Development of Lightweight Polymer Laminates for Radiation Shielding and Electronics Applications


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The present study portrays the development of lightweight epoxy laminates filled with boron carbide (B₄C) and lead (Pb) particles through a novel layered molding and curing route. Six different laminates of single and tri-layers were prepared with varying compositions and were subjected to thermal, radiation shielding, and dielectric studies. Radiation shielding test were done using a narrow beam setup with six different sources such as Cobalt-57 (Co⁵⁷-122 keV), Barium-133 (Ba¹³³-356 keV), Sodium-22 (Na²²-511 and 1275 keV), Cesium-137 (Cs¹³⁷-662 keV), Manganese-54 (Mn⁵⁴-840 keV), and Cobalt-60 (Co⁶⁰-1170 and 1330 keV). The dielectric studies were done to understand the dielectric constant, dielectric loss factor, and AC conductivity at different temperature and frequency ranges. From the characterizations, it was found that the thermal stability of the single-layered sample increased with respect to the addition of B₄C and Pb particles, which may be due to the thermally stable nature of the particles. The radiation shielding study of the samples witnessed the superior characteristics and radiation shielding ability of sample D (40% Pb) and sample E with Pb cladding at incident gamma radiation energy of 662 keV. The dielectric constant of the samples increased significantly at higher temperatures and the dielectric loss factor increased with an increase in temperature and decreased with an increase in frequency. The AC conductivity of the samples increased with respect to an increase in temperature and frequency.

1. Introduction

The ionizing radiation finds a great place in various industrial sectors such as medical, spacecraft, nuclear power sectors, and not limited to these. Exposure to ionizing radiation leads to harmful effects on both biotic and abiotic species around the globe. It is obvious that these mentioned sectors have to find a precautionary measure to shield these harmful radiations as well. Lead (Pb), a traditionally used shielding material, suits the purpose of shielding. However, due to its toxic nature, high density, and poor mechanical strength, there is a huge demand for alternative materials [1, 2]. Polymer composites have nowadays become a potential alternative for lead-based radiation shielding materials. Several researchers have focused on the development of particle-filled shielding materials based on rubber, epoxy, polyethylene glycol, and unsaturated polyester resins and reported their suitability for the radiation attenuation applications [3, 4]. Similarly, in microelectronics, the replacement of passive electronic components with passive embedded components attracts researchers due to the minimal utilization of size, reduction in cost, and flexibility in the circuit design. Particularly, in conductive polymer electronics, the need for a thin layer of dielectrics with good dielectric constant, loss factor, and conductivity makes researchers think toward a positive alternative [5].

Epoxy, a capable hinderer of radiation, is studied extensively by researchers due to its good characteristics such as...
density, mechanical property, and stability. Moreover, it could be manufactured easily when compared with metal matrix composites. Also, epoxy possesses good dimensional stability, good adhesion properties, high resistance to heat, and good chemical stability. Additionally, the presence of an aromatic ring in its chemical composition makes it suitable for gamma and neutron radiation shielding applications [6]. Boron carbide (B\textsubscript{4}C) among ceramic materials is nowadays a promising replacement for Pb owing to its superior hardness, neutron absorption capability, and high melting point [7–10]. Several B\textsubscript{4}C-based radiation-shielding materials were developed recently for neutron radiation-shielding applications [11–14]. However, works are limited to the fabrication of layered composite laminates for radiation shielding. On the other hand, epoxy displays a very low dielectric constant, which is less than 10 and is unfit for practical electronics applications. However, an increase in the dielectric constant can be achieved by adding filler particles to the epoxy matrix. This, in turn, leads to a detrimental effect on the mechanical properties of the material. Hence, proper care must be ensured for enhancing the dielectric constant by precisely altering the filler particle content [15]. Some works support the suitability of Pb and B\textsubscript{4}C filled in the epoxy matrix for X-ray attenuation and found an improvement in shielding efficiency with increased addition of particles [16].

Hence, in this work, efforts are made to manufacture single- and tri-layered epoxy-based laminates dispersed with B\textsubscript{4}C and Pb filler particles via a layered molding and curing route for shielding radioactive rays and to attempt the development of conductive polymeric laminates for electronics applications. The prepared laminates were subjected to gamma radiation, dielectric characterization, and the shielding characteristics, and electrical properties were studied.

2. Materials and Methods

2.1. Materials. Epoxy (Grade LY566) and the corresponding hardener (Grade HY951) used for this work were procured from Herenba Resins Pvt. Ltd., Chennai. Commercially available metallic particles B\textsubscript{4}C (99.9%) with particle size 10 μm were purchased from Neena Metal Mart, New Delhi, and the powdered lead (Pb) particles (99.9%) of particle size 10 μm were purchased from Alpha Chemika, Mumbai. The confirmation of the powdered particles was done by SEM equipped with an electrode dispersive spectrum analyzer using JEOL-JSM-5600LV under 20 kV and exposure time of 50 seconds and is depicted in Figures 1(a) and 1(b).

2.2. Experimental Methods. The composite laminates for radiation shielding were effectively prepared through a layered molding and curing route [17, 18], and are depicted in Figure 1(c). Rectangular molds of dimension 300 mm × 130 mm × 15 mm were used for making the laminates for radiation shielding. Four different samples of various compositions for single-layered studies and two different samples with three layers were made, and the properties of the prepared laminates were tabulated in Table 1. Initially, the epoxy matrix was taken in the beaker and the B\textsubscript{4}C and Pb filler particles were added. The particles were mixed thoroughly for 30 minutes using mechanical stirring to eliminate the formation of voids and for ensuring proper dispersion of particles. The procedure is followed by the addition of hardener in the epoxy-hardener weight ratio of 2:1, which is then mixed mechanically for 20 minutes. After thorough mixing, the solution was poured into the glass mold and was allowed to cure for 24 hours. Similarly, layered samples were made at a definite interval of 45 minutes after the pouring of the first and the subsequent layers. The same procedure was followed for the preparation of all the layered samples. The samples were allowed to cure for 24 hours before removing from the mold. Proper care and safety measures were ensured during the handling and preparation of lead samples. The samples prepared were as shown in Figure 1(d). The samples were powdered for studying the thermal degradation and the samples with dimensions 15 mm × 15 mm × 9 mm were made for studying the radiation-shielding properties. The samples were cut with dimensions 10 mm × 10 mm × 3 mm for performing the dielectric studies. The thermographs of the samples were recorded using a Thermogravimetric Analyzer (TGA-Q500TA Instruments, USA) with a range of 30–800°C in Nitrogen atmosphere at a heating rate of 20°C/min. Furthermore, the samples were subjected to density measurements through the Archimedes method utilized with calibrated single pan electrical balance and ethanol solution. The experimental apparent density is measured using the following equation for 3 samples for each composition:

\[ \rho_s = \frac{m_1}{m_2 - m_3} \rho_e, \]  

where \( \rho_s \) and \( \rho_e \) are the density of the sample and ethanol, respectively, \( m_1 \) and \( m_2 \) and \( m_3 \) are the mass of the sample weighed in the balance, mass of the sample hanging on the arm of the balance in the air, and mass of the sample hanging on the arm of the balance immersed in an ethanol solution, respectively.

2.3. Shielding Parameters. Mass attenuation coefficient (\( \mu_m \)) is the predominant parameter, which witnesses the shielding capacity of the material, explained as the ratio of linear attenuation coefficient and the density of the sample. It is measured through the narrow beam good setup. Furthermore, various parameters such as linear attenuation coefficient (\( \mu \)), half value layer (HVL), tenth value layer (TVL), and mean free path (MFP) were calculated using the basic relations as shown in the equations.

\[ \mu = \mu_m \rho, \]  

\[ \text{HVL} = \frac{\ln 2}{\mu}, \]  

\[ \text{TVL} = \frac{\ln 10}{\mu}. \]
Figure 1: Continued.
Table 1: Composition of the samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition of single-layered composites (wt%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_4C$</td>
<td>$Pb$</td>
</tr>
<tr>
<td>A</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

Composition of tri-layered samples (wt%)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>$Pb$-20</td>
<td>$B_4C$-20</td>
<td>$Pb$-20</td>
<td>2.099</td>
<td>1.998 ± 0.003</td>
</tr>
<tr>
<td>F</td>
<td>$B_4C$-20</td>
<td>$Pb$-20</td>
<td>$B_4C$-20</td>
<td>1.858</td>
<td>1.802 ± 0.010</td>
</tr>
</tbody>
</table>

Figure 1: (a) SEM-EDS confirmation of $B_4C$ particles; (b) SEM-EDS confirmation of $Pb$ particles; (c) manufacturing route-layered molding and curing, and (d) as-prepared samples for mechanical and radiation shielding studies.
The HVL and TVL are defined as the average distance required for attenuating the incident gamma radiation flux by a half and a tenth of its value, respectively. MFP could be understood as the average distance traversed by a gamma ray of given energy in a medium until it interacts with the same medium [19].

2.4. Radiation-shielding Studies. The prepared single- and tri-layered composite laminates were subjected to

\[ \text{MFP} = \frac{1}{\mu} \]  \hspace{1cm} (5)

Figure 2: Narrow beam setup for radiation studies.

Figure 3: (a) Primary thermograms of samples and (b) derivative thermograms of samples.

Table 2: Degradation temperature of the samples.

<table>
<thead>
<tr>
<th>Sample nomenclature</th>
<th>Degradation temperature (°C)</th>
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<tbody>
<tr>
<td></td>
<td>Onset</td>
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<tr>
<td>A</td>
<td>341</td>
</tr>
<tr>
<td>B</td>
<td>338</td>
</tr>
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<td>E</td>
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<tr>
<td>F</td>
<td>342</td>
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</tbody>
</table>
Figure 4: Continued.
radiation-shielding studies through the narrow beam good geometry setup as depicted in Figure 2. Co$^{57}$ (122 keV), Ba$^{133}$ (356 keV), Na$^{22}$ (511 and 1275 keV), Cs$^{137}$ (662 keV), Mn$^{54}$ (840 keV), and Co$^{60}$ (1170 and 1330 keV) are the six different sources of radioactive radiation. The NaI (Tl) scintillation detector was used to detect the gamma radiations. The signals from the detector (8.2% energy resolution at 662 keV) were recorded in an EG & GORTEC-13 bit plug-in card coupled with a PC/AT. The setup was checked for its stability and reproducibility prior to and after every set of runs.

2.5. Electrical Characterization. The samples prepared were subjected to electrical characterization to understand the various dielectric behaviors such as the capacitance $C_p$ and dielectric loss factor tan$\delta$. The studies were conducted at various temperatures ranging from 40$^\circ$C to 150$^\circ$C and also with a range of frequencies from 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz. LCR Meter Aglient 4284A through the parallel plate capacitor method was used for the study. The samples were subjected to annealing in the sample holder at 160$^\circ$C prior to observations. The temperature was in a controlled environment with an accuracy of $\pm 0.5^\circ$C and the readings were taken during the cooling process of the sample. The air capacitance $C_a$ was measured and the dielectric constant of the samples was calculated using the formula $\varepsilon_r = C_p/C_a$. It should be also noted that the AC conductivity of the prepared samples was determined by the following relation:

$$\sigma_{AC} = \varepsilon_0 \varepsilon_r \omega \tan \delta,$$

(6)

where $\varepsilon_0$ is the permittivity of free space and $\omega$ is the angular frequency and is given by $\omega = 2\pi f$, and $f$ is the applied frequency.

3. Results and Discussion

3.1. Thermal Studies. Figures 3(a) and 3(b) depicted above clearly elucidates the thermal stability of the as-prepared samples through primary and derivative thermograms. It is evident from Figure 3(a) that single-step degradation is observed in all the samples in a Nitrogen environment. The degradation temperatures (onset, inflection, and end-set) of the samples are tabulated in Table 2. The initial degradation temperature (onset) was determined at 5% weight loss of the samples. The inflection temperature and the end-set temperature were determined at the moment of sudden steep in weight loss and at the end of attaining constant degradation of the sample, respectively. It could be understood from Figure 3(a) that the onset temperatures of all the samples are between 330$^\circ$C and 360$^\circ$C. The rise in inflection temperature is attributed to the addition of thermally stable metallic particles such as B$_4$C and Pb. The derivative thermogram depicted in Figure 3(b) illustrates the shift in the plateau corresponding to sample D to the right side, which could be obviously due to the better thermal stability of the sample. On the other hand, the tri-layered sample with B$_4$C cladding has shown improved thermal stability when compared to
Figure 5: Dielectric constant as a function of temperature and frequency for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E and (f) sample F.
Figure 6: Dielectric loss factor as a function of temperature and frequency for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, and (f) sample F.
Figure 7: AC conductivity as a function of temperature and frequency for (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F.
that of the Pb cladding. The resulting thermal stability throughout the as-prepared samples could be resulted owing to the hindering effect of B\textsubscript{4}C and Pb on the mobility of polymer chain due to the inert characteristics of B\textsubscript{4}C and Pb [20].

3.2. Radiation-shielding Studies. Figure 4(a) shows the mass attenuation coefficient ($\mu_m$) of the samples with respect to the incident radiation energy. It is evident from the graph that $\mu_m$ for all the samples (both single and tri-layered) decreases with an increase in incident gamma energy. However, $\mu_m$ of the tri-layered sample showed exemplary results at low gamma energies. Particularly, the sample with Pb cladding has a very good mass attenuation coefficient (5 cm$^2$/g). On the other hand, the sample with B\textsubscript{4}C cladding showed a mass attenuation value of 2.85 cm$^2$/g, which is nearly half that of the Pb cladding. The reason for the phenomenon is obvious that the thickness of the sample plays a vital role in accessing the radiation-shielding performance [20]. However, the thickness beyond 10 mm reduced the dependency of shielding efficiency on the thickness of the samples [6]. Moreover, the decrease in $\mu_m$ values is attributed to Compton scattering, which is predominant in higher energy ranges [6]. The linear attenuation coefficient calculated by using the formula mentioned in equation (2) is in accordance with the measure of $\mu_m$ and the density of the samples and is depicted in Figure 4(b). It should be noted that HVL, TVL, and MFP are the other predominant parameters, which provide valid information about the penetration of radiation in a material and its shielding capabilities. The above parameters for the as-prepared samples are depicted in Figures 4(c)–4(e) and are obvious that these parameters increase with an increase in incident gamma energy. This could be ascribed due to the notion that an increase in incident energy leads to a decrease in the chance of interactions between the photons in the material [19]. Moreover, it is well known that the sample with lower HVL, TVL, and MFP values results in extraordinary shielding capabilities due to the shorter distance between two interactions of the radiation [19]. From Figures 4(c)–4(e), the performance of tri-layered samples is obvious owing to the above notions. However, among the single-layered samples, the one with 40% Pb (sample D) shows better shielding properties when compared with the other as-prepared samples. This could be attributed by the increased addition of Pb.

Radiation protection efficiency (RPE) is the measure of percentage effectiveness in shielding the incident gamma radiations. The RPE of as-prepared samples is illustrated in Figure 4(f), and it is obvious from the graph that all the samples showcase a similar trend in shielding radiation, that is, efficiency decreases with an increase in incident gamma energy. Among the samples, the tri-layered samples with Pb cladding showcases better shielding efficiency of nearly 50% at 662 keV owing to the increased presence of Pb. Moreover, the presence of Pb-epoxy layer could result in in-elastic and elastic scattering leading to increased radiation shielding. However, the mid layer with B\textsubscript{4}C-epoxy could result in photoelectric absorption and elastic scattering leading to shield low-energy gamma rays emerged from layer 1 [21]. On the other hand, the single-layered sample with 10% Pb displays poorer RPE owing to the reduced addition of Pb.

3.3. Dielectric Properties. Figures 5(a)–5(f) depicts the dielectric constant of sample A to sample F with respect to the temperature and frequency. It is obvious from the figure that dielectric constant increases significantly to a considerable extent with respect to temperature. The segmental mobility of polymer chains could be the possible phenomenon behind the increase in dielectric constant with respect to temperature. It is obvious that the enhancement of orientation of dipole due to segmental mobility leads to the increase in dielectric constant [22]. Moreover, at low frequencies, thermal activation predominates the dipole orientation and segmental mobility, resulting in increased dielectric constant. On the other hand, at higher frequencies, the molecular dipoles could not trace the increment in the frequency owing to lower thermal activation resulting in a lower dielectric constant in all the as-prepared samples. Nevertheless, an increase in particle addition (Pb addition up to 30%) led to an increase in the dielectric constant of the samples. This is because of the fact that the incorporation of conducting fillers in the conductor-insulator composites results in the formation of electrically heterogeneous material. Similarly, the sample with Pb core has showcased significant improvement in dielectric constant when compared to that of the B\textsubscript{4}C core. Furthermore, the improvement in dielectric constant due to particle addition could be attributed due to the increase in interfacial polarization [23, 24]. The samples invariably displayed a similar trend in the case of the dielectric loss factor (tan$\delta$) which is much obvious from Figures 6(a)–6(f). The dielectric loss factor found to increase with an increase in temperature and decrease with an increase in frequency and is owing to the thermal independence at higher frequencies. This is due to the inability of the molecular dipoles to follow the high frequency [25]. Figures 7(a)–7(f) illustrates the AC conductivity of the samples with respect to temperature and frequency. It is clear from Figures 7(a)–7(f) that the AC conductivity of the samples increases with respect to the increase in temperature and frequency. Here, both the single- and tri-layered samples exhibit enhanced AC conductivity when the particle composition is increased. The sample with Pb core displayed better AC conductivity than that of the B\textsubscript{4}C core. This could be owing to the fact that in conductor-insulator composites, electron tunneling, a phenomenon in which the electrons will tunnel in between clusters separated by insulated polymeric layers, is the very obvious reason for the enhancement in AC conductivity [25–28].

4. Conclusion

In this work, six different laminates of epoxy matrix dispersed with B\textsubscript{4}C and Pb particles were developed through a layered molding and curing route. The samples were subjected to radiation-shielding, thermal stability, and dielectric studies, and the results are concluded as below.
(i) The thermal stability of the single-layered sample increased with respect to the addition of B$_4$C and Pb particles, which may be due to the thermally stable nature of the particles. Similarly, the tri-layered samples with B$_4$C cladding portrayed better thermal stability compared to that of Pb cladding owing to the inert characteristics of B$_4$C that hinders the mobility of epoxy polymer chain due to the thermal effect.

(ii) The radiation shielding study of the samples witnesses the superior characteristics and radiation-shielding ability of sample D (40% Pb) and sample E with Pb cladding at incident gamma radiation energy of 662 keV.

(iii) At lower energies, all the samples possessed nearly 100% RPE and, at 662 keV, sample E possessed nearly 42% which is much higher than that of all the samples. This results in the usage of the as-prepared sample for radiation-shielding application of low-energy radiation involved in spent fuel casks and containers.

(iv) The dielectric constant of the samples increased significantly at higher temperatures, which could be due to the segmental mobility of polymer chains.

(v) On the other hand, at higher frequencies, the molecular dipoles could not trace the increment in the frequency owing to lower thermal activation resulting in a lower dielectric constant in all the as-prepared samples.

(vi) The dielectric loss factor found to increase with an increase in temperature and decrease with an increase in frequency and is owing to the thermal independence at higher frequencies.

(vii) The AC conductivity of the samples increased with respect to an increase in temperature and frequency, which could be owing to the phenomenon of tunneling of electrons.

Data Availability

None of the data are available elsewhere.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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