Development of Lead-Free Materials for Radiation Shielding in Medical Settings: A Review

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ABSTRACT

Radiation protection is an essential issue in diagnostic radiology to ensure the safety of patients, healthcare professionals, and the general public. Lead has traditionally been used as a shielding material due to its high atomic number, high density, and effectiveness in attenuating radiation. However, some concerns related to the long-term health effects of toxicity, environmental disease as well as heavy weight of lead have led to the search for alternative lead-free shielding materials. Lead-free multilayered polymer composites and non-lead nano-composite shields have been suggested as effective shielding materials to replace conventional lead-based and single metal shields. Using several elements with high density and atomic number, such as bismuth, barium, gadolinium, and tungsten, offer significant enhancements in the shielding ability of composites. This review focuses on the development and use of lead-free materials for radiation shielding in medical settings. It discusses the drawbacks of traditional lead shielding, such as toxicity, weight, and recycling challenges, and highlights the benefits of lead-free alternatives.

Keywords

Radiation Protection; Radiation; Radiography; X-rays, Lead-Free Shields; Multilayered Polymer Composites; Nano-Composite Shields

Introduction

Radiation protection standards play a crucial role in ensuring the safety of healthcare workers who are routinely exposed to ionizing radiation during various medical imaging procedures. These standards help to establish guidelines for dose limits, equipment maintenance, and proper use of protective measures to minimize the risk of radiation-related health issues among healthcare workers. Compliance with these standards is essential to safeguard the well-being of medical staff and maintain a safe working environment in healthcare facilities [1-3]. Shielding is one of the most critical matters of the protection methods to minimize radiation dose of patients, healthcare professionals, and the general public, other than minimizing exposure time and maximizing distance. The initial step towards identifying radiation shielding materials with suitable physical properties is to develop a comprehensive understanding of how gamma rays interact with matter. Materials containing elements with high atomic numbers (Z) and densities offer a greater likelihood of interactions and a more substantial energy transfer with gamma rays, making them an excellent choice for effective gamma shields. Heavy materials are particularly adept at attenuating gamma rays, making them highly desirable for radiation protection. Lead has been the most widely used shielding material due to its high Z, high density, and low cost. However, lead-based personal protective equipment [e.g., aprons, thyroid, and gonad shields] have several disadvantages including high toxicity, low flexibility, and ergonomic discomfort of wearing heavy shields. The potential health risks associated with lead exposure have prompted a quest for lead-free alternatives that can provide comparable protection. Lead is an extremely toxic material, and exposure to it may cause serious health concerns. It has been found that lead exposure can cause neurologic and psychiatric morbidity, developmental disorders, and thus, it may be responsible for various clinical conditions, especially in deprived areas [4-6]. Studies indicate that even low-level exposure (blood lead levels below 10 μg/dl) can lead to cognitive dysfunction, neurobehavioral disorders, neurological damage, hypertension, and renal impairment [7]. It can cause harm through acute neurotoxicity or gradual accumulation over extended periods. Both inorganic and organic forms of lead are primarily absorbed through ingestion and inhalation, with organic compounds potentially entering the body through the skin and crossing the placental barrier. In occupational environments, inhalation and absorption through the skin are the primary routes of exposure, while ingestion is more common among the general population [8-11]. The World Health Organization and the Centers for Disease Control and Prevention have made declarations stating that there is no safe level of lead in the bloodstream. Indeed, there is no safe threshold for lead exposure [12]. In addition to the points mentioned above, there is a growing body of evidence indicating that wearing lead aprons for extended periods can contribute to the development of low back and neck pain among radiation workers [13-15]. These professionals, who frequently work in environments with radiation exposure, rely on lead aprons as a protective measure. The weight and inflexibility of these aprons place significant strain on the spine and musculoskeletal system, leading to chronic pain and discomfort. Thereupon, it is crucial for healthcare institutions and radiation safety authorities to address this occupational hazard and explore alternative protective aprons or ergonomic solutions to mitigate the long-term health effects on radiation workers [16]. A comparison between the three groups of cardiologists, orthopedic surgeons, and rheumatologist physicians showed that cardiologists have more complaints of low back pain [17]. The weight of a 15-pound lead apron produces a pressure of up to 300 pounds per square inch of pressure on the vertebral discs. Of greater significance, lead-based shielding materials demonstrate a blind absorption zone in the 70-90 keV range, where they are less efficient in these energy ranges [18]. In summary, there is an urgent need for new shielding materials to replace conventional lead-based ones [19]. Using polymer matrix materials for radiation shielding has advantages such as flexibility, chemical stability, lightweight, low maintenance, good workability, low cost, etc. [20-22]. However, due to their low Z characteristics, polymers alone are unable to meet the required effective shielding. Consequently, efforts have been made to reinforce polymers with suitable fillers and additives, resulting in the development of polymer matrix composites [PMCs] as competent and efficient shielding materials. In addition to their shielding properties, these fillers also contribute to the improved physico-mechanical characteristics of PMCs. Polymer-based composites mixed with high Z micro/nanoparticles are typical trials to substitute for the lead-based shielding material. Due to the arrangement of atoms possessing diverse absorption edges and the substantial surface area of nanoparticles, polymer composites mixed with metallic nanoparticles exhibit superior shielding effectiveness compared to those filled with microparticles [23, 24]. Various types of polymers, including polyethylene (PE), polypropylene (PP), polystyrene (PS), poly methyl methacrylate (PMMA), Epoxy and phenolic resins, styrene-butadiene rubber [SBR], ethylene propylene diene monomer (EPDM), polyvinyl chloride (PVC), unsaturated polyester (UPS), and Natural polymers like chitosan, cellulose, and alginate have gained attention as eco-friendly alternatives for radiation shielding due to their biocompatibility and biodegradability. These polymers, among others, have been extensively studied to understand their radiation shielding capabilities and optimize their properties for specific applications in the field of radiation protection [25-28].

Silicon- and vinyl-based polymers, engineering thermoplastics, thermosetting resins, smart polymers, elastomers, as well as biopolymers, have been extensively investigated for their potential in fulfilling shielding requirements in recent decades. But in higher energy ranges such as in nuclear medicine, some metals like tungsten that has a higher density [19.3 g/cm^3] could be a better candidate for radiation attenuation. Thus, tungsten shields can be made thinner and more flexible with a higher dose reduction factor. In addition, various materials can be used alone or in combination for developing personal protective equipment [29, 30].

Therefore, it is crucial to replace lead with non-toxic alternatives. Presently, ongoing research aims to discover radiation shielding materials that are non-toxic, lightweight, flexible, and cost-effective [25, 31]. In the present study, we aimed to review the lead-free shields for personal protection.

Lead-free shields materials

In this section, we introduce basic non-lead materials used as radiation shields alone or in combination with other materials. In Table 1, the main physical properties of these elements contributing to radiation shielding are addressed. Based on pieces of literature, lead-free protective shields are manufactured more in composite structures. Further discussions and reviews on previous studies have been taken in the following parts.

Bismuth

Bismuth is a white crystalline metal with the highest electrical resistance and diamagnetic properties [32]. Studies show that bismuth provides adequate protection against photons produced by the photoelectric effect, as well as against high-energy X-rays and gamma rays that interact mainly through pair production [33]. Using bismuth as a radiation shield is an active area of research. There are several reports that show bismuth is a proper shield to reduce the dose from computed tomography [CT] to anterior radiosensitive organs, such as the breasts, eye lens, and the thyroid [34, 35]. Studies show bismuth is an easy-to-use, patient-friendly, light, and effective shield by a high dose reduction factor. However, bismuth shielding in CT has undergone scientific challenges regarding image quality, automatic exposure control, organ tube current modulation, and patient dose [36, 37]. The radiation dose received by breast in helical chest CT can exceed 50 mGy for an average-sized 60-kg woman. So, breast tissue dose in female patients who undergo chest CT is an important issue because it is a critical tissue for the development of long-term cancers after radiation exposure than other tissues. Several studies have indicated that using the bismuth shield in different CT and CT angiography modalities decreases radiation dose to the breast. Studies show the use of the bismuth shield is a better strategy compared to tube current modulation and optimization techniques [38, 39]. In contrast to breast shields in chest CT, current tube modulation provides a more efficient dose reduction for thyroid at neck CT and fetal dose at CT pulmonary angiography [40, 41]. The shielding effectiveness has been dependent on CT scan protocols and organs. The signal-to-

Table 1: The main physical properties of elements contributing to X-ray radiation shielding.

Element	Lead	Tungsten	Tin	Indium	Gadolinium	Cadmium	Bismuth	Barium	Antimony
Atomic number	82	74	50	49	64	48	83	35	51
Density	11.3	19.3	7.30	7.31	7.90	8.65	9.75	3.5	6.69
μ/ρ [cm²/g] [30 keV]	3.032E+01	2.273E+01	4.121E+01	3.949E+01	1.484E+01	3.765E+01	3.152E+01	9.904E+00	7.631E+00
μ/ρ [cm²/g] [50 keV]	8.041E+00	5.949E+00	1.070E+01	1.030E+01	3.859E+00	9.779E+00	8.379E+00	1.379E+01	1.120E+01
μ/ρ [cm²/g] [60 keV]	5.021E+00	3.713E+00	6.564E+00	6.306E+00	1.175E+01	5.975E+00	5.233E+00	8.511E+00	6.879E+00
μ/ρ [cm²/g] [80 keV]	2.419E+00	7.810E+00	3.029E+00	2.907E+00	5.573E+00	2.751E+00	2.522E+00	3.963E+00	3.176E+00
μ/ρ [cm²/g] [100 keV]	5.549E+00	4.438E+00	1.676E+00	1.609E+00	3.109E+00	1.524E+00	5.739E+00	2.196E+00	1.758E+00
μen/ρ [cm²/g] [30 keV]	2.536E+01	1.991E+01	1.490E+01	1.553E+01	1.333E+01	1.594E+01	2.617E+01	8.875E+00	6.755E+00
μen/ρ [cm²/g] [50 keV]	6.740E+00	5.050E+00	6.314E+00	6.262E+00	3.242E+00	6.115E+00	7.004E+00	6.534E+00	6.400E+00
μen/ρ [cm²/g] [60 keV]	4.149E+00	3.070E+00	4.211E+00	4.135E+00	4.722E+00	4.001E+00	4.320E+00	4.660E+00	4.311E+00
μen/ρ [cm²/g] [80 keV]	1.916E+00	2.879E+00	2.101E+00	2.043E+00	2.937E+00	1.957E+00	1.999E+00	2.501E+00	2.173E+00
μen/ρ [cm²/g] [100 keV]	1.976E+00	2.100E+00	1.189E+00	1.150E+00	1.849E+00	1.096E+00	1.951E+00	1.470E+00	1.237E+00
K-edge	88	69.5	29.2	27.9	50.2	26.7	90.5	37.4	30.5

noise ratio reduction has been generally just a few percent lower than unshielded irradiation, and artifacts have no significant effect on standard requirements for quality assurance. The American Association of Physicists in Medicine (AAPM) has provided a position statement that recommends considering alternatives to bismuth shielding for dose reduction in CT. These alternatives mentioned that by reducing the X-ray tube current and adjusting automatic exposure control parameters when the level of image noise is constant, the bismuth shield should provide a proper dose reduction in the anterior, posterior, and lateral surfaces of the patient's body [42].

A recent study developed a lightweight free-lead shield containing bismuth titanate particles [43]. These particles were mixed in an epoxy resin matrix and some shielding layers were provided equally to 0.35 mm Pb. Results of X-ray attenuation efficiencies showed a significant attenuation of X-rays (up to 97%) at 80 and 100 kVp. This compound showed that bismuth titanate with 0.35 mm lead equivalent attenuation has a half-weight compared to lead. A Monte Carlo analysis also showed that although most non-lead metals lose their attenuation efficiency in high energy levels (120 kVp), bismuth can act as a promising alternative for lead for higher energies [44].

Previous research at Los Alamos National Laboratory has examined the costs and benefits of replacing lead with bismuth for routine personnel protection from radioactive sources. Complete elimination of lead in the work environment is desired, especially in nuclear facilities. For radiation protection against low-energy sources under the photoelectric effect or high-energy X- and gamma rays that interact primarily through pair production, bismuth, a nonhazardous alternative, provides adequate protection without impairing worker safety and productivity. This can be concluded that the performance of bismuth is slightly more effective than the performance of lead in radiation protection [45]. Although bismuth is not considered a human carcinogen, its salts can cause kidney damage, and its large doses can be fatal. Also, inhalation and ingestion of bismuth may induce poisonous reactions and respiratory concerns. Another disadvantage of using bismuth is that it is fragile in its pure form and unsuitable for making bricks. Therefore, many commercial bismuth bricks are made from polymer bismuth mixtures [46].

Barium

Barium is an abundant natural silvery-white metal that can be found combined with other chemicals, such as sulfur, carbon, or oxygen. Barium is a light element that reacts with water, air, and almost all non-metals. It can be mined from barite ores and may be found in soils and food. Barium has many applications in industry and medicine [47, 48]. Radiation shielding using barium is an interesting issue due to the environmentally friendly nature of barium. Barium sulfate is a potential replacement for lead aprons that is not harmful to the human health [49]. Kim et al. developed a barium sulfate [mixed with silicon] sheet as a radiation shield. Their product had a feasible protective property and high flexibility. In another work, they used barium sulfate as a base to manufacture six types of radiation shielding sheets made from a combination of tungsten, molybdenum, rubber, and silicon with an optimal mixing process. They evaluated a shielding sheet from barium sulfate and liquid silicone resin mixtures at different energy ranges at 30, 60, 100, and 150 kVp. Results showed a similar shielding ability to an equivalent thickness of lead, and its flexibility was satisfactory. The authors proposed this compound as an economical and environment-friendly radiation shielding material instead of lead in radiology and nuclear medicine examinations [50]. The health consequences of barium are dependent on its dosage. There is no proof that barium can cause cancer. In 2011, Won-in et al. used barium to fabricate lead-free radiation shielding glass [51]. In their study, lead-free glass samples were prepared from 40% by weight of local quartz sand and different concentrations of $BaCO_3$ (20-40% weight) as a base material in order to investigate the 662 keV gamma attenuation characteristics from Cs-137. Attenuation coefficients increased linearly with increasing $BaCO_3$ content. It can be concluded that a higher density lead-free glass with a high refractive index, will enhance the attenuation property and can be used as gamma ray protective glass to replace lead. Also, the radiation dose reduction and level of comfort provided by bilayer barium sulfate–bismuth oxide composite (XPF) was analyzed during fluoroscopy-guided interventions and compare with standard 0.5-mm lead-equivalent thyroid collars (TCs). Results show that XPF TCs provided superior shielding efficiency and were a lightweight, comfort alternative to standard 0.5-mm lead-equivalent TCs [52].

Tungsten

Tungsten is a well-known metal with special characteristics such as a high melting point and high density of 19.25 g/cm^3. It has played a unique role in X-ray tube construction as an element in the anode and cathode. The amount of tungsten in nature is very low, and there are few tungsten mines across the world. Tungsten has a wide application in microchip technology and liquid crystal displays [53, 54]. In recent decades, tungsten has been introduced as one of the most important alternatives to lead for radiation shield, because of its relatively high Z [=74] and mass density. For radiation shielding against higher energy ranges in diagnostic radiology in which Compton scattering becomes the dominant photon interaction mechanism, tungsten, with a density approximately twice that of lead, is the efficient shielding material of choice [55]. Neeman et al. reported a significant reduction in radiation doses to the patient and operator using tungsten antimony shielding during computed tomographic (CT) fluoroscopy [56]. Also, the use of a tungsten-antimony bilayer shield compared to tungsten or antimony alone can provide a more dose-efficient reduction for radiation workers during fluoroscopy [57]. Furthermore, using a tungsten-antimony composite shield can reduce the absorbed radiation dose in the female breast during chest multidetector CT (MDCT) up to approximately 70% [58, 59]. The results of a study aimed at protecting against low-energy gamma- and X-rays by Monte Carlo simulation in 2011 indicated that tungsten and tin elements are valid alternatives of lead for radiation protection in diagnostic range. In addition to the lower thickness, the shields made in this study had significant mechanical properties and chemical stability [25]. Another experiment evaluated the attenuation efficiency of W and Sn in a CT scan using Monte Carlo and a phantom model. This combination was assessed as a thyroid shield to protect against scattered radiations in brain CT scans. Results showed that a combination of 45% Tungsten-55% Tin was able to provide nearly 15% more radiation attenuation compared to lead shield. They concluded that a combination of W and Sn is more effective with lesser toxicity for the thyroid in brain CT scans [60].

Gadolinium

According to K-edge at 38–63 keV and large neutron capture cross-section, rare earth elements are promising efficient fillers for fabricating shielding materials [61, 62]. Gadolinium is a member of the lanthanide group (Z=64) in the periodic table. It has low toxicity but may irritate skin and eyes [63]. Gadolinium oxide (Gd_2O_3) based glasses have been fabricated and studied as a radiation shield. Kaewjang et al. found the density, attenuation coefficients, the effective Z and effective electron densities of the glass increased as Gd_2O_3 concentration was increased in the 223-662 keV energy range [64].

Polymer materials

The desire to use environmentally friendly and lead-free shielding materials has increased because, as mentioned, lead poses a significant risk to both human health and the environment. The urgent need for alternative materials in radiation protection motivated the synthesis and fabrication of polymer and plastic materials, which became the basis of the materials science industry. Polymers in the form of linked molecules have been proposed in the radiation shielding industry due to their remarkable properties such as flexibility, adaptability, low cost, and lightness that make them attractive candidates for radiation attenuation [65]. In addition, polymers are materials that contain low-Z elements such as carbon (C), hydrogen (H), oxygen (O), and nitrogen (N), which are very important in medical and protective applications and also as tissue-equivalent phantom materials. The interaction between organic matter and radiation is controlled by many mechanisms, such as oxidation, gas production, and polymerization [66]. In polymers, photon interaction mechanisms depend on the amount of oxygen and the volume of the material. X-ray and gamma-ray shielding properties of silicone polymers such as polymer A-polydimethylsiloxane (C_2H_6O-Si), polymer B-polymethylhydro-siloxane (CH_4SiO), polymer C-per hydropolysiloxane (H_3SiN), polymer D-polydi Methylsiloxane (C_2H_6Si), polymer E-methylsilses quinoxaline ($C_{12}H_{32}O_8Si_8$), and polymer F silalkylyene polymer (SiC_3H8) were recently studied, so that polymethyl hydrosiloxane (CH_4SiO) had the lowest half-value layer (HVL), tenth value layer (TVL), mean free path (MFP), and the highest attenuation coefficient [67]. In another study, several types of polymer mixtures were prepared through compression molding. The MCNP5 simulation was used to study the radiation shielding properties of polyamide 6 (PA-6)/acrylonitrile butadiene styrene (ABS) mixtures against gamma rays for different energies. The results indicated the dependence of the mass attenuation coefficient (μ_m) on the weight percentage of the elemental composition of the manufactured polymers so that with an increase in weight percentage of the ABS and the thickness of the polymer, μ_m also increased [68]. The Shielding behavior of six polymer materials, bone equivalent plastic (B-100), PVC, air-equivalent plastic (C-552), radio chromic dye film (nylon base), polyethylene terephthalate (Mylar), PMMA, and concrete was investigated in the energy ranges 10-1400 keV. PVC showed the highest radiation shielding efficiency against gamma rays in the energy range 10-110 keV from the selected samples [69]. Four types of resin of different densities and elemental composition were studied by Elmahroug et al. to calculate the cross-sections of photons interactions with matter in the energy range from 1 keV to 1 GeV using WinXCom code. Their results showed the total µm is dependent on the incident photon energy and chemical content as well as the attenuation coefficient of two epoxy resin and resin (with 1.8 g/cm^3 density) are slightly higher than those of the other resins. Furthermore, epoxy resin and resin showed somewhat better protection against gamma rays than other resins due to their slightly higher density [70]. Using Monte Carlo simulations, bone-equivalent plastic, polyvinylidene chloride, air-equivalent plastic, radiochromic color film, polyethylene terephthalate, polymethyl methacrylate, concrete and water were investigated according to the values of the μ_m and HVL in the energy of 59.5, 80.9, 140.5, 279, 356.5, 511, 661.6, 1173.2, 1332.5 keV. Gurler et al. showed that nylon-based radiochromic dye film has a better shielding efficiency than concrete for energies above 100 keV [71]. Kilicoglu et al. analyzed the polymers used to manufacture N95 masks to investigate gamma ray attenuation. The findings showed that having the lowest TVL, HVL, and MFP, the N2 sample (polyvinyl chloride (PVC)) was best suited and the most promising mask sample for gamma-ray attenuation [72]. These studies confirm that it is very useful to use polymer materials to make flexible radiation shields. In addition, it can be noted that researchers should focus on thermoplastic materials such as polyetherimide, captone, polysulfone, polypropylene, polyether ketone, polymethyl methacrylate, poly (butylene terephthalate), poly (ether sulfone), polymethylpentane, poly (butyl meta), poly (phenylene oxide), high-density polyethylene, and poly (ethylene isophthalate) helping control of the plastic pollution because they are recyclable [73].

Other Lead-free shields materials

Antimony

Antimony is a semimetal found in two forms: metallic and nonmetallic. Antimony has poor heat and electricity conductivity and is stable in acids and dry air. Antimony can be found free, but stibnite (Sb_2S_3) and valentinite (Sb_2O_3) ores are common sources of this element. The main application of antimony is in some types of semiconductors [74, 75]. Antimony has found much interest in shielding in combination with other shielding materials due to its high Z. Its combination with lead makes an alloy that increases lead's durability. There is no evidence for using antimony alone as a shield, but it is used for stability and weight reduction. Some studies showed the feasibility and advantages of tungsten–antimony shields for breast CT scanning [76, 77]. The health effects of antimony are based on different human and animal studies. Exposure to high amounts of antimony for a long time induces irritation of the eyes, skin, and lungs. If this exposure continues, gastrointestinal and cardiovascular diseases may be developed. There are no reports of antimony carcinogenesis [78].

Cadmium

Cadmium is a lustrous silver-white metal. It is a suitable filter for removing low-energy photons in mammography because of the X-ray absorption in the K-edge region (26.7 keV). As a shielding choice, cadmium has been used in powder form and combination with other materials. Cadmium may induce lung damage, high blood pressure, liver disease, and nerve or brain damage [79]. As a part of a low-melting point lead alloy in composition shields, Cadmium can endanger the health of exposed technicians by producing toxic gas during manufacturing and use [80].

Tin

Tin is a silvery-white metal that very rarely occurs free in nature and is widely used for food preservation and wrapping as a coating on the surface of other metals to prevent corrosion. Also, it is used in dental amalgams and toothpaste ingredients. Tin is considered to be non-toxic, but most tin salts and organometallic compounds of tin are toxic. The uptake of tin may cause some effects such as eye and skin irritations and liver damage [81, 82]. Tin is used in radiation shields in combination with other materials. A comparative study showed that using tin and a compound of 80% tin and 20% bismuth for radiation-protective clothing in 60, 75, and 120 kVp energy ranges X-rays is full of debate. Schlattl et al. showed that the shielding efficiency depends strongly on the X-ray spectrum. On the other hand, the amount of scattered radiation emitted by tin is more pronounced than in lead. However, these are not detected in the narrow-beam but considered in the broad-beam configuration. The shielding deficits for the 60 and 120 kVp spectra are much more pronounced in broad-beam geometry than in narrow-beam geometry. Thus, broad-beam geometry more faithfully represents exposure to radiation in occupational practice. In comparison with lead, the shielding efficiency of the lead-free materials was lower, and the effective dose increased by 60%, 6%, and 38% for tin, and 14%, 3%, and 35% for tin/bismuth shielding for 60, 75, and 120 kVp, respectively [8].

Nanomaterial-based radiation shields

Studies show that an 8 mm thickness of Gd nanocomposite with a volume fraction (φs) of 0.10, 0.12, and 0.14 can reduce the transmitted X-ray intensity by about 93-99%. Also, a 16 mm composite thickness (φs=0.12) can protect more than 99 % obtained in the energy ranges of 60-120 kVp. These samples show attenuation efficiency comparable to pure lead sheets with thicknesses of 0.25, 0.35, 0.5, and 1 mm standardly used in radiological protection. The mass of the Gd nanocomposite (φs=0.14, thickness 8 mm) X-ray shielding plate is significantly lighter than the sample made of concrete, glass, and wood at the same attenuation performance (97-99% attenuation) [83].

Another study also showed that a 16 mm thick sheet of Gd2O3 composite made with φs of 0.08 and 0.1 can shield more than 95% and 99%, respectively, of a primary X-ray beam in the ranges of 60-120 kVp. At the same X-ray attenuation (99% attenuation), the sample is 7, 8.5, and 16 times lighter than wood, glass, and concrete, respectively. At 0.5 mm lead equivalent, the composite also has 4.5-19.4% less weight per unit area than current non-lead commercial products [84].

Polymer-based radiation shields

Nanomaterials include particles with dimensions in the ranges of 1 to 100 nm. Particles in these dimensions have magic features not observed in other sizes [85]. Nanotechnology has opened a new horizon in the development of new innovative systems and structured materials for any field. Several studies show that the attenuation of ionizing radiation changes as the particle size of attenuated material changes [86-88]. For example, the attenuation coefficient of gamma radiation emitted from ^{137}Cs changes inversely with size (particle diameter), in the ranges of 200 μm to 2.5 mm. This difference is due to empty spaces between lead particles [89]. This could be a reason for the better attenuation of nanoparticles than microparticles. Some studies have shown copper oxide nanoparticles have better attenuation than microparticles for low-energy X-rays [90]. Noor Azman et al. studied the effect of particle size on the X-ray radiation attenuation in the energy range of 40 to 120 kVp [88].

Their finding confirmed nanoparticles have better attenuation compared to microparticles against low X-ray energy (25-35 kVp). In another study, CuO nanoparticle shield showed a 14% higher attenuation at 26 kVp and 30 kVp but not at 60 kVp and 102 kVp [91]. A comparison of nano- and micro-sized WO_3 as filler for epoxy resin and polyvinyl chloride (EPVC) indicated that nano-sized WO_3 has better attenuation for lower tube voltage. Furthermore, the attenuation of nano-sized particles has a better ability to attenuate the X-ray beam generated by general radiography compared to mammography units [92]. Polydimethylsiloxane (PDMS) nanocomposites including BO nanoparticles in different weight percentages showed a good attenuation at diagnostic X-ray energy (40 to 150 kVp). Studies suggest PDMS nanocomposites can be used as protective cloth and for gonad and thyroid shielding [93].

An experiment investigated the attenuation effect of micro and nano-sized WO_3 in the diagnostic energy ranges. WO_3 particles were embedded into the EPVC polymer matrix and exposed to different X-ray energies. Results showed that nano-sized WO_3 particles are more effective in attenuating X-rays compared to microparticles. Furthermore, results indicated that the nano-sized WO_3 particles have better attenuation efficiency for lower energy ranges. However, at higher X-ray energies like 100 kVp, micro and nano-sized WO_3 particles have similar attenuation efficiency [22]. Recently, an experiment investigated the attenuation efficiency of barium-doped PVC/Bi_2WO_6 composites. In this experiment, barium-doped Bi_2WO_6:Ba^{2+} nanoparticles were evaluated for X-ray attenuation at diagnostic energy ranges. Then, the mentioned structure was embedded into PVC with various thicknesses. Results indicated that the best attenuation coefficients can be observed at lower energy ranges (about 40 kVp). However, an increase in the concentration of barium can improve attenuation coefficients in all energy ranges. This experiment recommended that using barium-doped PVC/Bi_2WO_6 shields with higher concentrations of barium may be useful to replace lead shields in diagnostic radiology [94]. Although most experiments show that nanoparticles can effectively attenuate ionizing radiation for low-energy X-rays, a Monte Carlo study suggested that a composite containing PVA polymer with WO_3 nanoparticles is more effective for the attenuation of high-energy photons of ^{60}Co, ^{137}Cs and ^{152}Er [95]. However, these results need to be confirmed by experimental studies. According to the results of a 2020 meta-analysis, -shields showed higher X-ray attenuation compared to micro-shields, especially at low energies [96].

Discussion

Lead-free shields play an essential role in radiation protection by providing a safe and effective barrier against harmful radiation exposure, ensuring the safety of individuals working in environments with high levels of radiation [95]. According to the above-mentioned disadvantages of lead and the introduction to lead-free shielding materials, radiation protection can be improved with health concerns as low as possible. The comparison of lead and lead-free aprons needs to be studied in different situations, such as interventional radiology. A study showed that lead and lead-free aprons with a similar lead-equivalent have very similar protection for physicians in interventional radiology [97]. Hubbert et al. showed the use of different high-Z materials combined with lead provides better X-ray attenuation compared to lead alone. Using a composite material that includes tungsten, antimony, and lead has better attenuation for 120 kVp X-ray photons (HVL: 4.5 ml Al). This study proposed a composite shield structured with high-Z material with different K-edges that can be more effective for radiation protection at fluoroscopic and radiology procedures [98].

A Monte Carlo simulation and an experimental study showed a composite of tungsten and tin have a better attenuation in the diagnostic ranges. In this study, different weight percentages of tungsten and tin were studied, and a 45% tungsten and 55% tin composition has been found as the best protective structure [25]. In another study, a comparison of lead and a lead-free shield containing tin and tungsten showed that the lead-free shield attenuates 60-120 kVp X-rays as the same as lead when it is 20% lighter. This composite apron is highly recommended for interventional radiology staff [99]. A composite of silver/copper/tin was tested for shielding in different energy ranges of X-rays (10 keV to 10 MeV). The radiation attenuation of different amounts of these materials was examined and feasible results have been obtained [100]. As a composite structure, a two-layer shield containing tungsten/bismuth with 36% less weight has found a similar attenuation to 0.5 mm lead in the energy range of 70 to 90 keV [19].

McCaffrey et al. compared the attenuation effects of lead and several lead-free shields [including cadmium, indium, tin, antimony, cesium, barium, cerium, gadolinium, tungsten, and bismuth] using experimental and simulation studies. This study showed metals with high-Z and low density have a proper dose reduction in the 39 to 206 kVp energy range. In another work, they showed for 30-150 kVp X-rays, shielding using two-layer structures containing a high- and a low-Z material is a better choice than a high-Z metal only [101]. These two layers were barium/bismuth, antimony/tungsten, and antimony/bismuth. These studies concluded radiation shielding can be more effective with a combination of high-Z and low-density materials [102]. An experiment showed interesting properties of tungsten and tantalum-containing composites for attenuating X-rays in medical applications. In this study, tungsten shields were provided as WO_3 or Na_2WO_4 particles within a polydimethylsiloxane composite. Furthermore, tantalum shields including Ta and Ta_2O_5 particles developed in silicone composites. Results showed that tantalum-containing composite is more effective for radiation shielding in the diagnostic energy ranges [33].

There are different commercially available lead-based and lead-free protective devices. New protective cloths are being developed capable of attenuating X- or gamma rays in the diagnostic energy ranges. The most common lead-free protective shields in healthcare are EarthSafe, Xenolite, and Demron™ composites. The manufacturers of these shields claimed that these composites have attenuation coefficients the same as lead-based shields. An interesting issue concerning materials contributing to these shields is that the exact composition of these materials is proprietary and is protected by patents. However, based on Scuderi et al. "both Earth Safe and Xenolite are composed of varying amounts of tin, antimony, arsenic, and cadmium in addition to other unknown materials". Demron is a matrix of chemical resistant polymers and microscale metal particles, including bismuth, barium, tungsten, iodine, as well as proprietary nanocomposites. The manufacturers of these available protective devices have claimed that their products are safe, flexible, non-toxic, and environmentally friendly. Scuderi et al. evaluated the protective radiation efficiency of these garments in terms of transmission, attenuation, lead equivalencies, and also weight and then compared them with a standardized lead protective shield in the energy range of 60-120 kVp. Their results showed EarthSafe and Xenolite have a 0.5 mm lead equivalency protection at 80 and 100 kVp, but not at energies higher than 100 kVp, while Demron was able to shield radiation in higher energies [>100 kVp]. Regarding weight, all these lead-free materials are lightweight to produce less fatigue and musculoskeletal complaints [103].

Conclusion

Lead-free shields are newly developing protective materials in medical imaging. There is plenty of data that shows promising results for lead-free radiation shielding. In the present study, we reviewed current evidence and materials as lead-free protective devices. Composite, polymer and nano-based lead-free shields showed credible results as lead replacements in radiology departments. Finding new materials and developing composite shields are in progress in many research departments. Radiation shielding has many challenges from theory to practice. Many Monte Carlo and experimental studies have been done to find the best materials to replace lead. As the main factor, the geometry of measurement plays a determinant role. The main studies which reported new lead-free shields were based on lead equivalence values that were done in narrow beam geometry measurement. This geometry ignores secondary radiation generated by photon interactions inside the shield and only measures the primary radiation attenuation. In this light, the geometry of measurement should be taken into account.

Authors' Contribution

A Safari and SMJ Mortazavi designed the study. They drafted the manuscript. All authors reviewed and revised the manuscript.

Conflict of Interest

SMJ. Mortazavi, as the Editorial Board Member, was not involved in the peer-review and decision-making processes for this manuscript.

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