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Comparative Evaluation of Eggshell-Reinforced Epoxy and Vinyl Ester Polymer Composites for Sustainable Radiation Shielding Applications

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ABSTRACT
Polymer materials of epoxy resin and vinyl ester with composites varied at different mass percentages of egg shells used as filler were studied for their structural, thermal, and shielding properties. The scanning electron microscopy showed a difference in the particle arrangement for the epoxy resin and vinyl ester polymers; however, the particles from the developed composites from each polymer were found to be of the same arrangement. There was an observed increase in the carbon and oxygen content of the developed composites as compared with epoxy resin and vinyl ester polymer from the Energy Dispersive X-Ray Spectroscopy. From the thermogravimetric analysis results, at approximately 300 °C, the epoxy resin and its composite (88% TGA) showed a higher level of thermal decomposition than vinyl ester and its composite (95% TGA). As a result of this, vinyl ester and its composite are better considered for thermal reliability. The radiation shielding efficiency, which measures how effective a given material is at radiation shielding, revealed that the epoxy/egg shell composites are higher than the vinyl/egg shell composites when compared at the same 45% filler composition. The epoxy/45% egg shell composite had a higher linear attenuation value of 0.59 at 100 kVp than the vinyl/45% egg shell composite with a linear attenuation value of 0.52. The low Mean Free Path (MFP) values for the epoxy/45% egg shell composites at 100 kVp, 80 kVp, 60 kVp, and 40 kVp levels of radiation exposure are better considered when compared with the vinyl/45% egg shell composite.

INTRODUCTION

Ionizing radiation exposure has proved to have application across the fields of medical diagnostics, medical therapy, nuclear power generation, pharmaceuticals, medicine, space exploration, archeology, geology, paleontology, hydrology, agriculture, energy production, military and other industrial purposes, (Al Nabhani, 2021; Erdogan et al., 2025). Research reports presented so far have demonstrated that radiation shielding is of critical importance to the specific type of ionizing radiation that successfully diminishes its damaging effects on humans as well as the environment from the emitted radiation dose (Abu El-Soad et al., 2025; Mortazavi et al., 2024; Tashlykov et al., 2022; Han et al., 2025). Due to the limitations for some shielding materials like lead, iron, concrete, that involves toxicity, brittleness, management, corrosion, formation costs, environmental disposal problems, blind absorption zone (ranging 70–90 keV), chemical instability, and weight, attention in radiation shielding have prompted researchers to explore to other alternative materials such as polymers and its composites that will overcome these limitations while providing non-toxic, lightweight, and flexible characteristics (Abu El-Soad et al., 2025; Mortazavi et al., 2024; Fayyadh & Ahmed 2024). The improvement of polymers with different forms of fillers for use in radiation shielding is of the major importance, which motivates one to study for the effective diminishing of the damaging effect of ionizing radiation.

The attention to polymer materials and their composites as applied for radiation shielding has grown due to their remarkable features such as high cross-link density, bonding with oxides, metal fillers, high tensile/flexural strength, good creep resistance, thermal stability, abrasion resistance, and chemical resistance (Erdogan et al., 2025). The incorporation of fillers into these polymer matrices in order to obtain micro- or nano-particles has helped to enhance radiation shielding, thermal stability, mechanical properties, and process ability while reducing material costs (Erdogan et al., 2025).

Epoxy resin is one of the most widely investigated thermosetting polymers for the development of radiation-shielding composites because of its high mechanical strength, chemical resistance, dimensional stability, process ability, and availability (Zheng et al., 2009; Bazrgari et al., 2018; Higgins et al., 2019; Ghani et al., 2025; Huo et al., 2025; Verma et al., 2025). These properties have contributed to the extensive application of epoxy resins in coatings, adhesives, lamination, and construction materials (Naous et al., 2006; Zheng et al., 2005; Protyai et al., 2024; Guo et al., 2024). In radiation-shielding applications, epoxy is predominantly attractive as a polymer matrix because it can accommodate relatively high concentrations of inorganic fillers while maintaining structural integrity and allowing the composite to be fabricated into different shapes and thicknesses.

The incorporation of suitable fillers into epoxy resin has been widely reported as an effective approach for improving the radiation-shielding performance of polymer composites, where the shielding efficiency of these materials depends strongly on the type, concentration, particle size, density, and elemental composition of the incorporated filler (Bijanu et al., 2021; More et al., 2021; Zeng et al., 2023; Aygün et al., 2025). High-density and high-atomic-number fillers are particularly important for photon shielding because they increase the probability of photon interactions within the composite, whereas low–atomic-number fillers are more effective for neutron moderation (Poyraz, 2026). Consequently, the selection of an appropriate filler is essential for obtaining a balance between radiation attenuation, mechanical performance, density, process ability, and cost.

Several studies have investigated relatively inexpensive mineral fillers for epoxy-based composites. Dhandapani and Santhanam (2020) reported the use of calcined clay as a reinforcing filler in epoxy composites. Calcined clay is of interest because of its availability and its ability to modify the structural characteristics of the polymer matrix while potentially reducing fabrication costs (Dhandapani and Santhanam 2020). Egole et al. (2024) noted that there were various economic benefits related to the use of readily available fillers. In particular, the researchers found that a composite made of 50 wt% cured epoxy and 50 wt% calcined clay had the highest density of approximately 1.366 g/cm³ (Dhandapani and Santhanam 2020). Makinde et al. (2026) reported that increasing the Epoxy-Based filler loading of Bi_2O_3 from 14.29% to 85.71% resulted in a corresponding increase in composite density, from 2.65 g/cm³ to 5.86 g/cm³. However, according to Abu El-Soad et al. (2025), calcined clay might have little impact on shielding effectiveness at higher photon energies since increasing filler content did not necessarily lead to proportional improvements in photon attenuation. This example showed that it was important to consider not only filler content but also filler interaction mechanisms and elemental composition.

In addition to the capacity for radiation shielding, much research has been devoted to the enhancement of the mechanical performance of epoxy resins by the modification of fillers. Thus, for instance, according to Bekeshev et al. (2023), functionalization of the nano-filler could greatly impact the mechanical performance of epoxy nano-composites since the researchers found that the functionalization of aluminum nitride by amino-acetic acid increased the hardness and tensile strength of the composite. Similarly, Amirbeygi et al. (2019) investigated the effect of silane-modified graphene on the mechanical properties of epoxy-based nano-composites and found that 0.3 wt% of silane-modified graphene resulted in maximum interlaminar shear strength and compressive strength. Thus, appropriate surface modification and filler concentration contributed to the enhancement of the interaction between filler and polymer matrix.

More recently, Ghani et al. (2025) introduced new epoxy composites, reinforced with tungsten carbide (WC), titanium dioxide (TiO_2) and carbon fiber for improving the mechanical performance of the composites. According to Ghani et al. (2025), the addition of 1.5% of TiO_2 resulted in approximately 420% improvement in impact resistance compared with the unfilled epoxy. These results are important for radiation-shielding materials since shielding components should be mechanically stable and able to withstand mechanical handling and structural loads. Consequently, the development of epoxy composites should take into account both radiation attenuation properties and mechanical performance.

Another important thermosetting polymer for the development of radiation-shielding composites is vinyl ester resin. Its applicability is due to the favorable combination of mechanical strength, chemical resistance, dimensional stability, and environmental endurance. Therefore, vinyl ester can be applied in environments where shielding components can be subjected to aggressive environmental conditions, due to its high resistance to acids, alkalis, moisture and corrosive environments (Zhao et al., 2023; Sati, 2024). Corrosion resistance can increase the long-life and durability of the shielding structure in industrial, medical, or nuclear environments (Zhao et al., 2023).

Environmental and radiation stability is another important characteristic for radiation shielding applications. The investigations of ultraviolet exposure and electron-beam irradiation showed that vinyl ester could maintain substantial structural and chemical stability in conditions of prolonged environmental and radiation exposure, although there was certain degradation, which depended on the exposure conditions and resin composition (Signor & Chin, 2001; Zhu et al., 2023). These properties are especially important for radiation-shielding components, which will be subject to repeated use, since the degradation of the polymer matrix can impact mechanical strength and radiation-shielding properties of the material (Signor & Chin, 2001; Zhu et al., 2023).

Fillers can modify not only the radiation-shielding properties, but also the mechanical and environmental performance of vinyl ester composites. Ahmad et al. (2024) found that the appropriate fillers could increase the chemical resistance and barrier characteristics of vinyl ester composites, thus increasing their resistance to environmental degradation. Wu and Xiao (2025) noted that the mechanical strength and radiation stability of vinyl ester composites were important for structural applications, associated with the generation of radiation. These properties show that vinyl ester could act not only as the matrix for the radiation-attenuating fillers, but also as a structural material.

Vinyl ester-based materials have also been investigated for protective and equipment-related applications, where their resistance to heat, chemicals, and environmental degradation makes them potentially suitable for coatings and protective components associated with X-ray and radiotherapy equipment (Papadopoulos & Bank, 2023). In addition, the incorporation of high-density and non-toxic fillers into vinyl ester matrices has been explored as part of the broader effort to develop alternatives to conventional lead-based shielding materials (Papadopoulos & Bank, 2023). Such alternatives are desirable because of the environmental and health concerns associated with lead.

The relatively low density and mold ability of polymer-based composites also provide advantages for applications requiring lightweight and customized shielding components. Vinyl ester composites can potentially be fabricated into different geometries and configurations, including protective panels and wearable shielding components (Kumar et al., 2023). Studies on polymer-based radiation-protection materials have reported their potential application in wearable devices such as protective aprons and gloves for reducing occupational and patient exposure to scattered radiation (Kumar et al., 2023; Gilys et al., 2022; Almurayshid et al., 2021). Compared with conventional lead shielding, polymer composites offer the possibility of producing lighter and more easily moldable protective materials, although their shielding effectiveness depends strongly on the type and concentration of the incorporated high-density filler.

Generally speaking, epoxy resin and vinyl ester resin demonstrate great flexibility and are promising alternative polymer matrices for radiation-shielding because it is highly dependent on filler composition. As a result of this, recent researches focus on the development of alternative fillers, which are relatively cheap and environmentally friendly and can enhance radiation shielding capability of the epoxy-based and vinyl ester-based materials without compromising the mechanical and other properties of the polymer matrix.

This work concentrates on the design, production, and comparative evaluation of epoxy composites and vinyl ester composites reinforced with egg shell waste for radiation shielding purposes. Both composites were fabricated according to the formulation: a control (0 wt% filler) and composites of egg shell particulates containing 25 wt%, 35 wt%, and 45 wt%. The impact of insertion of egg shell waste on the structural and radiation attenuation characteristics of the developed polymer composites was examined for the structural properties using scanning electron microscopy. The thermal and decomposition properties were investigated using a thermogravimetric analysis, while the radiation shielding effect was used to study the attenuation and absorption competencies of X-ray for the various composites.

MATERIALS AND METHODS

Epoxy and vinyl ester polymer composites were prepared via direct mixing of the matrix and filler (egg shell). The egg shells, used as reinforcement, were collected from food waste, washed with detergent to remove oil residues, and rinsed repeatedly with distilled water to eliminate contaminants. The egg shells were dried at room temperature for a period of 48 hours, it was milled into fine particulates, and then sieved to obtain uniform particle size of 10 mm.

The epoxy resin, methyl ethyl ketone peroxide (catalyst), and cobalt naphthenate (accelerator), each with 98% purity (Sigma-Aldrich), were mixed in stoichiometric proportions according to the manufacturer's specifications. Three other preparations were created with the filler composites containing 25 wt%, 35 wt%, and 45 wt% of the egg shell particulates. These steps were later repeated by using the vinyl ester polymer, methyl ethyl ketone peroxide (catalyst), and cobalt naphthenate mixed in stoichiometric proportions, and three other preparations were also created with the filler composites containing 25 wt%, 35 wt%, and 45 wt% of the egg shell particulates. Each mixture was magnetically stirred at 600 revolutions per minute to ensure homogeneous distribution of the polymer compounds and the egg shell. The mixtures were each cast into a mold of size 150 mm × 75 mm × 5 mm and were allowed to cure at room temperature for a period of 24 hours. Upon de-molding, all the composites were hard and exhibited a light brownish coloration that intensified with increasing filler percentage concentration, while the epoxy and vinyl polymer without filler (egg shell) remained comparatively lighter in color.

Morphological analysis was carried out using a scanning electron microscope (ZEISS Gemini SEM 500) in order to determine the particle arrangement and the elemental composition. Thermal behavior was assessed using TG-DTA and TMA (Rigaku Evo Plus II, Japan) at a heating rate of 10 °C/min so as to ascertain the level of its thermal decomposition, thermal reliability, and suitability for practical applications. At the Department of Radiation Medicine, University of Nigeria Teaching Hospital, Ituku/Ozalla, Enugu State, Nigeria, radiation shielding performance for the polymer and its composite materials were investigated in order to reveal how effective a given material is to radiation shielding. The irradiation and measurements were carried out using an X-ray tube system (Canon Electron Tube and Devices Co., Ltd. 1385, Shimoishigami, Otawara-shi, Tochigi, 324-8550 Japan) and a Cobia X-ray Analyzer Multimeter (RTI Electronics Inc., USA). The source-to-detector distance was fixed at 100 cm, and the beam was collimated to match the sample dimensions (150 mm × 75 mm × 5mm) placed above the detector. The effectiveness of radiation shielding on each of the samples irradiated was achieved by an X-ray machine, using a broad-beam geometry at various radiation levels set across tube voltages of 40, 60, 80 and 100 kVp at a constant tube current of 5mAs. The measurements were obtained with an X-ray machine built on the STATIX column-mounted tube stand manufactured by Italy S.r.l, with a permanent filtration equivalent of 0.9mm Al at 75KVp.

RESULTS AND DISCUSSION

Morphological and Elemental Analysis

Scanning electron microscopy (SEM) was used to inspect the morphology and filler-background interface of the polymer materials, eggshell-reinforced epoxy and vinyl ester composites. The SEM micrographs in Fig. 1 showed differences in the surface morphology of the developed samples. The Micrographs were acquired at magnifications of ×300 and ×500 to assess overall filler dispersion, particle morphology, and interfacial characteristics. The second image, recorded at higher magnification for each composition, was used as a guide for clearer identification of arrangement from the surface. The SEM images for the epoxy polymer in Fig. 1a point out a difference in the surface structure, roughness, and strands at different points. It comprises long flat strands at some points and rough irregular particles. Fig. 2b shows the SEM image of the epoxy/egg shell composite material obtained at 45% wt. Its surface morphology appeared to be totally different from the epoxy polymer, as the structures comprises both large and small irregular particles with, some that are spherical in shape after the mechanical grinding. The morphology of the vinyl ester polymer in Fig. 1c showed a smooth surface with some particles that are tiny though, with some other large irregular particles. There was no form of uniformity as regards the arrangement of the detected particles from its magnified image. The morphology of the vinyl ester/45% wt egg shell composite showed large irregular structures of particles that are not evenly distributed and with some shallow points indicated, as shown in Fig. 1d. Its arrangement is quite different from the result obtained from vinyl ester morphology. Generally, from these observations, we can presume that varying the weight percent of fillers used on polymer materials had a strong influence on the structural and morphological properties of the composites developed. Chang et al., (2023) reported that the prepared HDPE/m-BN composites with homogeneous filler dispersion exhibited superior neutron shielding performance.

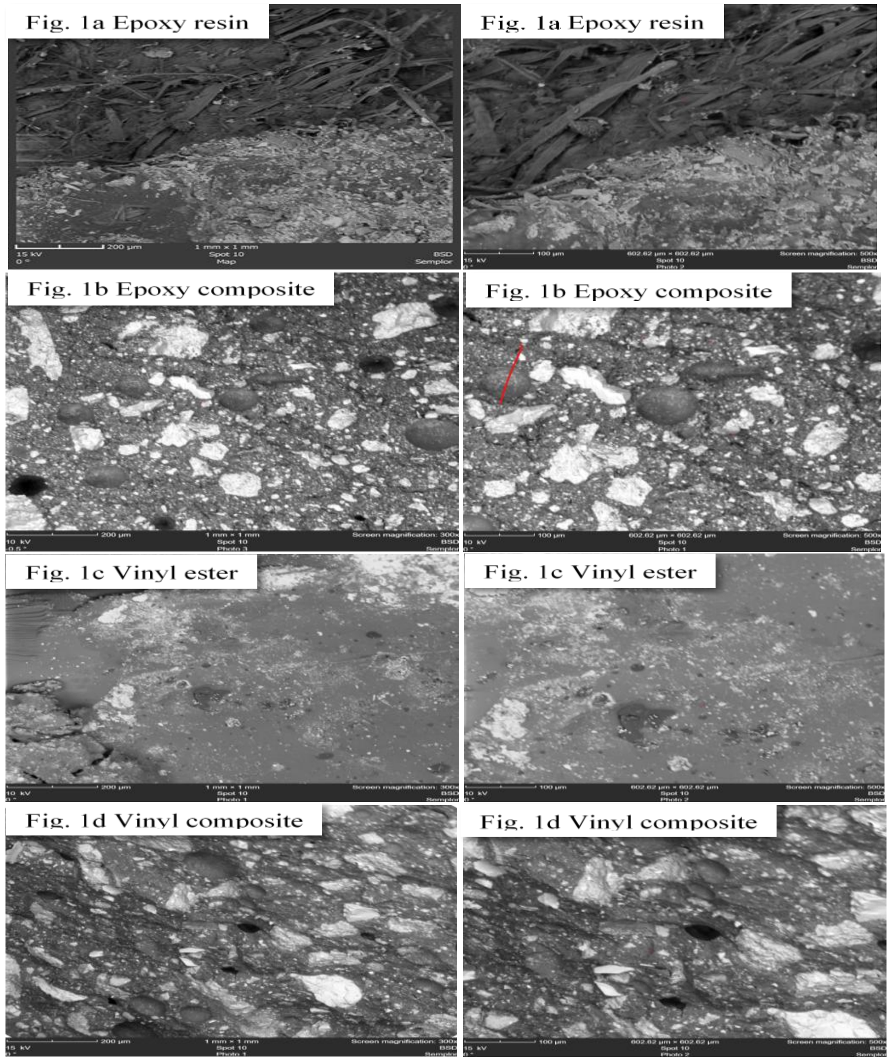

Figure 1: SEM Images that Depict the Surface Morphology of (a) Epoxy Resin, (b) Epoxy Composite at 45% wt, (c) Vinyl Ester, and (d) Vinyl Ester Composite at 45% wt

Energy Dispersive X-Ray Spectroscopy (EDS) was used to examine the spectra and percentage weight of the elements it revealed for the polymer materials, eggshell-reinforced epoxy and vinyl ester composites (Fig. 2a-d). The elements identified from the EDS spectrum in Fig. 2a, which is for the epoxy polymer, are carbon (C), oxygen (O), Calcium (Ca), silicon (Si) and Bromine (Br) with carbon having the highest weight percent from the inset and followed by oxygen, and calcium. The other elements found (silicon (Si) and Bromine (Br)) are with insignificant traces. Fig. 2b shows the spectrum and the identified elements for the epoxy composites (45% egg shell) which are carbon (C), oxygen (O), Silicon (Si), Aluminum (Al), Calcium (Ca), and Palladium (Pd). There was a significant increase in the percentage weight of Carbon, and Silicon from the inset and a drop in the quantity of calcium as compared with the epoxy polymer. Aluminum, as a new element identified displaced bromine from the spectrum, and Palladium as another new element, was found as a trace quantity.

The EDS spectrum in Fig. 2c, which is for the vinyl ester polymer identified several elements, of which the major ones with the highest percentage by weight from the inset are carbon and oxygen. Fig. 2d shows the spectrum and the identified elements for the vinyl ester composite (45% egg shell) which are carbon (C), oxygen (O), Silicon (Si), Aluminum (Al), Phosphorus (P), and chlorine (Cl). From the inset, there was a significant drop in the percentage weight of Carbon, but with an increase in Oxygen, Silicon and Aluminum when compared with the vinyl ester polymer, and so many elements were displaced this time from the spectrum of the vinyl ester composite.

According to Ofor, (2021) and Owuamanam & Cree, (2019), EDS conducted on eggshell-filled polymer composites regularly revealed that the polymer matrix gives mainly carbon (C) and nitrogen (N) signals, while the eggshell filler presents calcium (Ca) and oxygen (O) accompanied with $CaCO_3$, along with some trace amounts of Mg, P, Fe, Al, and other elements. The matrix in epoxy-based systems, is composed mainly of C, H, and O, with rare N from amine hardeners, so EDS spectra of eggshell/epoxy composites normally reveal strong C and O peaks from both phases and distinct Ca peaks from the filler (Sanjay et al., 2019; Prabu & Manikandan, 2020). Comparable elemental behavior is predictable in vinyl ester composites, whose backbone also consists mainly of C, H, and O (More et al., 2021). The low-intensity signal tentatively assigned to palladium (Pd) from the produced EDS analysis was not intentionally added to the eggshell–epoxy formulation. Since EDS identification may be influenced by spectral overlap, contamination, coating materials, and software-based peak fitting, this observation cannot be regarded as conclusive. Replicate point analyses, and elemental mapping, though not studied in this report, are required for further confirmation.

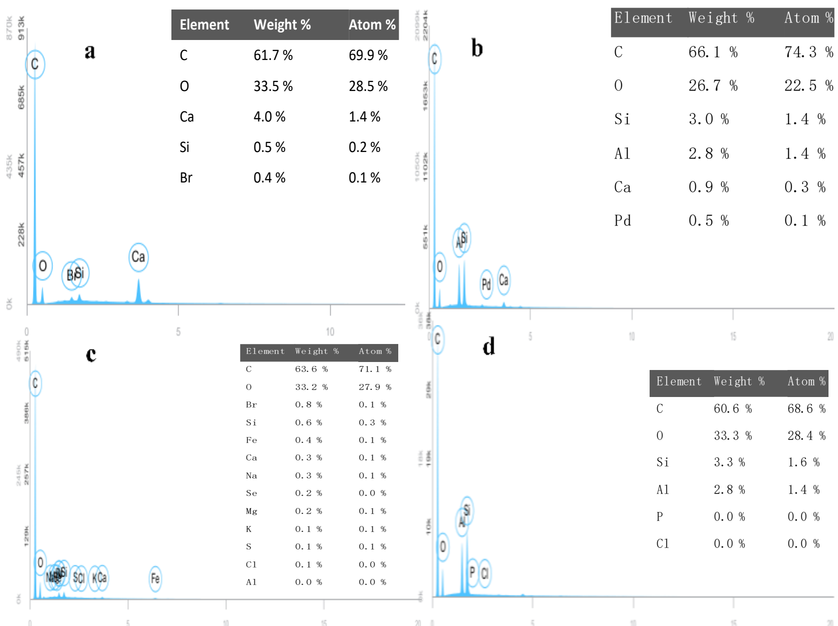

Figure 2: EDS Spectrum of the Materials (a) Epoxy Resin (b) Epoxy Composite at 45% wt (c) Vinyl Ester, and (d) Vinyl Ester Composite at 45% wt

Thermal Gravimetric Analysis

The thermal gravimetric analysis (TGA) assesses the extent of reaction in the chemical structure that occurred and the stability of the developed polymer and its composite samples, which concerns their thermal and chemical composition. The plot of thermal gravimetric analysis (TGA) versus temperature from 0 to 850 ºC was performed for the epoxy resin, vinyl ester, and its composites. The Epoxy resin plot in Fig. 3a showed a gradual drop in its trend as it starts from 0 ºC (at 100% TGA) to 296 ºC (at 88% TGA) before a steep drop was followed to a temperature of 447 ºC (13 % TGA). A gradual drop was maintained again till it reached 850 ºC at 4% TGA. The epoxy/ ES at 45% composite in Fig. 3a also starts from 0 ºC at 100% TGA as it maintained a gradual drop to 160 ºC (96 % TGA) before an increase to 216 ºC at 97% TGA. A steep drop in the trend was followed to a temperature of 387 ºC (13% TGA) before a slightly horizontal trend was observed till it reached 850 ºC at 9% TGA.

The vinyl ester plot in Fig. 3b showed a gradual drop in its trend from 0 ºC (at 100% TGA) to 300 ºC (at 95% TGA). An abrupt drop was traced in the trend till it got to 456 ºC at 27% TGA before a slightly horizontal trend was maintained to 850 ºC at 24% TGA. The vinyl ester composite (ES at 45%) still in Fig. 3b starts from 0 ºC at 100% TGA also maintained a gradual drop same as the vinyl ester polymer to 301 ºC (96% TGA) before a steep decrease to 365 ºC at 70% TGA. This was then traced to 414 ºC at 66% TGA and the steep was maintained to 543 ºC at 21% TGA. A bit horizontal trend was observed till it got to 850 ºC at 16% TGA.

The gradual drop from the starting point in the polymer materials and their composites is a result of weight loss due to the level of water molecule content within the materials (Alshoaibi et al., 2026). The major cause of the increase observed in the trend for the percentage TGA of epoxy composite (ES at 45%) to its maximum, is as a result of uncorrected instrumental artifacts that led to such apparent mass gain (XRF Scientific, 2025; Alshoaibi et al., 2026). The abrupt drop traced from all the samples from a high percentage TGA to a low one is as a result of decomposition of the polymer compound due to bond breaking and thermal degradation (Alshoaibia et al., 2025). By comparing of epoxy resin polymer and vinyl ester polymer based on the level of thermal decomposition, epoxy resin polymer (850 ºC, TGA is 4%) from the plots decomposes more than the vinyl ester polymer (850 ºC, TGA is 24%). Also from the initial drop in the trend to about 300 ºC, the epoxy polymer decomposes to 87% TGS while the vinyl ester polymer decomposes to 95% TGA. As for the composites, vinyl ester composites are also better than the epoxy resin composite in terms of the level of its thermal decomposition. Based on this Zhao et al., (2023) reported that vinyl ester resins are known for their superior properties, which help protect the shielding material from environmental degradation, thereby extending service life in harsh conditions. Papadopoulos & Bank (2023) reported that vinyl ester-based coatings enhance the durability and heat resistance of devices exposed to radiation during imaging or therapy.

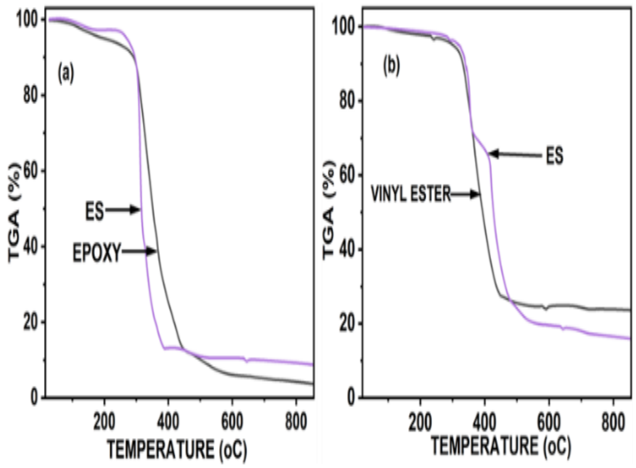

Figure 3: The TGA Plots Against Temperature for (a) Epoxy Polymer and its Composite (45% Egg Shell) (b) Vinyl Ester Polymer and its Composite (45% Egg Shell)

Radiation Shielding Effect

Radiation shielding involves the attenuation of ionizing radiation (X-rays, neutrons) as it passes through a material. The success involved in shielding highly depends on the material density, atomic number (Z) of the elements, thickness of material, and the energy of incident radiation. The plots for radiation exposure dose versus the peak potential energy for the different samples of epoxy resin, epoxy resin/egg shell composite are shown in Fig. 4a, while that of vinyl ester and vinyl ester/egg shell composites are shown in Fig. 4b. The radiation shielding effect were analyzed at different exposure energy levels (40, 60, 80, 100 kVp), each at tube current-seconds of 5 mAs and at material thickness of 5 mm. From each of the plotted graphs, the unshielded radiation was compared with each of the developed materials at the given radiation level. From both plots in Fig. 4(a, b), as the peak potential applied increases from 40 kVp to 100 kVp for each of the samples, the radiation exposure dose likewise increases. At each peak potential applied, there is an observed drop in the radiation exposure dose from the unshielded, epoxy resin or vinyl ester polymer, 25% egg shell composite, 35% egg shell composite and then to 45% egg shell composite respectively. This showed that the effectiveness of radiation shielding occurred as the developed materials (epoxy resin or vinyl ester polymer, 25% egg shell composite, 35% egg shell composite and 45% egg shell composite) attenuated ionizing radiation at different levels.

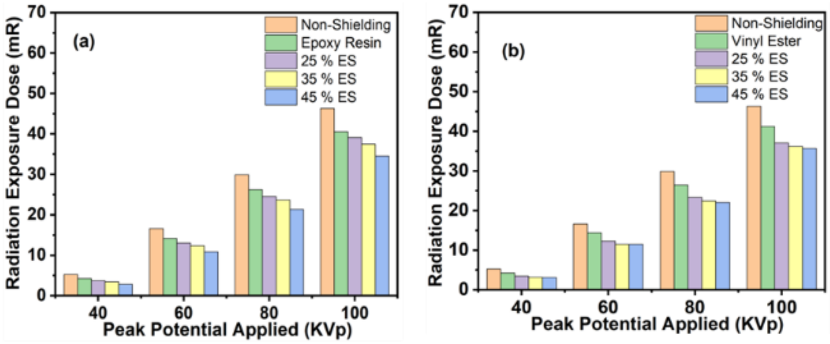

Figure 4: The plot of Radiation Dose Measurements Versus Peak Potential Applied for (a) Epoxy Resin Polymer and its Composites (b) Vinyl Ester Polymer and its Composites

Radiation Shielding Efficiency (%)(RSE)

The essential parameter mostly used in the study of radiation shielding is known as radiation shielding efficiency (RSE) because it directly measures how effective a given material diminishes the intensity of a given incident radiation. The shielding efficiency is usually expressed as a percentage fraction of attenuated radiation by a material and it is considered by using the given equation:

$$E\ (\%) = \frac{N - S}{N} \times \frac{100}{1}$$

Where E is the shielded rate expressed as a percentage, N is the non-shielded radiation beam and S is the shielded beam with a known material. Fig. 5a shows the plot for the radiation shielding efficiency for the epoxy resin polymer, epoxy/25% egg shell composite, epoxy/35% egg shell composite, epoxy/45% egg shell composite at different exposure levels of 40, 60, 80 and 100 kVp. Fig. 5b shows the plot for the radiation shielding efficiency for the vinyl ester polymer, vinyl/25% egg shell composite, vinyl/35% egg shell composite, vinyl/45% egg shell composite at different exposure levels of 40, 60, 80 and 100 kVp. The shielding rate calculated for both the polymer and its composites was found to be high at low radiation exposure of 40 kVp because of its high level of attenuation, and the trend which results to a drop was followed as radiation exposure increased to 60 kVp, 80 kVp and then to 100 kVp as seen in Fig. 5(a, b). The values for the RSE for the epoxy/45% egg shell at 40 kVp, 60 kVp, 80 kVp and 100 kVp are 45.9%, 34.9%, 28.6% and 25.6% while the RSE values for the vinyl ester/45% egg shell at the same radiation exposure are 40.5%, 30.8%, 26.1% and 22.9% respectively. From each of the level of the exposed radiation in Fig. 5a, the epoxy resin polymer showed the list shielding efficiency then followed by an observed increase for the epoxy/25% egg shell composite, epoxy/35% egg shell composite and then to epoxy/45 % egg shell composite. The epoxy/45% egg shell composite had the highest percentage attenuation for each level of radiation exposure and the margin it had with the former (epoxy/35% egg shell) was observed to be higher. The vinyl ester polymer in Fig. 5b, also showed the list shielding efficiency for each of the level of the exposed radiation. This was followed by an observed increase for the vinyl/25% egg shell composite, vinyl/35% egg shell composite and then to vinyl/45% egg shell composite. The vinyl/45% egg shell composite had the highest percentage attenuation for each level of the radiation exposure but the margin it hard with the vinyl/35% egg shell composite was observed to be almost the same with percentage values less than one.

The decrease in the percentage attenuation of the polymer materials and their composites generally from the different levels of radiation exposure (40 kVp to 100 kVp) is as a result of the increase in the photon beam energy from the X-ray machine used for the irradiation of the samples. The drop in attenuation of vinyl/45% egg shell composite when compared to vinyl/35% egg shell composite in Fig. 5b is as a result of the saturation of the egg shell fillers used. The vinyl/egg shell composites had higher radiation shielding efficiency values at filler weights of 25%, and 35% when compared to the epoxy/egg shell composites at the same weight but the epoxy/egg shell composites values for radiation shielding efficiency are higher at 45% filler weight. Moonkum et al., (2026), reported that the radiation shielding performance of epoxy resin and Portland cement composites enriched with bismuth oxide (Bi_2O_3) fillers at weight ratios of 20%, 30%, 40%, and 50%, across photon energies (122 to 662 keV) of which the results indicate radiation protection efficiency from 26 to 99% and at thickness from 0.16 to 2.1 cm. Abu El-Soad et al., (2025) reported that at high filler percentage weight (50 wt% calcined clay), the composite with the highest density of 1.366 g/cm^3, does not greatly influence the shielding efficacy. According to Moonkum et al., (2026), at 122 kVp, the radiation shielding efficiency values of Portland cement of thicknesses 1.0, 2.0, 3.0, and 4.0 cm were 47.90%, 72.86%, 85.86%, and 92.63%, respectively, as compared with a lead block of thickness 2.5 cm, to be 99.77%.

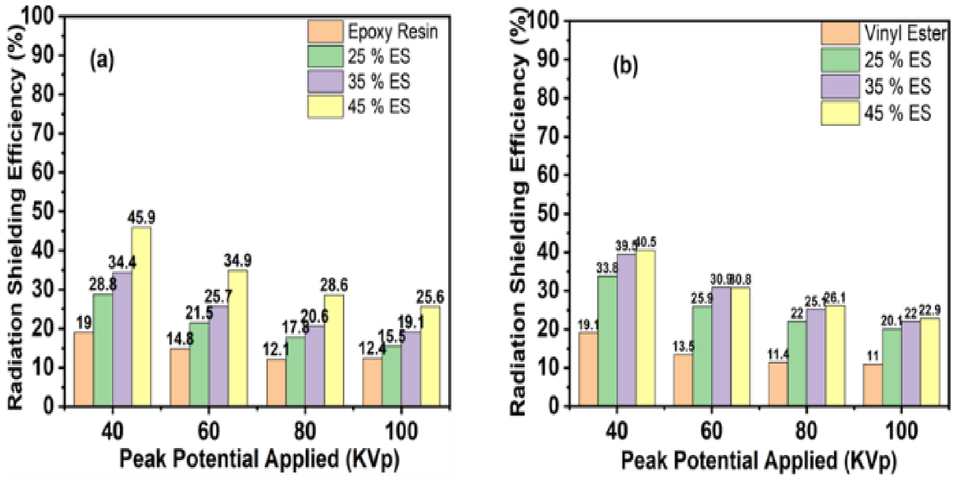

Figure 5: The Radiation Absorption Efficiency for (a) Epoxy Resin Polymer and its Composites (b) Vinyl Ester Polymer and its Composites.

Linear Attenuation Coefficient

The fraction of photons removed from a monochromatic X-ray beam by a homogeneous absorber per unit length is described by a constant known as linear attenuation (μ). The values of the constant can be obtained by using the Beer-Lambert equation

$$I = I_o e^{-\mu x}$$

Where I_0 is the count rate with no shielding material, I is the count rate with shielding material of known thickness x and μ is the constant for the linear attenuation coefficient (Chang et al., 2015). The plot of the linear attenuation coefficient values obtained from the samples of epoxy resin, epoxy/25% egg shell composite, epoxy/35% egg shell composite and epoxy/45% egg shell composite is shown in Fig. 6a. Fig. 6b shows the plot of the linear attenuation coefficient values obtained from the samples of vinyl ester, vinyl /25% egg shell composite, vinyl /35% egg shell composite and vinyl /45% egg shell composite.

There was an observed decrease in the values of linear attenuation coefficient for each of the samples from the plots as the radiation exposure increases. The linear attenuation coefficient was also observed to cluster together for the exposure levels for the epoxy resin polymer and the vinyl ester polymer but spread out as the percentage increase in the filler content used tends to increase as seen from both plots. The 45% egg shell filler used from both plots has the widest separation. The epoxy/45% egg shell composite has a higher linear attenuation value of 0.59 at 100 kVp than the vinyl/45% egg shell composite with a linear attenuation value of 0.52, though the vinyl ester/45% egg shell composite tends to curve at high filler weight. According to the report from Moonkum et al. (2026), Portland cement demonstrated μ values of approximately 0.652, 0.501, and 0.378 cm^{-1} across the photon energy spectrum of 122, 356, and 662 kVp, respectively. The report presented by Aldhuhaibat et al., (2021) states that the attenuation coefficient for epoxy resin polymer measured at different radiation energies remains comparatively close to one another, as a result of the absence of heavy elements that limits the variation in interaction probability, particularly in the photoelectric region. As the filler for the bismuth-based polymer composites increases, the attenuation coefficient values become increasingly separated because the composite's effective atomic number and the density as reported by Putra et al., (2025) increased. This confirms well with the epoxy resin and vinyl ester polymer composite samples reported. According to Putra et al., (2025), such filler arrangement is observed greatly to enhance photoelectric absorption at lower energies and also increases the probability of Compton interactions at intermediate energies, since the attenuation mechanisms become more energy dependent, the differences in μ values between radiation energies become more pronounced, causing the curves to spread apart. Though the effective atomic number of the composites is not measured in this report, the attenuation coefficient results had already been proven from the EDS that the elements obtained from the fillers are of low atomic number.

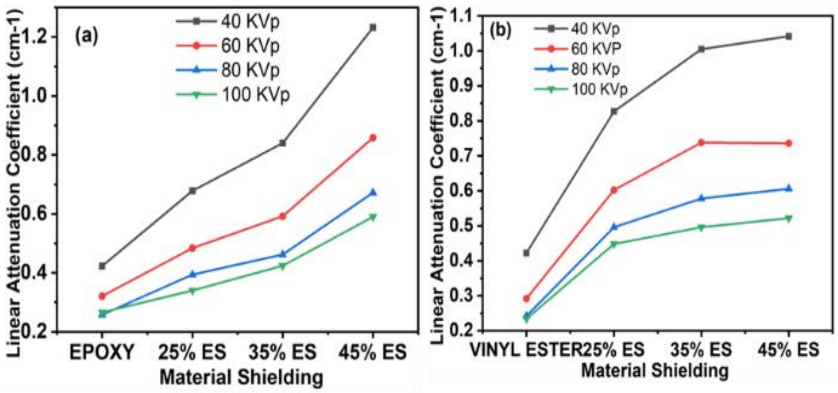

Figure 6: Plot for the Linear Attenuation Coefficient Versus Shielding Material for (a) Epoxy Polymer and its Composite (b) Vinyl Polymer and its Composite

Half Value Layer and Tenth Value Layer

The thickness of a shielding material required to reduce the intensity of incident X-ray radiation by 50% is a major parameter known as the half value layer (HVL). It is mathematically represented using the given equation:

$$Half\ Value\ Layer\ (HVL) = \frac{In2}{\mu}$$

Where μ is the linear attenuation coefficient. The plot for the HVL versus the epoxy resin, epoxy/25% egg shell composite, epoxy/35% egg shell composite, and epoxy/45% egg shell composite are shown in Fig. 7a, while that of the vinyl ester polymer, vinyl/25% egg shell composite, vinyl/35% egg shell composite, and vinyl/45% egg shell composite are shown in Fig. 7b. There was an observed increase in the values of HVL for each of the samples from both plots as the radiation exposure level increases. The HVL was also observed from Fig. 7a and Fig. 7b to spread out at different exposure levels for the pure epoxy and vinyl ester samples but cluster together gradually as the percentage increase in the fillers used for the composites tends to increase. In these plots, the epoxy/45% egg shell composites and the vinyl/45% egg shell composites had the list separations when compared with other samples like the epoxy resin, epoxy/25% egg shell composite, epoxy/35% egg shell composite and the samples of vinyl ester, vinyl /25% egg shell composite, vinyl /35% egg shell composite. Low HVL values indicate superior shielding efficiency, as less material thickness is required to attenuate the radiation. According to Kharita et al., (2008), HVL is strongly energy-dependent, at low photon energies, the photoelectric effect dominates, resulting in higher attenuation and consequently low HVL values. Conversely, at higher photon energies, as reported by Zahran et al., (2022) Compton scattering becomes the predominant mechanism, which reduces photon-matter interaction probability and leads to high HVL values (Gouda et al., 2024).

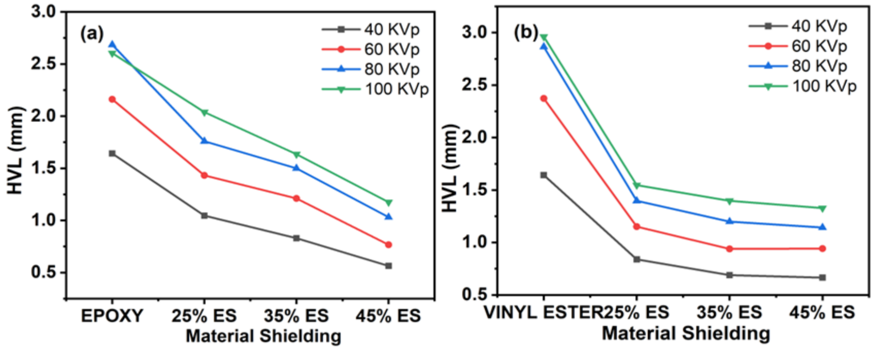

Figure 7: Plot for the HVL Versus Shielding Material for (a) Epoxy Polymer and its Composite (b) Vinyl Polymer and its Composite

The thickness of a shielding material required to reduce the incoming radiation intensity by 90% is known as the tenth value layer (TVL). This is statistically represented in the given equation:

$$Tenth\ Value\ Layyer\ (TVL) = \frac{In10}{\mu}$$

Where μ is the linear attenuation coefficient. The TVL versus the epoxy resin, epoxy/25% egg shell composite, epoxy/35% egg shell composite, and epoxy/45% egg shell composite plot is shown in Fig. 8a, while that of the vinyl ester polymer, vinyl/25% egg shell composite, vinyl/35% egg shell composite, and vinyl/45% egg shell composite plot is shown in Fig. 8b. There was an observed increase in the values of TVL for each of the samples from both plots as the radiation exposure level increases when compared with the HVL. The TVL spreads out at different exposure levels for the epoxy resin polymer and vinyl ester polymer as the trend was observed to cluster together gradually as the percentage increase in the fillers used was increased. The TVL values for both samples from the plots at high percentage filler composition and radiation exposure level are low. Haque et al., (2019) reported that TVL provides a more rigid measure for shielding performance, as it is predominantly important in environments that demand high attenuation, such as nuclear medicine, reactor shielding, and aerospace applications.

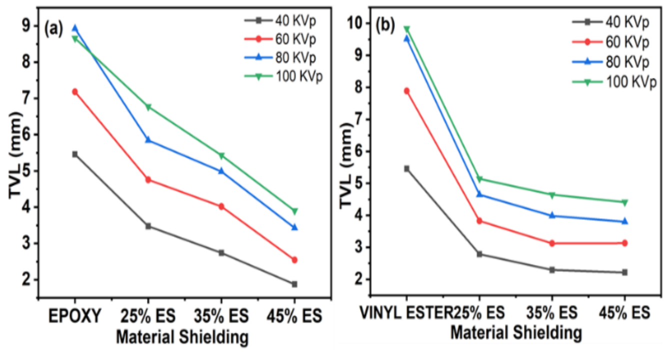

Figure 8: Plot for the TVL Versus Shielding Material for (a) Epoxy Polymer and its Composite (b) Vinyl Polymer and its Composite

Mean Free Path (MFP)

The average distance at which radiation is motionless within a given shielding material, as defined by Biswas et al., (2016), is known as the mean free path (MFP). The MFP is calculated using the stated equation:

$$MFP = \frac{1}{\mu} cm$$

Where µ is already defined as linear attenuation coefficient. The detailed values for the mean free path for the epoxy resin, the other developed polymer composites, and at various radiation exposure rates are shown in Table 1. There was an observed increase in the values of the mean free path for the epoxy polymer and the various developed composites as the radiation dose increased from 40 kVp to 100 kVp. Alternatively, a decrease in the values was observed from the order (epoxy resin, ES 25%, ES 35% and ES 45%) for the various radiation doses. The obtained values for the MPF at low radiation exposure (40 kVp) for the epoxy resin, epoxy/ES 25% composite, epoxy/ES 35% composite and epoxy/ES 45% composite are 2.369$\pm$0.003, 1.474$\pm$0.002, 1.190$\pm$0.001 and 0.813$\pm$0.001 while for the high radiation exposure (100 kVp) are 3.959$\pm$0.001, 2.941$\pm$0.002, 2.358$\pm$0.002 and 1.695$\pm$0.003 respectively.

Table 2 also shows the values for the mean free path for the vinyl ester and other developed polymer composites at various radiation exposure rates. An increase in the values of the mean free path was observed for the vinyl ester polymer and the various developed composites as the radiation dose increases from the 40 kVp, 60 kVp, 80 kVp to 100 kVp. On the other hand, a decrease in the values of the MPF was observed in the order (vinyl ester, vinyl/ES 25%, vinyl/ES 35%, and vinyl/ES 45%) for the various radiation doses. The obtained values for the MPF at low radiation exposure (40 kVp) for the vinyl ester, vinyl/ES 25% composite, vinyl/ES 35% composite and vinyl/ES 45% composite are 2.370$\pm$0.001, 1.210$\pm$0.002, 0.995$\pm$0.002 and 0.959$\pm$0.001 while for the high radiation exposure (100 kVp) are 4.274$\pm$0.002, 2.232$\pm$0.001, 2.016$\pm$0.001 and 1.916$\pm$0.002 respectively.

The reduction in MFP values with increasing filler (egg shell) concentration indicates an improvement in the shielding usefulness of the epoxy and vinyl ester composites. Therefore, the integration of egg shell fillers into the polymer materials has proved to intensify the density and effective atomic number of the composite material. The egg shell used as filler is rich in calcium carbonate ($CaCO_3$) and comprise of bit quantities of heavy elements from the EDS report that add to greater photon interaction probabilities. The deeper penetration of photons into the polymer or composite material before interaction leads to high MFP values (Hubbell & Seltzer, 2004; Knoll, 2010). Tekin et al., (2021) reported that photons involve shorter distances to interact within composites comprising higher filler percentages, as it exhibits greater radiation attenuation capability when compared with pure epoxy resin. A perfect suggestion from the results proves that the low MFP values indicate that photons are attenuated over shorter distances within the highly filled composites, approving the usefulness of the egg shell fillers, which improves radiation shielding performance at low radiation energy. The two composites, when compared from the results prove that the polymers (epoxy resin and vinyl ester) have the same attenuation effect (MPF values the same) at low energy exposure, while at high energy exposure the epoxy resin polymer is better than the vinyl ester polymer because the MPF value is smaller. Alternatively, the epoxy composites are better than the vinyl ester composite in both high and low radiation exposure because of their small MFP values.

Table 1: The Values of the Mean Free Path for the Epoxy Resin Polymer and its Composite

	MFP (cm)			
Material	**40 kVp**	**60 kVp**	**80 kVp**	**100 kVp**
Epoxy resin	2.369±0.003	3.119±0.002	3.875±0.002	3.959±0.001
25% ES	1.474±0.002	2.066±0.002	2.538±0.002	2.941±0.002
35% ES	1.190±0.001	1.747±0.001	2.165±0.002	2.358±0.002
45% ES	0.813±0.001	1.106±0.001	1.488±0.001	1.695±0.003

Table 2: The Values of the Mean Free Path for the Vinyl Ester Polymer and its Composite

	MFP (cm)			
Material	**40 kVp**	**60 kVp**	**80 kVp**	**100 kVp**
Vinyl ester	2.370±0.001	3.425±0.001	4.132±0.001	4.274±0.002
25% ES	1.210±0.002	1.661±0.001	2.016±0.001	2.232±0.001
35% ES	0.995±0.002	1.356±0.001	1.730±0.002	2.016±0.001
45% ES	0.959±0.001	1.359±0.001	1.650±0.001	1.916±0.002

CONCLUSION

Polymer materials of epoxy resin and vinyl ester, with their composites at varied compositions of egg shell were successfully synthesized. The difference in the obtained structural and morphological arrangement of the epoxy resin and vinyl ester polymers when compared with the composites was a result of the strong influence of the egg shell that was used. The major elements like carbon (C), oxygen (O), and Calcium (Ca) identified from the EDS results for the epoxy polymer and the vinyl ester polymer increased as compared to the developed composites, which was due to the presence of calcium carbonate content from the egg shells that were used as the filler. The TGA results at a given temperature of approximately 300 ºC for the vinyl ester polymer and its composites (95% TGA) are better considered for thermal reliability and suitability for practical applications than the epoxy resin and its composites (88% TGA). This is because the level of vinyl ester polymer and its composite's thermal decomposition is lower and will not have much alteration in its result when used at such a level of temperature. The observed drop in radiation exposure dose analyzed for the epoxy resin polymer, vinyl ester polymer, and each of its composites at different exposure energy levels (40, 60, 80, 100 kVp), showed the effectiveness of radiation shielding occurred for all the developed materials. The radiation shielding efficiency employed revealed that the epoxy/egg shell composites are higher than the vinyl/egg shell composites when compared at the same 45% filler composition. The epoxy/45% egg shell composite had a higher linear attenuation value of 0.59 at 100 kVp than the vinyl/45% egg shell composite with a linear attenuation value of 0.52. The low Mean Free Path (MFP) values for the epoxy/45% egg shell composites are better than those for the vinyl/45% egg shell composite at 100 kVp, 80 kVp, 60 kVp, and 40 kVp levels of radiation exposure. The epoxy/egg shell composite had better shielding capability than the vinyl/egg shell composite, but the vinyl/egg shell composite decomposed less from the thermal analysis result, which makes it better suited to be used as a shielding material in areas where thermal and harsh environmental applications are involved than the epoxy/egg shell composite.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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