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Preparation and characterization of γ-ray radiation shielding $PbWO_4$/EPDM composite

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Abstract A novel composites based on ethylene-propylene-diene monomer (EPDM) rubber for gamma shielding were prepared by using carbon blacks (CB) and ball milled $PbWO_4$ (PWO) powder as fillers. The microstructure of ball milled PWO powder which has a uniform morphology in these composites was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD). The mechanical and shielding tests were performed to determine mechanical and radiation attenuation properties, respectively. The results show these materials exhibit excellent mechanical and radiation-resistance properties.

Keywords EPDM · $PbWO_4$ · Gamma shielding · Radiation resistance · Mechanical properties

Introduction

With radiation technology exploited widely in industry and medicine, radiation hazard has inevitably become a noticeable issue in the world range. In this regard, the preparation of flexible and light materials that efficiently protects radiation workers and the environment become a research focus [1]. Edyta Kusiak prepared the EPDM composites filled with selected fillers as radiation shielding substance. Radiation absorption substances were bismuth (II) oxide (Bi_2O_3), gadolinium (III) oxide (Gd_2O_3), tungsten (III) oxide (WO_3) and antimony (III) oxide (Sb_2O_3) [2]. Jaewoo Kim presented a kind of polymer composites which were prepared by dispersing nano-W into ethylene-propylene-based polymer mixture using melt mixing, and the attenuation of gammas for the composites was enhanced up to ~75 % for Ba-133 (~0.3 MeV) [3]. However, when these shielding polymers are exposed continuous irradiation, the energy absorbed by the polymer backbone initiates a free radical process which should be responsible for the degradation of the material [4], poor radiation resistance properties of materials applied in nuclear environment become an another problem [5]. Therefore, reinforcement of polymer with micro- or nano-materials to improve radiation-resistance properties attracts increasing attention from a number of technologists [6]. In zhang's work, they found that the layers of organophilic clay can not only absorb a large amount of radiation to protect the chains of the tri-block copolymer styrene–butadiene–styrene (SBS) from being irradiated, but also produce a large number of free radicals to recombine the chain free radicals of SBS by means of electron spin resonance (ESR) and gel fraction measurements [7]. Tiwari et al. observed that the degradation had been considerably suppressed in nanocomposites through cross-linking of polymer chains, providing a suitable high energy [8]. Therefore, the aim of this study is to develop a novel radiation protection composite with a good combination of high strength and radiation-resistance functions [9]. EPDM has been chosen in this study because of its distinguished physical properties. Firstly, radiation attenuation performance is positively correlated with the amount of filled

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functional fillers. EPDM which has the least density of only 0.86–0.90 kg/m^3 in all rubber materials can be accepted large amounts of fillers. Secondly, EPDM would not easily undergo chain scission due to saturated and nonpolar chains when exposed to continuous irradiation.

Generally, photon energy attenuate gradually through electron pair effect and Compton scattering effect when γ-rays collide with iron (Fe), lead (Pb), tungsten (W) or other high Z material, and vanish through photoelectric effect at last. According to the absorption edge effect, it is considerable probability that photoelectric effect appears when photon energy is equal to or slightly higher than element inner electron binding energy, and the efficiency of attenuation rises if equivalent absorption edges exist in the material for photon beam. Therefore, using the different binding energy of different element legitimately can improve shielding effect of different energy photons. Furthermore, among those heavy elements, Pb which is most popularly and widely used by far and W that could be an excellent shielding material should be chosen as shielding elements [10]. Simultaneously, smaller powder distributed uniformly in material form a compact shielding layer to prevent penetration of photons, reducing unwanted exposure dosage of the radiation workers. [11] Thence, polymer composite containing PWO can be a new kind of protection material and used as gamma radiation shielding garments or sheets.

In this investigation, a fabrication method is developed by dispersing PWO into EPDM composites via melt mixing. Attenuation properties have been studied in an attempt to understand the mechanism of shielding in such systems. Some mechanical properties such as tensile strength, elongation at break, hardness, and radiation-resistance properties of the composites were also studied in order to evaluate their potential in industrial applications.

Experiment

Materials

Solid ethylene-propylene-diene monomer (4045 M, ENB-EPDM) with 44.5 % ethylene was supplied by Mitsui Chemicals. Carbon black (N330) was obtained from Longchang Carbon Black Company, China. Submicron sized powder of lead tungstate (PWO) were prepared by reacting aqueous solutions of lead nitrate and sodium tungstate (0.05 mol L^{-1} each) at 30 °C and ball milled with silane coupling agent (KH570) in order to improve their dispersity in the matrixes. The physical characteristics of carbon black, lead tungatate powder was presented in Table 1. Dicumyl peroxide (DCP, melting point 41–42 °C, purity of 98 %) was procured from Sinopharm Chemical Reagent Co., China. Triallyl isocyanurate (TAIC, melting point 26–28 °C, purity of 98 %) and N-isopropyl-N′-phenyl-4-phenylenediamin (antioxidant 4010NA, melting point 70–90 °C) was supplied by Jiangsu Huada Chemical Group Co., China.

Sample preparation

Formulation of the composites was given in Table 2. PWO powders were added into melt EPDM with other compounding agents, such as zinc oxide (ZnO), stearic acid (SA), paraffin wax, carbon black (N330), etc. Mechanical stirring was also used for better powder dispersion. The mixing rubber was vulcanized by using rubber flat vulcanizing machine under a pressure of 15 MPa at 160 °C for 30 min. These cured samples were tested after 24 h at room temperature. Radiochemical ageing was performed at ArcNucléart (CEA/Grenoble, France) using Co-60 gamma sources. Samples were irradiated in a container with an oxygen flow of 0.5 L min^{-1} at 20 °C, for total doses between 30 and 220 kGy at the dose rate of 130 Gy min^{-1}.

Characterization

Mechanical properties such as tensile strength and elongation at break were measured using a universal testing machine (QJ-2104) as per ASTM standard testing method with a cross speed of 500 mm min^{-1} at room temperature. The hardness of the composites was measured using a Shore A durometer according to the standard ASTM D2240 testing method. For hardness measurement, the samples having an effective thickness of 6 mm were used. The SEM observation of fracture surface of these samples was made using a scanning electron microscope (EVO 18). The samples of SEM analysis were immersed in liquid nitrogen for more than 10 min to cool down and then fractured immediately. Experimental procedure used for evaluation of the composite shields and their attenuation properties was based on the utilization of HPGe spectrometry.

Results and discussion

Characteristics of milled lead tungstate

Through ball milling process, continuous collisions among the particles and the opportunities of contact between the particles and the coupling agent result in the decrease of size of the PWO fillers. The raw PWO powder through chemical precipitation method with average size of ~4 μm were showed in the SEM image in Fig. 1a, while 1b showed the milled PWO powder whose size is decreased to ~200 nm. The XRD analysis of the raw and milled

Table 1 Physical characteristics of carbon black and $PbWO_4$ powder

Carbon black		$PbWO_4$ powder	
DBP absorption	114 mL/100 g	Powder size	200 nm
I absorption	82 mg/g	Specific surface area	4.6 m^2/g
Ash, weight	0.05 %		
PH value	8–10		
Specific surface area	82 m^2/g		

Table 2 Mass fractions of elastomeric composites, phr

Sample	EPDM	TAIC[a]	DCP[a]	ZnO	SA	Paraffin wax[b]	CB	$PbWO_4$
S-0	100	5	3.5	5	1	10	30	–
S-100	100	5	3.5	5	1	10	30	100
S-200	100	5	3.5	5	1	10	30	200
S-300	100	5	3.5	5	1	10	30	300
S-400	100	5	3.5	5	1	10	30	400

Phr, parts per hundred

[a] Curing agent (Dicumyl peroxide-DCP; Triallyl isocyanurate-TAIC)

[b] Softener (Paraffin wax)

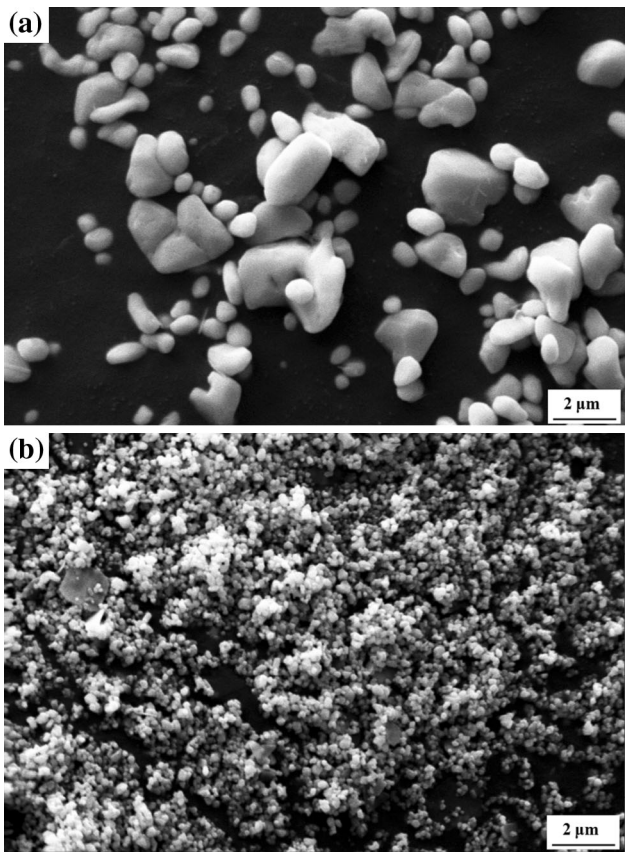

Fig. 1 SEM of lead tungsten powder; **a** raw powder and **b** milled powder

powder modified with KH570 were shown in Fig. 2. The Miller indices of XRD patterns of raw and milled powder (JCPDS NO.19-0708) are identical as marked, while

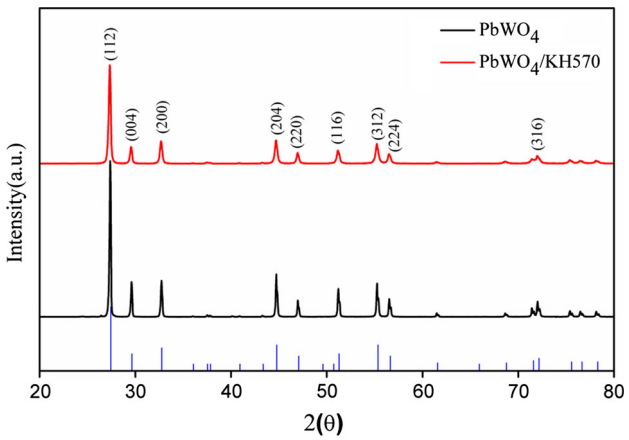

Fig. 2 XRD patterns of raw and milled PWO powder

diffraction intensities of (112), (220) and (204) for milled powder reduced obviously and peak areas decreased. This means that the process of ball milling induces the decrease of the crystallinity of milled powder, the structural change of powder has not changed. Also, impurities other than PWO were not observed from milling balls.

SEM analysis of composites

The EPDM composites containing 0–400 phr PWO powder with an average size of ~200 nm were prepared by melt mixing using a two-roll mill. Figure 3a and b show the SEM images of the microstructures of 100 and 400 phr $PbWO_4$ powder dispersed in the EPDM matrix, respectively. The dispersion uniformly in polymer composites can not only improve the potential mechanical

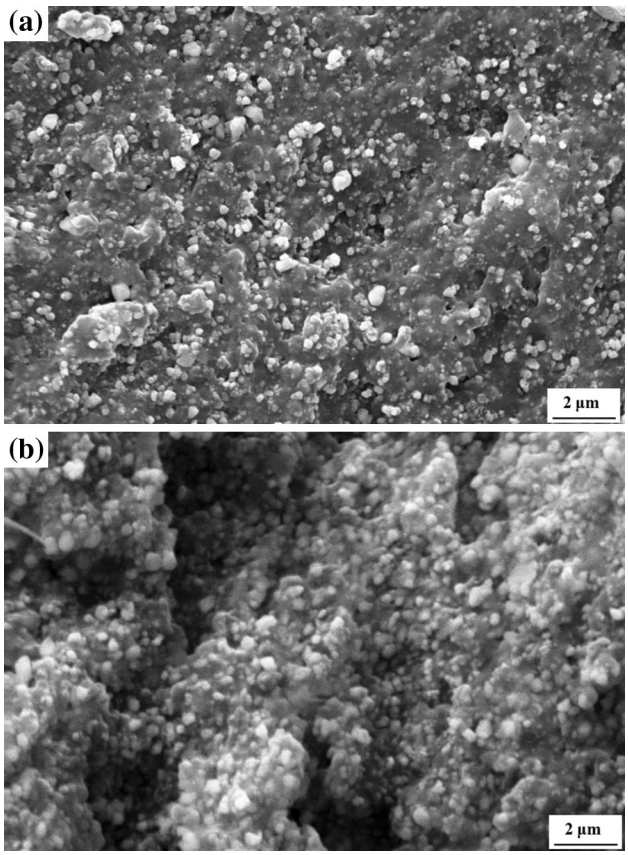

Fig. 3 SEM images of **a** 100 phr, **b** 400 phr $PbWO_4$ dispersed EPDM composites

properties, but also prevent gamma photons from possible vacancies in the matrix. Based on these SEM images, it is confirmed that substantially uniform and dense structures of the PWO powder existed in polymer matrix at lower concentration, whereas powder at higher concentration shows a visible agglomeration phenomenon. Thence, high concentration fillers that were in dispersed state led the increase of lacunae in EPDM composites inevitably [12]. Strong adhesion is also very important for shielding materials since weak adhesion may act as a void for shielding. In general, the inorganic powder has poor compatibility with organic material, which leads poor mechanical properties and use performance. KH570 can be cross-linked with rubber through vulcanization reaction, the interfacial effect between PWO fillers modified by the silane coupling agent and rubber is higher than that of naked fillers and matrix. However,adhesion for 400 phr PWO/EPDM composites looks better than 100 phr PWO/EPDM composites, which can be explained that the adhesion between filler and matrix was observed in Fig. 3a, but the adhesion between filler and filler was observed mostly in Fig. 3b.

Mechanical properties of composites

There was a balance problem between mechanical properties and energy attenuation of gamma shielding rubber. The effect of powder content on the performance of gamma shielding rubber was shown in Table 3. It can be seen that PWO powder had great effect on the mechanical properties of shielding rubber. In the experimental range, the tensile strength and hardness of EPDM composites increased gradually while the elongation at break decreased sharply as the concentration of PWO powder increased. The PWO fillers are dispersed uniformly in rubber matrix at relatively concentration, which can keep the bonding force between fillers and matrix to improve the tensile strength. As the weight fraction of PWO powders increased, the average distance between powders that were in the dispersed state was shorter and shorter. Therefore, the composites are more easily destroyed resulting decrements in the tensile strength and elongation at break of composites. At the same time, with the increase of powder content, the motion of molecular chains is restricted due to the interaction between fillers and rubber molecular chains, which also lead to the decrement in elongation at break. For the composites loaded together with 30 phr CB and 400 phr PWO powder, the Shore A hardness was up to 92.9, the tensile strength and elongation at break were 9.95 MPa and 73.4 %, respectively.

Despite increasing the weight fraction of shielding fillers can enhance the gamma attenuation of composites, the processing energy consumption increase and mechanical properties of composites get worse. Therefore, on the premise of attenuation properties, shielding filler contents should be limited as low as possible.

Table 3 Effect of shielding filler content on properties of EPDM composites

Properties			
Sample	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness (HA)
S-0	2.56 ± 0.03	146.6 ± 6.5	64.1 ± 1.1
S-100	4.15 ± 0.02	107.5 ± 4.3	71.0 ± 0.8
S-200	4.86 ± 0.04	99.2 ± 2.1	80.4 ± 1.5
S-300	7.20 ± 0.04	78.9 ± 4.4	87.5 ± 1.7
S-400	9.95 ± 0.02	73.4 ± 5.5	92.9 ± 0.9

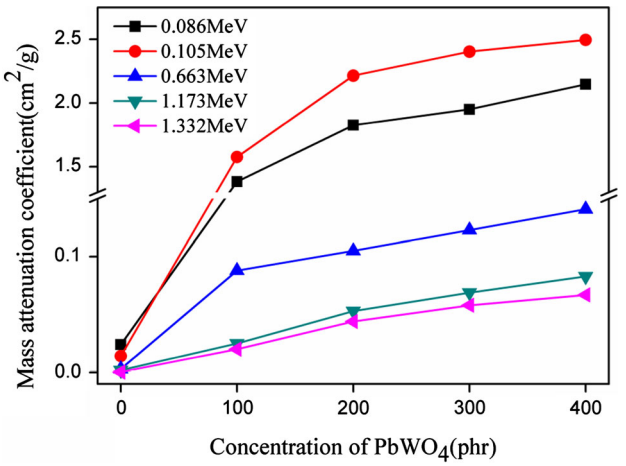

Fig. 4 The mass attenuation coefficient with mixing concentration for different γ-ray energy

Effect of $PbWO_4$ filler loading on gamma energy attenuation

The attenuation behavior of high energy photons can be simply expressed by the following formula [13]:

$$I(t) = I_0 e^{-\mu_m \rho t} \quad (1)$$

where I(t) and I_0 are the intensity of the transmitted and incident radiations respectively, μ_m is the mass attenuation coefficient depend on energy and material, ρ is the volume density, and t is the thickness of the material.

Experimentally, three gamma sources (Eu-155, Cs-137, Co-60) were used to evaluate the attenuation behavior of the PWO dispersed EPDM composites. The relation between the mass attenuation coefficient and mixing ratio seems to follow a strong linear relationship as shown in Fig. 4. Figure 5 represents the average values of linear

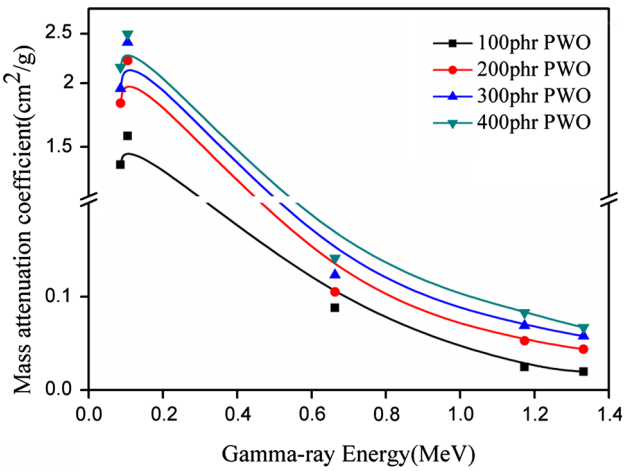

Fig. 5 the mass attenuation coefficient with gamma–ray for different mixing ratios

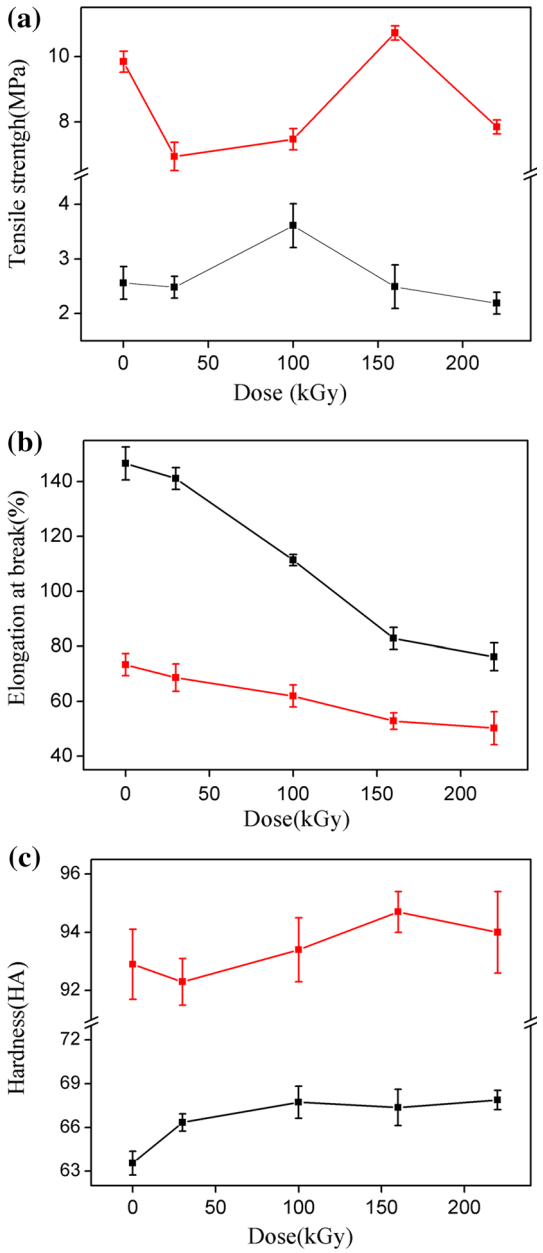

Fig. 6 Effect of gamma irradiation on the mechanical properties of EPDM composites under irradiation dose (— ■ —, PWO-free EPDM composites;— ■ —, 400 phr PWO/EPDM Composites)

mass attenuation coefficient versus the incident photon energy at different concentrations. This figure shows that the average values of mass attenuation coefficient decreases rapidly as energy increases.

When the gamma photons interact with the bounded electrons of Pb and W atoms, the photoelectric effect is dominant for low gamma energy (Eu-155), while the photoelectric effect and Compton scattering are equally dominant for medium energy (Cs-137). For Co-60, photon interactions are mainly governed by Compton scattering, which is least affected by interaction cross-section among

three energy sources [14]. Because Pb atoms have a weak absorption region (40–88 keV) in photoelectric effect, the attenuation for 0.086 MeV mainly depends on W atoms, while Pb and W have a common and great shielding attenuation for 0.105 MeV. This is why the mass attenuation coefficient for 0.105 MeV is higher than that for 0.086 MeV.

The effect of gamma radiation aging

In nuclear reactor, rubbers filled with different shielding fillers are widely used as gamma shielding materials. However, these polymer chains are sensitive to continuous irradiation. Upon photon irradiation, the gamma radiation interacts with polymers in two ways: chain scission, which results in reduced tensile strength and elongation, and cross linking, which increases tensile strength but reduces elongation [15].

Figure 6 shows that the mechanical properties of PWO-free EPEM composite and 400 phr PWO/EPDM composite which were irradiated with the different doses from 30 to 220 kGy under oxygen. For PWO-free EPDM composites, the tensile strength increases initially and after decreases for high dose, finally that of irradiated samples decreases very sharply as shown in Fig. 6a, which is consistent with the research of Tonguç [16]. The decrease of elongation at break and the increase of hardness might possibly be related to cross-linking and breaking of molecular chains via continuous irradiation. When 400 phr PWO dispersed into rubber, the change of tensile strength of composite lags with increasing radiation dose, whereas the hardness undergoes only a minor change, which indicates PWO fillers can be used to absorb part of the energy to weaken the process of radiochemically aged EPDM elastomer. Therefore, it is worthy that PWO filler as shielding component and absorbing additives applied in nuclear field.

Conclusion

In this investigation, we presented a series of gamma radiation shielding materials consist of PWO fillers dispersed EPDM rubber composites whose attenuation is greatly enhanced. For all PWO/EPDM composites, the hardness and tensile strength increased while elongation at break decreased as the weight fraction of PWO powder increased. SEM results showed that fillers were uniformly distributed in matrix and trend to agglomeration easily as the content of fillers increased. Meanwhile, elongation at break of composites decreased while the tensile strength and the hardness increased rapidly as the weight fraction of PWO fillers increased. In addition, a comparison of the mechanical properties of composites before and after irradiation aging showed decrease in the tensile strength and elongation at break while an increase in the hardness. Finally, we can say that increasing PWO percentage in rubber can enhance gamma-ray shielding property effectively. So, these samples can be used as covering walls of nuclear energy centrals, protection clothing in nuclear medicine departments and investigation centers, etc., to protect damage from γ-ray.

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References

1. Nambiar S, Yeow JTW (2012) Polymer-composite materials for radiation protection. Acs Appl Mater 4(11):5717–5726
2. Szajerski P, Zaborski M, Bem H, Baryn W, Kusiak E (2014) Optimization of the heavy metal (Bi–W–Gd–Sb) concentrations in the elastomeric shields for computer tomography (CT). J Radioanal Nucl Chem 300(1):385–391
3. Kim J, Seo D, Lee BC, Seo YS, Miller H (2014) Nano-W dispersed gamma radiation shielding materials. Adv Eng Mater 16(9):1083–1089
4. Clayton LM, Gerasimov TG, Cinke M, Meyyappan M, Harmon JP (2006) Dispersion of single-walled carbon nanotubes in a non-polar polymer, poly(4-methyl-1-pentene). J Nanosci Nanotechnol 6(8):2520–2524
5. Ei-Sayed AA, Ali MAM, Ismail MR (2003) Natural fibre high-density polyethylene and lead oxide composites for radiation shielding. Radiat Phys Chem 66(3):185–195
6. O'Rourke PA, Clayton L, D'Angelo J, Harmon JP, Sikder AK, Kumar A, Cassell AM, Meyyappan M (2002) Effects of gamma radiation on poly(methyl methacrylate)/single-wall nanotube composites. J Mater Res 17(10):2507–2513
7. Zhang W, Zeng J, Liu L (2004) A novel property of styrene–butadiene–styrene/clay nanocomposites: radiation resistance. J Mater Chem 14(2):209–213
8. Tiwari VK, Kulriya PK, Avasthi DK, Maiti P (2009) Poly (vinylidene fluoride-co-hexafluoro propylene)/layered silicate nanocomposites: the effect of swift heavy ion. J Phys Chem B 113(34):11632–11641
9. Fan H, Geng L, Wang S, Zheng Z (2009) A novel radiation protection material: BaPbO3/Al composite. Mater Des 30(3):862–866
10. Erdem M, Baykara O, Dogru M, Kuluozturk F (2010) A novel shielding material prepared from solid waste containing lead for gamma ray. Radiat Phys Chem 79(9):917–922
11. Tanimoto T, Uchida N, Kodama Y, Teshima T, Taniguchi S (2011) Safety of workers at the Fukushima Daiichi nuclear power plant. Lancet 377(9776):1489–1490
12. Ding XJ, Wang JW, Zhang S, Wang J, Li SQ (2015) Composites based on CB/CF/Ag filled EPDM/NBR rubber blends with high conductivity. J Appl Polym Sci 132(4):41357–41364
13. Xu SQ, Bourham M, Rabiei A (2010) A novel ultra-light structure for radiation shielding. Mater Des 31(4):2140–2146
14. Durante M, Kronenberg A (2005) Ground-based research with heavy ions for space radiation protection. Adv Space Res 35(2):180–184

15. Sharma T, Aggarwal S, Kumar S, Mittal VK, Kalsi PC, Manchanda VK (2007) Effect of gamma irradiation on the optical properties of CR-39 polymer. J Mater Sci 42(4):1127–1130
16. Özdemir T (2008) Gamma irradiation degradation/modification of 5-ethylidene 2-norbornene (ENB)-based ethylene propylene diene rubber (EPDM) depending on ENB content of EPDM and type/content of peroxides used in vulcanization. Radiat Phys Chem 77(6):787–793