright 2004 Royal Society of Chemistry.

the SBS/OMMT nanocomposites may have undergone both cross-linking and main-chain scission when exposed to γ radiation. The DMA results showed that the storage modulus of both pure SBS and SBS/OMMT nanocomposite decreased with increase in dosage for temperatures above the glass transition temperature of one of the major constituent polymeric blocks in SBS—the polybutadiene (PB). However, the decrease in the storage modulus of the nanocomposite was found to be relatively less than that of the pure SBS. The ESR spectra and the gel fraction measurements showed that the nanocomposites formed more free radicals and favored gel-formation, respectively, compared to the pure polymer. On the basis of all the characterization techniques, the authors concluded that the OMMT layers protected the SBS chains from irradiation through grafting of the broken chains of SBS on the OMMT. A similar study on another type of polymer/clay composite was conducted by the same research group.⁴³ Zhang and Fang⁴³ investigated the effects of γ radiation on the morphology and material properties of two kinds of clay minerals used as filler materials with ethylene-vinyl acetate

(EVA) copolymer. In this study, two different kinds of OMMT were prepared through cationic exchange between the sodium-MMT and a clay-modifying agent in an aqueous solution denoted as HOM (prepared through exchange of 12.5 g of Na-MMT and 4.6 g of hexadecyltrimethylammonium bromide) and DHOM (prepared through exchange of 12.5 g of Na-MMT with 5.8 g of 2-methacryloyloxyethylhexadecyldimethylammonium bromide). XRD analysis of the two kinds of nanocomposites, EVA/HOM and EVA/DHOM, showed that the interlayer spacing and the peak intensities of the EVA/DHOM were greater than those of the EVA/HOM nanocomposite, indicative of good intercalation and ordered structure of the clay layers of DHOM within the EVA matrix. Similar to their previous study, the mechanical and thermal properties of the EVA/DHOM nanocomposites showed significant radiation resistance compared to the pure EVA polymer.

Tiwari et al.⁴⁴ were the first to report the effects of swift heavy ions (SHI) on poly(vinylidene fluoride) (PVDF)/clay nanocomposites. They studied the structural properties, thermal behavior, and morphological changes of the pure polymer and the intercalated PVDF/clay nanocomposites before and after exposure to SHI with various ion fluences. From the XRD results, they concluded that the intercalation of the nanoclay (Cloisite 30B [bis(hydroxyethyl)methyl tallow ammonium ion exchanged montmorillonite]) with the PVDF increased with fluence (i.e., the interlayer spacing between the nanoclay layers increased). Moreover, at higher fluencies, the PVDF/clay nanocomposites were able to recrystallize (marginal degradation) when compared to the pure PVDF, which completely degraded to form a brittle structure (Figures 7 and 8). The crystallinity and the heat of fusion of pristine PVDF significantly reduced after SHI irradiation, whereas the nanocomposites showed relatively small changes even at higher fluences. The damage effects on the surface and bulk of the

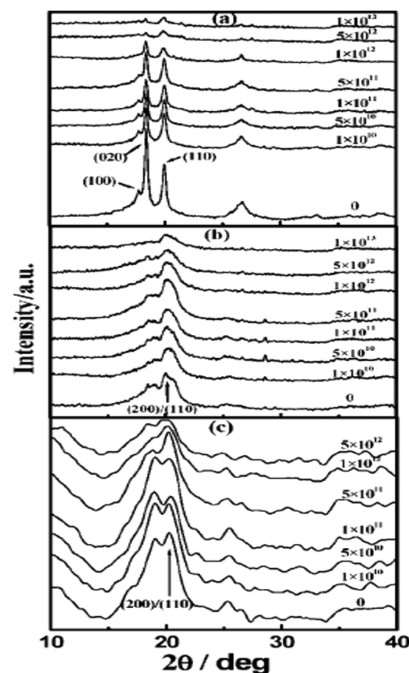


Figure 7. Wide-angle XRD patterns of (a) pure PVDF, (b) 4 wt % nanoclay in PVDF, and (c) 8 wt % nanoclay in PVDF at indicated fluences: “0” to 5×10^{12} ions/cm². Reprinted with permission from ref 44. Copyright 2009 American Chemical Society.

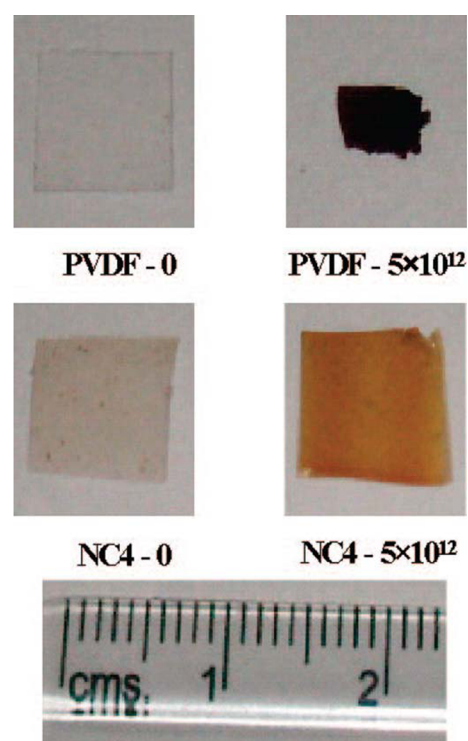


Figure 8. Optical micrographs of PVDF and its nanocomposite (4 wt % of nanoclay in PVDF denoted as NC4) with indicated fluence: “0” and “ 5×10^{12} ” ions/cm². Reprinted with permission from ref 44. Copyright 2009 American Chemical Society.

PVDF and the nanocomposites upon SHI irradiation, as quantified with atomic force microscopy through calculation of the pitting dimensions, showed that the degradation was considerably suppressed in nanocomposites making it a suitable high-energy radiation-resistant thermoplastic polymer.

A similar study was conducted by the same group on a different polymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) (HFP) and the same type of nanofiller.⁴⁵ The mechanical, thermal and morphological characterization yielded results similar to those of the PVDF nanocomposites. Additionally, they conducted gel-fraction and molecular weight measurements on both pristine and nanocomposites of HFP. The increased gelation and molecular weight of the nanocomposites at higher fluences indicated that exposure to the SHI mainly induced chain scission in pure HFP whereas cross-linking was the major phenomenon in nanocomposites. Recently, Tiwari et al.⁴⁶ developed multifunctional nanocomposites of poly (vinyl-

idene fluoride-cochlorotrifluoroethylene) (CTFE) with 4 and 8 wt % nanoclay (Cloisite 30B) that showed significant enhancement in toughness, SHI resistance and piezoelectric properties when compared with pristine CTFE. The authors concluded that the increased radiation resistance of the CTFE/clay nanocomposites, in comparison to the pure polymer, was due to the predominance of the cross-linking mechanism through parallel chain conformation of CTFE molecules onto the surface of the layered nanoclay (i.e., recombination of free radicals formed during SHI exposure).

4. CONCLUSIONS

The increasing demands for radio-protective gear and structural materials in various industries are discussed in Section 1. The shielding effectiveness of any material, in addition to its material properties, is also largely dependent on a variety of factors that include the type of radiation, its origin (cosmos, nuclear reactor, laboratories, natural radioactivity, etc), the range of energies involved, exposure time, secondary radiations and other external parameters such as temperature, pressure, etc. Additional factors involved in selecting an effective shielding material include conformability, cost-effectiveness, weight factor, toxicity, durability, etc. In this regard, polymer composites offer numerous advantages over conventional materials. Based on the studies covered in Section 3, we can conclude that polymers reinforced with micro- or nanoscale structures have great potential to be used as radiation shielding materials in all the three industries discussed in this review. Moreover, the general trend seems to be toward development of novel, multifunctional polymer nanocomposites exploiting the properties of nanofillers. It should be noted that the radiation-resistant properties of the nanomaterials under different types of radiation still remain to be fully understood.

In nuclear industry, low *Z* materials alone are not often successful in attenuating highly penetrative rays such as γ rays. One of the emerging solutions is the use of a graded shield material that contains heavy atoms impregnated within hydrogen-rich polymer matrix along with other micro- or nanomaterials such as boron, metal oxides, graphitic fibers, metal whiskers, etc. Materials consisting of a mixture of different atomic numbers incorporated within hydrogenous polymer-matrix along with some neutron absorbers are especially suited for shielding applications in nuclear reactors. The inelastic scattering by heavy atoms and elastic scattering by hydrogen could effectively block fast and intermediate neutrons, and the neutron absorbers can reduce secondary gamma radiations and thermal neutrons.¹²

Table 2. Comparison of Polymer Composite-Based Shielding Materials with Conventional Material

industry	material type	standard material	material properties compared to standard material				
			mass density	thermal conductivity & material strength	toxicity	conformability	dose equivalent compared to standard material
aerospace	(i) neat polymers (epoxy, PE, polyether-imide, poly sulfone, PBI)	Al	low	low		high	low
	(ii) polymer + micro/nanofillers (carbon/graphite fibers, CNTs, BN, HGM, nanoclay)		low	equivalent		high	low
healthcare	(i) polymer + lead-based fillers (lead oxide, lead particles)	lead	low		equivalent, or higher for lead oxide composites.	high	equivalent
	(ii) polymer (LDPE, natural rubber, PDMS) + nonlead based fillers (tungsten, tin, bismuth oxide)		low		very low	high	equivalent

A qualitative comparison between polymer composites and conventional material used in aerospace and healthcare industry is provided in Table 2. Overall material properties and their shielding effectiveness are indicated as “low”, “high”, or “equivalent” in comparison with conventional material.

Heavy metal elements (high Z materials) such as lead, tungsten, bismuth, lead oxide or composites of these materials have been traditionally used for protection against X-rays or γ rays because of their higher mass densities. The use of lead-based aprons in interventional radiological procedures and related applications tend to cause occupational health hazard because of the toxicity and weight factor associated with lead products. Alternatively, polymer-based shielding materials are lightweight, conformable, and they can be designed to include nontoxic, high-Z filler materials that provide effective X-ray protection.¹⁹ The size effects (nanoparticles versus microparticles) on X-ray attenuation properties of copper oxide (CuO) embedded in bee wax has been recently reported by Botelho et al.⁵⁴ The CuO nanoparticles showed enhanced attenuation characteristics at the low X-ray energies (26 and 30 kV) when compared to the microparticles. The selective enhancement of radiation attenuation by the nanomaterials at the lower energies was attributed to the increased number of particles per gram and grain-size effects. Although such investigations need to be extended to other high Z materials in order to fully understand and exploit the unique properties offered by nanosized materials, such studies offer a basis for further research efforts on non-lead-based polymer nanocomposites for shielding against low-energy diagnostic applications such as mammography.

Aluminum has been traditionally used as a structural material in spacecrafts, however, it is heavy when compared to other shielding materials especially polymers. Moreover, Al provides limited shielding effectiveness because of its low electron density and issues related to production of secondary particles.⁵⁵ Subsequently, composites of hydrogen-rich polymers with various fillers began to be investigated. Carbon/graphite fiber reinforced plastics (CFRP) is one such composite material that has been widely used as structural materials due to their high stiffness-to-weight ratio, and superior mechanical and thermal properties. However, high-energy particle radiation in space can accelerate the degradation of CFRP materials if additional shielding technique is not applied.⁵⁶ The concept of “self-healing or self-repair” of microcracks has been well explored to address the issues of material degradation in polymers including advanced composites such as CFRPs.^{47,57} Among a number of approaches adopted for self-repair or enhancing the impact tolerance of polymers, the most studied is the inclusion of micrometer-sized hollow glass fibers or microcapsules filled with healing agent.^{47,57} Although investigations into radiation-induced chemical and structural changes on stand-alone CNT films (both single-walled and multiwalled) have reported severe bending, decrease in diameter, and surface oxidation,⁵⁸ the use of CNTs as filler material in polymeric matrix has been shown to impart significant reinforcement to the pristine polymer and also improve its resistance toward radiation.^{25,28,48} As discussed in section 3.3, the nanoclay filler materials act as free-radical recombination, enhancing the resistance of polymer nanocomposites under high-energy radiation. With the advancements in nanotechnology, the current trend is toward exploiting the properties of nanoscale structures in creating advanced polymer nanocomposites for effective, lightweight, durable radiation-resistant materials.

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Notes

The authors declare no competing financial interest.

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