



# Volcanic Rock Reinforced Epoxy Composites for Gamma Ray Shielding

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## Abstract

In the present study, gamma ray shielding capability of epoxy resin polymer matrix was tried to enhance with three volcanic rock powders collected from different regions of Van, Turkey. The chemical contents of the volcanic rocks were determined by X-ray Fluorescence spectroscopy. The novel epoxy/volcanic rock composites were prepared with different volcanic rock contents varying from 0 % wt. to 40% wt. The gamma ray shielding performances of the samples were measured experimentally by NaI(Tl) detector for the photons with of 81 keV and 356 keV energies emitted from Ba-133 point radioactive source. The abilities of the samples to shield gamma radiation were evaluated in terms their mass attenuation coefficient, half layer value thickness and mean free path distance. It was determined that the low cost epoxy/volcanic rock composites have a promising potential to be utilized as a radiation shielding medium for the gamma rays. In particular, among all volcanic rock additives the volcanic rock additive having the highest hematite content gained the best gamma ray shielding ability to pure epoxy for both photon energies.

**Keywords:** Epoxy Resin, Volcanic Rock, Composites, Mass attenuation coefficient, HVL.

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## 1. Introduction

The production of non-toxic, low cost and lightweight radiation shielding materials has become an important necessity to protect against the radiation which rapidly enters into our daily lives. As is known, polymers consisting of the elements with low atomic numbers such as carbon, hydrogen, oxygen, and nitrogen provide good shielding for neutrons. Due to neutron shielding property of polymers, instead of toxic and heavyweight lead, polymer composites prepared with inorganic fillers, have been suggested as gamma ray shielding materials in recent years (Nambiar & Yeow, 2012; Thibeault et al., 2015). In polymer composites, micro- or nano-fillers have been dispersed in a polymer matrix to produce a material having good radiation shielding property. In designing the radiation shielding materials, deciding the polymer matrix and inorganic filler depend on the radiation type and its energy. For example, Abdel-Aziz et al. achieved to produce a good neutron shielding material by preparing the ethylene-propylenediene rubber/low density polyethylene/ boron carbide composite structure which contains 54% boron carbide (Abdel-Aziz, Gwaily, Makarious, & Abdo, 1995). Among various polymers, epoxy resins have a crucial place in radiation shielding technology due to their good mechanical properties, high resistance to chemicals, high stability and adhesive strength (P. Chen & Wang, 2011). It was also shown that epoxy resins achieve to decelerate fast and intermediate fast neutrons due their rich contents of hydrogen atoms (Nambiar & Yeow, 2012). Therefore, enhance of the radiation shielding ability of the epoxy resins against different type of radiations such as X-ray, gamma-ray etc. have been investigated by many research groups. Additionally, many efforts have been made for producing new high performance epoxy based radiation shielding materials. The develop the X-ray shielding capability of pure epoxy, the inorganic fillers with high atomic numbers such as tungsten, tungsten oxide, lead, bismuth were tried (N. N. Azman, Siddiqui, Hart, & Low, 2013; N. Z. N. Azman, Siddiqui, & Low, 2013). From this point of view, low cost volcanic rocks (VRs) which have not been chemically treated, were chosen as additives for epoxy polymer in the present study. The main focus of the present study is to determine the radiation shielding parameters of the epoxy/basalt composites for low and medium-high gamma rays emitted from Barium-133 point radioactive source.

## 2. Radiation Shielding Parameters

As is known, when electromagnetic waves interact with a matter, various interactions can happen between the electromagnetic wave and atoms, electrons or nuclei in a material. As a result of these interactions, incident gamma rays can be either absorbed or scattered by the matter.

According to Beer-Lambert law, when gamma ray interact with a matter, a considerable change in the intensity of the incident gamma beam is observed. The change in the intensity is represented by Eq. (1) which is known as Beer-Lambert equation:

$$-\frac{dI}{dx} = \mu I \quad (1)$$

In Eq. (1), while  $x$  is the thickness of the absorber material,  $\mu$  represents the total linear attenuation coefficient of the material. The total linear attenuation coefficient is independent of the phase of the absorbing medium.  $\mu$  also defines the probability of interaction with gamma ray per unit length in the absorbing medium and has the unit of  $\text{cm}^{-1}$ .

Under the assumptions that all incident gamma rays are mono energetic and the photons are reduced under ideal geometric conditions, the intensity of the photons passing through an absorber of  $x$  thickness,  $I(x)$  is defined by Eq. (2):

$$I(x) = I_0 e^{-\mu x} \quad (2)$$

In Eq. (2)  $I_0$  is the intensity of the incident beam, and  $I(x)$  is the intensity of the transmitted gamma ray.

Instead of dealing with linear mass attenuation coefficient, mass attenuation coefficient  $\mu/\rho$ , which is known as the normalization of the linear attenuation coefficient per unit density of a material, is mostly preferred in determining gamma ray shielding ability of an absorber material. Mass attenuation coefficient is also a measure of the probability of interactions of gamma ray with matter and has the unit of  $\text{cm}^2\text{g}^{-1}$  (Sayed, 2016a). The mass attenuation coefficient is derived from Eq. (2):

$$\frac{\mu}{\rho} = -\frac{1}{\rho x} \ln\left(\frac{I}{I_0}\right) \quad (3)$$

Mass attenuation coefficient of a chemical compound or a mixture of elements is also defined by Eq. (4):

$$\mu/\rho = \sum_i w_i (\mu/\rho)_i \quad (4)$$

where  $w_i$  is the fractional weight of the  $i$  th constituent in the mixture (Sayed, 2016b).

As well as mass attenuation coefficient, half layer value (HLV) and mean free path,  $\lambda$  are also other important parameters in determining the gamma ray shielding performance of a material. While HVL is defined as the width of a material required to reduce the air kerma of an gamma ray to half its original value,  $\lambda$  represents the average distance at which a gamma ray travels in the absorber without any interaction (K. Singh et al., 2002; S. Singh, Kumar, Singh, Thind, & Mudahar, 2008). The definitions of HVL and  $\lambda$  are given in Eqs. (5) and (6), respectively (N. Singh, Singh, Singh, & Singh, 2006).

$$HVL = \frac{\ln 2}{\mu} \quad (5)$$

$$\lambda = \frac{1}{\mu} \quad (6)$$

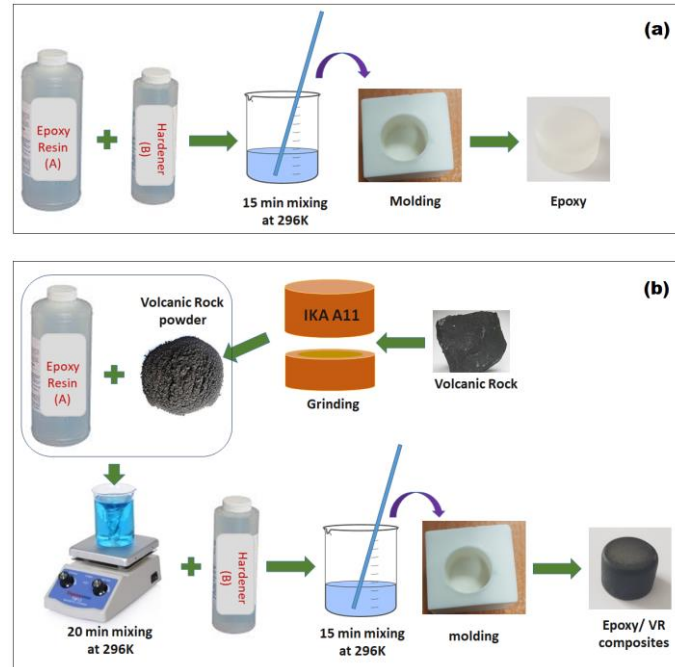
### 3. Experimental

#### 3.1 Materials

Liquid, unmodified bisphenol A-epichlorohydrin epoxide resin with the product code of AC510 UV (Taiwan) was purchased from Armor Chemical. Isophorone diamine with the product code of AC510 UV (Germany) was used as a hardener and it was supplied from Armor Chemical. Three different volcanic rocks coded as VR-1, VR-3 and VR-3 were collected from Van, Turkey.

#### 3.2 Preparation of the Composites

The preparation process of the Epoxy/VR composites were shown in Figure 1 (a) and (b).. 2-4 g liquid, unmodified bisphenol A-epichlorohydrin epoxide resin (Part A) was used for preparing pure epoxy polymer matrix. 1-2 g isophorone diamine hardener (Part B) was added to the liquid epoxy and then the mixture were mixed mechanically to obtain homogenous mixture for 15 min (Mixing ratio: 2 (Part A) +1 (Part B) by weight). Then the solution was molded into a circular shaped teflon mold. Following this step, the sample was kept at room temperature in the mold for drying 24 h (Figure 1(a)). The Epoxy/VR composites were also prepared in similar way. Before preparing the composites, the VRs were grinded with IKA A11 basic analytical mill with the rotational speed of 10000 rpm. The mixing time per VR was 15 min. After obtaining fine VR powders, the 2-4 g liquid unmodified bisphenol A-epichlorohydrin epoxide resin was mixed with each VR with the appropriate masses to obtain the epoxy composites containing 10 wt. %, 20 wt. % and 40 wt. % VRs. Then, the epoxy and VR mixtures were stirred in magnetic stirrer for 20 min. and as a second step the hardener was added to the resultant mixture with an appropriate masses. After this stage, the mixtures were mixed mechanically for 15 min to obtain homogenous VR distribution in the epoxy and finally the solutions were poured into the mold and kept at room temperature in the mold for 24 hours. After the drying process for 24 hours, the samples were removed from the molds (Figure 1(b)). Each sample was produced for two different thicknesses. Thus, gamma radiation shielding measurements were carried out with two different thicknesses of the same sample. While the radius of the samples was 1.15 cm; their thickness were varying between 0.6 cm and 1.4 cm.



**Figure 1.** Schematic diagram of the preparation process of the (a) pure Epoxy (b) Epoxy/VR composites.

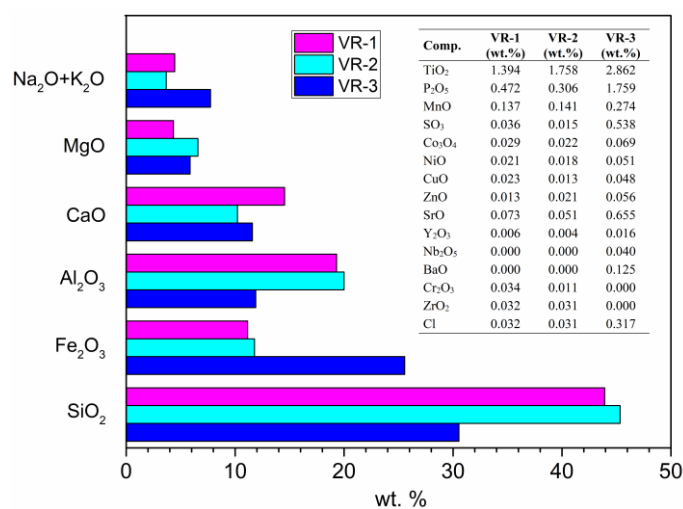
The mass density of each sample was determined by Archimedes' principle and listed in Table 1. The mass amounts in gram units of epoxy and VRs in the samples were also given in Table 1.

**Table 1.** The weight percentages of epoxy, hardener, and VRs in in the samples along with the mass density of the samples.

Sample	Resin (wt.%)	Hardener (wt.%)	VR (wt.%)	Mass density (g/cm <sup>3</sup> )
Epoxy	65	35	0	1.301±0.072
Epoxy/ 10% VR-1	60	30	10	1.365 ±0.019
Epoxy/ 20% VR-1	53.5	26.5	20	1.502 ±0.027
Epoxy/ 40% VR-1	40	20	40	1.694 ±0.012
Epoxy/ 10% VR-2	60	30	10	1.371 ±0.035
Epoxy/ 20% VR-2	53.5	26.5	20	1.465 ±0.051
Epoxy/ 40% VR-2	40	20	40	1.697 ±0.033
Epoxy/ 10% VR-3	60	30	10	1.362 ±0.021
Epoxy/ 20% VR-3	53.5	26.5	20	1.515 ±0.094
Epoxy/ 40% VR-3	40	20	40	1.668±0.010

### 3.3 X-Ray Fluorescence Spectroscopy Analyses of the Volcanic Rocks

The chemical analyze of VRs was determined by X-Ray fluorescence (XRF) measurements performed with the equipment model no PANalytical B.V.–Axios Advanced The chemical contents of the VRs collected from different regions of Van, Turkey were given in Figure 2.

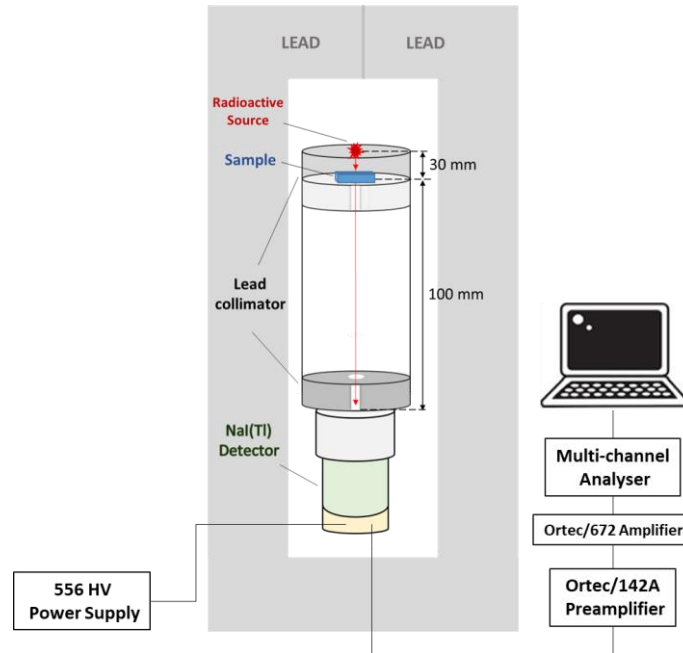


**Figure 2.** The chemical content of the VRs.

Total Alkali Silica (TAS) classification (Le Bas, Le Maitre, & Woolley, 1992) was used to classify the VRs. According to TAS classification, depending on the SiO<sub>2</sub> and (Na<sub>2</sub>O+K<sub>2</sub>O) percentages of the rock, it can be classified as foidite, basalt, tephrite-basanite, picro-basalt or basaltic andesite and etc. As illustrated in Figure 2, the VR-1, VR-2 and VR-3 powders contain 43.93%, 45.34% and, 30.54% SiO<sub>2</sub> and 4.45%, 3.67%, and 6.51% (Na<sub>2</sub>O+K<sub>2</sub>O). From this point of view, VR-1, VR-2 and VR-3 additives were classified as “tephrite basanite”, “basalt”, and “foidite”, respectively.

### 3.4 Experimental Setup for the Gamma Ray Shielding Performance of the Samples

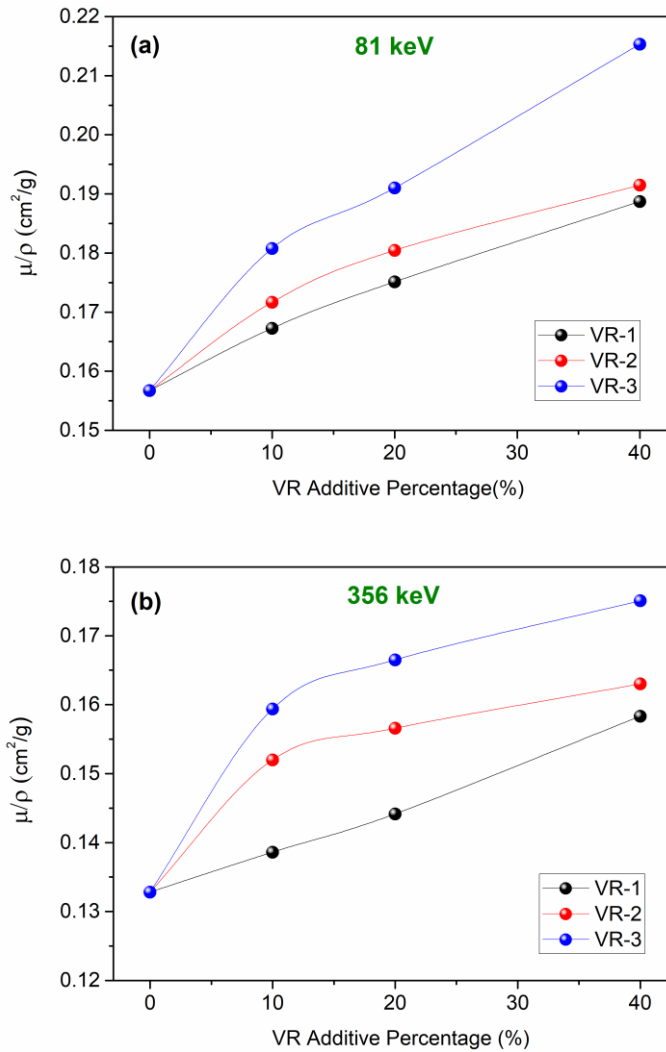
The mass attenuation coefficient of the samples were calculated by measuring an attenuated and un-attenuated intensities ( $I$  and  $I_0$ ) from the Ba-133 radioactive source with NaI(Tl) detector with dimension of  $7.62 \text{ cm} \times 7.62 \text{ cm}$ . The gamma rays emitted from the Ba-133 point radioactive source were 81 keV and 356 keV. The model of the with NaI(Tl) detector was 905-4 Ortec-Amtek. The photomultiplier tube (PMT) base, digiBASE (Ortec) had also 6.3 cm diameter and 8.0 cm length. The FWHM was equal to 46 keV at 662 keV and 65 keV at 1330 keV. NaI crystal was separated from the PMT by a glass window with the thickness of 5 mm. The experimental data were analyzed by the Maestro software. Additionally, it was collected into 2048 channels of the MCA. Total count of the photon peak was received after subtracting of the background counts and fitted by Gaussian function. Counting time was set fifteen minutes such that total counts were recorded under each photon peak and the counting was conducted for three times to ensure that error of the photon count was under 1%. The schematic representation of the experimental setup was also shown in Figure 3.



**Figure 3.** The experimental setup for the measurements of an attenuated and un-attenuated intensities from the Ba-133 radioactive source.

## 4. Results and Discussions

The mass attenuation coefficients of the samples were calculated by using the attenuated and un-attenuated intensities ( $I$  and  $I_0$ ) measured by the NaI(Tl) detector. By using  $I$  and  $I_0$  values, mass attenuation coefficients were calculated by Eq. (3) for the gamma photons with the energies of 81 keV and 356 keV. The variations of the mass attenuation coefficient of pure epoxy with both the type of VR additive and the additive percentage were shown in Figure 4(a) and (b) for the 81 keV and 356 keV, respectively.

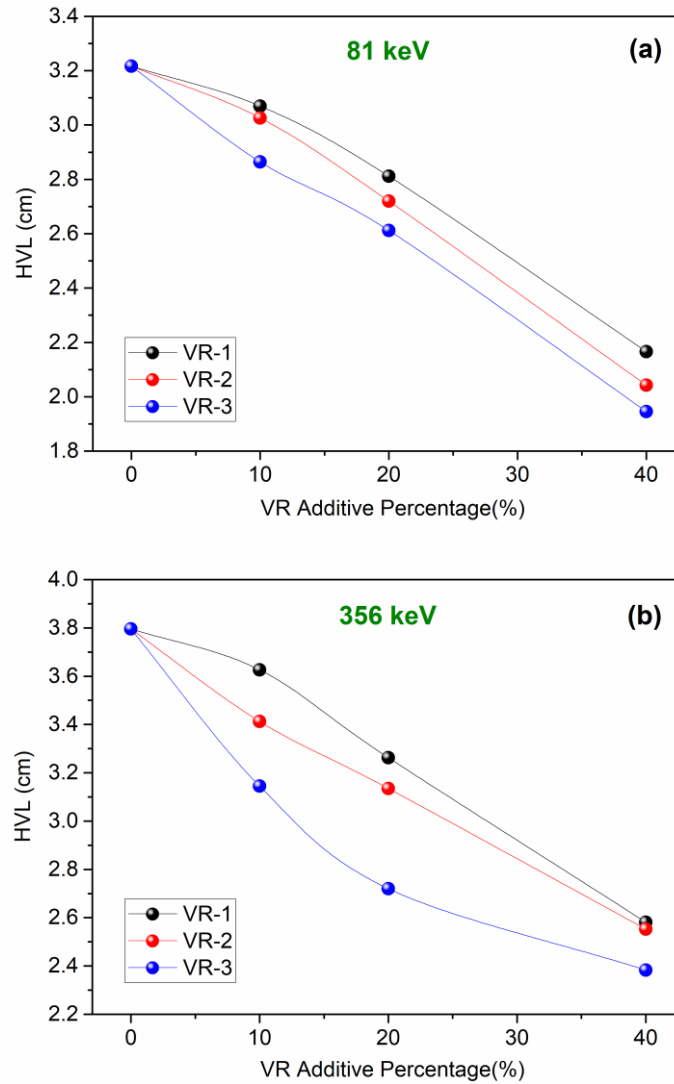


**Figure 4.** The mass attenuation coefficient of the epoxy based volcanic rock composites along with the pure epoxy polymer at (a) 81 keV and (b) 356 keV photon energies.

As shown in Figure 4, the pure epoxy has the lowest mass attenuation coefficients for 81 keV and 356 keV due to its element content having low atomic numbers such as hydrogen, carbon, oxygen and nitrogen (Li, Gu, Zhang, et al., 2017). On the other hand, as is observed in Figure 4(a), the mass attenuation coefficient of pure epoxy is increased with all VR additives with different ratios at 81 keV. Additionally, a gradual increase in the  $\mu/\rho$  with increasing VR additive was observed for the three different types of additives. This is mainly due to the fact the possibility of the observation of photon absorption via photoelectric effect is high at the lower photon energies such as 81 keV. The probability of observation of photoelectric effect is also linearly proportional to the third power of ratio of  $(Z/E)$ , where  $Z$  is the atomic number of absorbing element and  $E$  is photon energy (N. N. Azman et al., 2013). In this respect, addition of VRs that contain the elements with high atomic numbers such as Ti, Mn, Fe and Ba results in much stronger photon absorption performance relative to pure epoxy. The highest increase in  $\mu/\rho$  value of pure epoxy due to VR additive was also recorded for the VR-3 additive with the increment of 36% at 81keV. When the photon energy is increased to 356 keV, increased VR contribution to epoxy resin leads to the higher mass attenuation coefficients at 356 keV. Furthermore, as in the case of 81 keV, the highest increase in  $\mu/\rho$  value of pure epoxy was determined for the 40 % VR-3 additive with the increment of 31 % (See Figure 4(b)). Since mass attenuation coefficient indicates the possibility of the interaction of the gamma ray with the material, such as in increase in  $\mu/\rho$  for both energies shows that the gamma ray interacts more with the epoxy composites containing the VRs than pure epoxy. From this point of view, it was deduced that the epoxy composite containing the highest percentage of VR-3 exhibited the best gamma ray absorption for the photon energies of 81 keV and 356 keV. On the other hand, the lowest increase in the mass attenuation coefficient of pure epoxy was determined for VR-1 for both photon energies. When the VRs used in the composites are compared in terms of their gamma radiation absorption performances, VR-3 was found to be the most effective additive that enhances the ability of absorption of gamma radiation of pure epoxy. In this respect, it can be thought that the differences in the chemical content of the VRs causes this result. When the chemical contents of all VR additives are investigated, it was determined that among all additives, VR-3 has the lowest silicon dioxide ( $\text{SiO}_2$ ) and the highest hematite ( $\text{Fe}_2\text{O}_3$ ) contents. The best gamma ray absorption performance of the VR-3 additive for epoxy can be explained by its high hematite content, since hematite is commonly used additive for producing high density concrete for X-ray and gamma-ray shielding (Oto, Yıldız, Akdemir, & Kavaz, 2015).

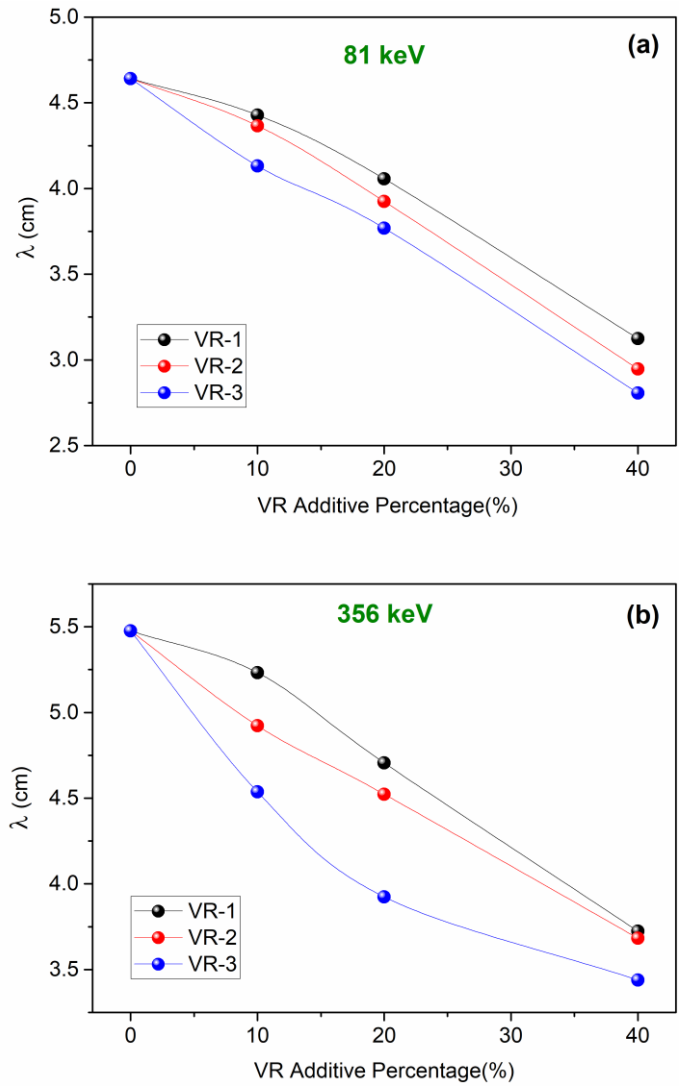
On the other hand, it was observed that the mass attenuation coefficients at 356 keV for each sample are lower than that of 81 keV. Such a decrease in  $\mu/\rho$  value for the higher energetic photons can be associated with the fact that the dominant interaction between gamma-ray and material alters from photoelectric effect to Compton scattering as the photon energies changes from 81 keV to 356 keV (Limkitjaroenporn, Chewpraditkul, Kaewkhao, & Tuscharoen, 2011). When the photon energy reaches to 356 keV, the Compton scattering becomes dominant relative photoelectric effect (S. Chen, Bourham, & Rabiei, 2015). Such high energy photons are generally attenuated by materials via Compton scattering and then the scattered photons with lower energies are absorbed by photoelectric effect. Due to this reason, mass attenuation coefficients decrease significantly at 356keV (Li, Gu, Wang, et al., 2017).

The variations of the radiation shielding parameters of HVL and  $\lambda$  of pure epoxy with both the type of VR additive and the additive percentage at 81 keV and 356 keV photon energies were given in Figure 5 and 6, respectively.



**Figure 5.** The half layer value of the epoxy based volcanic rock composites along with the pure epoxy polymer at (a) 81 keV and (b) 356 keV photon energies.

As is illustrated in Figure 5 and 6, HVL and  $\lambda$  parameters decrease considerably with all VR additive types for both photon energies. Since HVL is defined as the attenuating material thickness required reducing the intensity as one half of its original intensity, the decrease in the HVL parameter with VR additives also showed the increased gamma ray shielding capability of epoxy.



**Figure 6.** The mean free path of the epoxy based volcanic rock composites along with the pure epoxy polymer at (a) 81 keV and (b) 356 keV photon energies.

Similar to HVL, mean free path of the epoxy also reduces significantly with volcanic rock additives. From this point of view, it was concluded that by referring the highest increase in the  $\gamma$ -ray ( $\mu/\rho$ ) coefficient and the maximum decrease in the HVL and  $\lambda$  parameters for the pure epoxy, the VR-3 additive can be suggested as the best natural doping material among three additive for pure epoxy.

## 5. Conclusions

This work is devoted to increase the gamma ray shielding performance of epoxy resin by incorporating three VRs collected from Van, Turkey. The novel Epoxy/VR composites having 0 %, 10%, 20%, and 40% wt. volcanic rocks were prepared in the present study. The chemical content analyses of the VRs revealed that they can be classified as tephrite basanite”, “basalt”, and “foidite. The gamma ray shielding parameters such as  $\mu/\rho$ , HVL, and  $\lambda$  were determined experimentally by NaI(Tl) detector for the two photon energies (81 keV and 356 keV) emitted from Ba-133 source. It was pointed out that while the mass attenuation coefficient increases gradually with all VR additives as the additive percentage increases in the composite, the HVL and  $\lambda$  also decrease considerably. Especially, it was revealed that the VR additive having the highest  $Fe_2O_3$  content exhibits the best gamma radiation shielding performance for epoxy resin relative to the other VR additives used in the present study. In the light of this comparative study of VRs’ gamma ray shielding capability, VRs having high hematite content collected from different volcanic regions of the earth can be suggested as a good candidate in producing gamma ray shielding materials based on epoxy.



## References

- Abdel-Aziz, M., Gwaily, S., Makarious, A., & Abdo, A. E.-S. (1995). Ethylene-propylene diene rubber/low density polyethylene/boron carbide composites as neutron shields. *Polymer degradation and stability*, 50(2), 235-240.
- Azman, N. N., Siddiqui, S., Hart, R., & Low, I.-M. (2013). Effect of particle size, filler loadings and x-ray tube voltage on the transmitted x-ray transmission in tungsten oxide—epoxy composites. *Applied Radiation and Isotopes*, 71(1), 62-67.
- Azman, N. Z. N., Siddiqui, S. A., & Low, I. M. (2013). Synthesis and characterization of epoxy composites filled with Pb, Bi or W compound for shielding of diagnostic x-rays. *Applied Physics A*, 110(1), 137-144.
- Chen, P., & Wang, D. (2011). Epoxy resin and its application. *Chemical Industry Press, Beijing*, 78.
- Chen, S., Bourham, M., & Rabiei, A. (2015). Attenuation efficiency of X-ray and comparison to gamma ray and neutrons in composite metal foams. *Radiation Physics and Chemistry*, 117, 12-22.
- Le Bas, M., Le Maitre, R., & Woolley, A. (1992). The construction of the total alkali-silica chemical classification of volcanic rocks. *Mineralogy and Petrology*, 46(1), 1-22.
- Li, R., Gu, Y., Wang, Y., Yang, Z., Li, M., & Zhang, Z. (2017). Effect of particle size on gamma radiation shielding property of gadolinium oxide dispersed epoxy resin matrix composite. *Materials Research Express*, 4(3), 035035.
- Li, R., Gu, Y., Zhang, G., Yang, Z., Li, M., & Zhang, Z. (2017). Radiation shielding property of structural polymer composite: continuous basalt fiber reinforced epoxy matrix composite containing erbium oxide. *Composites Science and Technology*, 143, 67-74.
- Limkitjaroenporn, P., Chewpraditkul, W., Kaewkhao, J., & Tuscharoen, S. (2011). Effective atomic number of lead sodium borate glass systems at 662 keV. *Energy Res. J*, 2(1), 29-33.
- Nambiar, S., & Yeow, J. T. (2012). Polymer-composite materials for radiation protection. *ACS applied materials & interfaces*, 4(11), 5717-5726.
- Oto, B., Yıldız, N., Akdemir, F., & Kavaz, E. (2015). Investigation of gamma radiation shielding properties of various ores. *Progress in Nuclear Energy*, 85, 391-403.
- Sayyed, M. (2016a). Bismuth modified shielding properties of zinc boro-tellurite glasses. *Journal of Alloys and Compounds*, 688, 111-117.
- Sayyed, M. (2016b). Investigation of shielding parameters for smart polymers. *Chinese journal of physics*, 54(3), 408-415.
- Singh, K., Singh, H., Sharma, V., Nathuram, R., Khanna, A., Kumar, R., . . . Sahota, H. S. (2002). Gamma-ray attenuation coefficients in bismuth borate glasses. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 194(1), 1-6.
- Singh, N., Singh, K. J., Singh, K., & Singh, H. (2006). Gamma-ray attenuation studies of PbO–BaO–B<sub>2</sub>O<sub>3</sub> glass system. *Radiation Measurements*, 41(1), 84-88.
- Singh, S., Kumar, A., Singh, D., Thind, K. S., & Mudahar, G. S. (2008). Barium–borate–flyash glasses: as radiation shielding materials. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 266(1), 140-146.
- Thibeault, S. A., Kang, J. H., Sauti, G., Park, C., Fay, C. C., & King, G. C. (2015). Nanomaterials for radiation shielding. *MRS Bulletin*, 40(10), 836-841.