Chapter 4
Synthesis and Characterization of Pb, Bi or W Compound Filled Epoxy Composites for Shielding of Diagnostic X-Rays

Abstract Lead chloride, bismuth oxide and tungsten oxide filled epoxy composites with different weight fractions were fabricated to investigate their X-ray transmission characteristics in the X-ray diagnostic imaging energy range (40–127 kV) by using a conventional laboratory X-ray machine. Characterizations of the microstructure-properties of the synthesized composites were performed using synchrotron radiation diffraction, backscattered electron imaging microscopy, three-point bend test and Rockwell hardness test. As expected, the X-ray transmission was decreased by the increment of the filler loading. Meanwhile, the flexural modulus and hardness of the composites were increased through an increase in filler loading. However, the flexural strength showed a marked decrease with the increment of filler loading ($\geq$30 wt%). Some agglomerations were observed for the composites having $\geq$50 wt% of filler.

4.1 Introduction

X-rays/gamma-rays are the most penetrating of ionizing radiation than is known to be harmful to human health and heredity. Hence there is no doubt that the attenuation of them through composite materials has attracted much attraction amongst the researchers especially for medical studies [1–3]. The most important quantity to characterize the attenuation of photons (X-rays/gamma-rays) within the extended material they pass through is the linear attenuation coefficient (μ) or mass attenuation coefficient (μ/ρ). This quantity is needed in solving various problems such as in radiation dosimetry and radiation shielding application [1, 4, 5].

Lead-glass is one of the materials used for shielding of ionizing radiations, but it is heavy, expensive and very brittle. So, it is not surprising that the application of polymers in X-ray shielding technology is increasing steadily. This is due to several advantages that glass could not meet because of their unique properties, such as low manufacturing cost and rugged shatter-resistant material. In addition, the improved dispersion of fillers within polymer will enable the formation of mechanically stable materials and the possibility to modify both chemical composition and the related physical properties of polymers by easy-to-control fabrication parameters [6–10].

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However, the use of polymers is still limited, because of their inherent softness and low thermal stability [11–13].

Recently, many researchers have tried to synthesize new filler-reinforced polymer composites for radiation shielding and as the replacement for lead glass which is heavy and very fragile [14–17]. The X-ray shielding properties of the filler-reinforced polymer composites generally increase with a good dispersion degree of the filler within the polymer [18]. One modern example of the filler-reinforced polymer used for radiation shielding is lead-acrylic [19, 20]. The lead acrylic of the same size of lead glass with equal lead equivalence, the lead acrylic has nearly twice the weight of lead glass and it is even thicker than lead glass if just looking for the same lead equivalent factor, hence reducing the observation capabilities.

The comprehensive literature survey reveals that the gamma/X-ray shielding characteristics of filler-reinforced epoxy resins have not been attempted. In a recent work on WO_3-filled epoxy composites [21], we investigated only the effect of nano-sized and micro-sized fillers on X-ray attenuation in the energy range of 22–127 kV but the mechanical properties of these composites were not investigated. The results showed that nano sized WO_3 was more effective than micro-sized WO_3 in X-ray attenuation only at the low energy range of 22–35 kV but this size effect was not apparent at the higher energy range of 40–120 kV.

Thus, the aim of this study was to prepare, characterize and compare the physical, mechanical and X-ray transmission properties of epoxy composites filled with Pb, Bi or W compound. The feasibility of these composites for use in X-ray shielding is compared with the commercial lead glass.

4.2 Results and Discussion

4.2.1 Density

From Table 4.1, the apparent density of each sample of the same filler type increased with the increment of filler content, a phenomenon which was also observed by

Table 4.1 Density of filler-epoxy composite samples

% Weight	Density (cm^3/g)					
	$PbCl_2$-epoxy		Bi_2O_3-epoxy		WO_3-epoxy	
	(e)	(t)	(e)	(t)	(e)	(t)
10	1.24 ± 0.02	1.25	1.26 ± 0.01	1.26	1.24 ± 0.03	1.26
30	1.47 ± 0.05	1.52	1.55 ± 0.03	1.56	1.50 ± 0.02	1.54
50	1.85 ± 0.03	1.92	2.00 ± 0.03	2.04	1.87 ± 0.06	1.98
70	2.54 ± 0.06	2.63	2.68 ± 0.07	2.95	2.71 ± 0.03	2.79

(e)—experiment, (t)—theory

Harish et al. [14]. However, the results did not agree very well with the theoretical values, especially when the filler loading was more than 30 wt% due to lack of epoxy to fully cover the surfaces of filler powder, resulting in the concomitant increase in the number of pores and thus reducing the density of the composite. Equation (4.1) was used to compute the relative errors for density measurements relative to the theoretical density values:

$$\delta\rho_s = \left(\frac{\delta m_1}{m_1} + \frac{\delta m_2 + \delta m_3}{m_2 - m_3} + \frac{\delta \rho_e}{\rho_e} \right) \times \rho_s \tag{4.1}$$

where $\delta\rho_s$ is the apparent density uncertainty of the sample, δm_1, δm_2 and δm_3 are the mass uncertainty of the sample weighted in the balance, the sample hanging on the balance arm in the air and the sample hanging on the balance arm immersed in ethanol respectively. $\delta\rho_e$ is the density uncertainty of ethanol calculated from the error of its measured density and its accepted density.

The theoretical density values (ρ_{comp}) were calculated from Eq. (2.2) with an assumption of the samples being void-free.

The computed errors for density values relative to the theoretical density values are in the acceptable limit (i.e. <10.0%).

4.2.2 Effect of Filler Loading on the X-Ray Transmission (I/I_o) by Epoxy-Based Composites

The plots in Fig. 4.1a show that for the same filler type and at the same X-ray tube voltage, X-ray transmission value was decreased by the increment of the filler loading. For example (Fig. 4.1b), at 60 kV X-ray tube voltage, X-ray transmission for the 10 wt% of Bi_2O_3-epoxy composite is about 57 times greater than the X-ray transmission value for the 70 wt% of Bi_2O_3-epoxy composite. This was due to the amplification of elemental composition of the composite with the increment of filler loading in the epoxy base which play an important role in absorbing the X-ray passing through them. A similar result in X-ray transmission as a function of filler loading was obtained for epoxy composites filled with $PbCl_2$ and WO_3.

In order to ascertain the shielding ability of the composites, these results were compared with commercial lead glass (thickness: 10 mm) which contained 56 wt% of Pb (information provided by Gammasonics Institute for Medical Research Pty Ltd.) (see Fig. 4.1a). Bi_2O_3-epoxy composite having 70 wt% of Bi_2O_3 gave nearly the same (I/I_o) value as compared to lead glass and other composite samples even though it is thinner than lead glass. Hence the usage of lead in X-ray shielding can be substituted by Bi_2O_3 whereby Bi is classified as least toxic compared to Pb. In addition, even though the 70 wt% WO_3-epoxy composite with 8 mm thickness shows higher (I/I_o) values when compared to lead glass (Fig. 4.1c), WO_3-epoxy composite also can be a substitute material for Pb in X-ray shielding by increasing its thickness

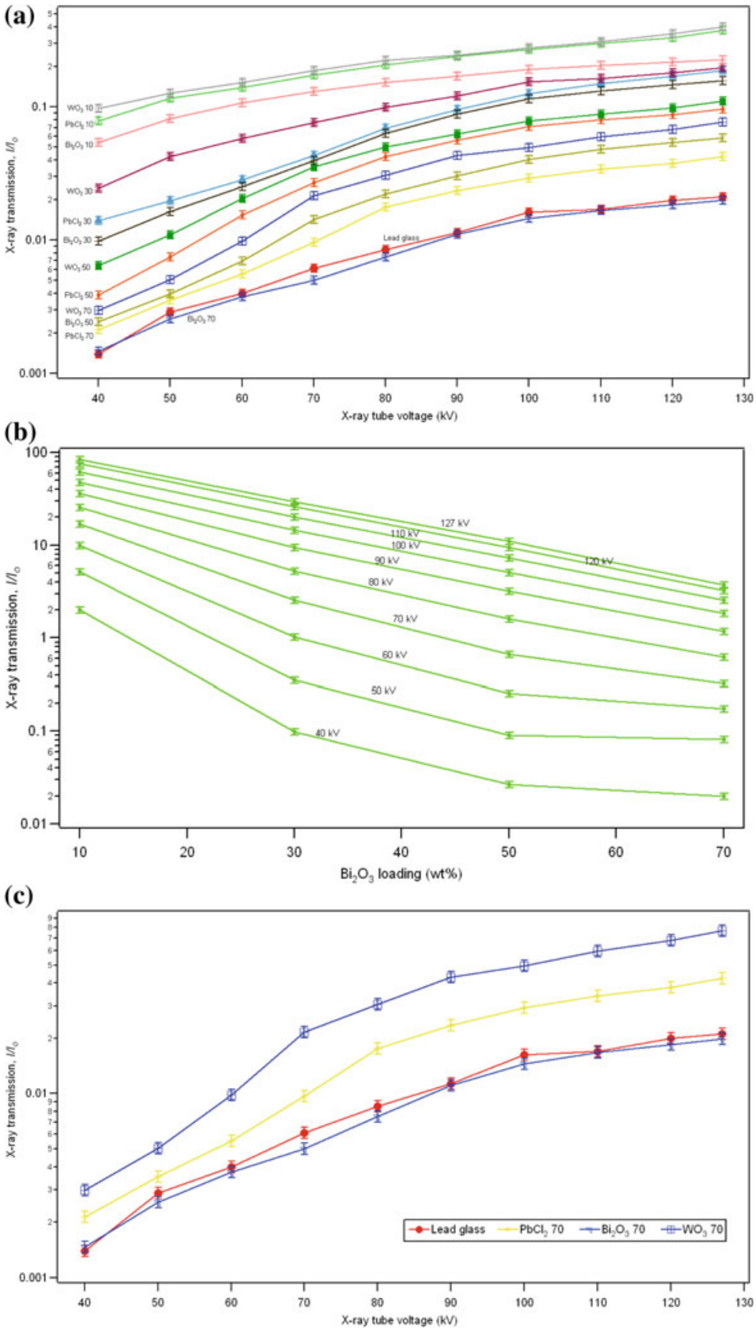

Fig. 4.1 **a** X-ray transmission (I/I_o) as a function of X-ray tube voltage for all composites and commercial lead glass; **b** X-ray transmission (I/I_o) as a function of Bi_2O_3 loading (wt%) showing that (I/I_o) was decreased by the increment of the filler loading; and **c** X-ray transmission (I/I_o) as a function of X-ray tube voltage for epoxy composites filled with 70 wt% of $PbCl_2$, Bi_2O_3 and WO_3 [23]

so that it can provide similar X-ray transmission characteristic as lead glass. The usage of $PbCl_2$-epoxy composite with larger thickness can also be considered as a lighter alternative for lead glass in X-ray shielding.

4.2.3 Phase Compositions

The reference for fitting the peaks was taken from International Centre for Diffraction Data (ICDD) PDF-4 + 2009 database. The wavelength for all of these databases was chosen to be the same as the wavelength of the synchrotron radiation used.

The Powder Diffraction (PD) pattern in Fig. 4.2a shows that all the peaks belong to orthorhombic $PbCl_2$ (PDF files 04-005-4709). For composite filled with Bi_2O_3, all the peaks were identified as monoclinic Bi_2O_3 (PDF file 00-050-1088) as shown in Fig. 4.2b and the diffraction peaks shown in Fig. 4.2c belong to monoclinic WO_3 (PDF file 00-043-1035). These results indicate that $PbCl_2$, Bi_2O_3 and WO_3 were single-phase pure without impurities.

4.2.4 Microstructure Analyses

The surface features of samples in Fig. 4.3, which uses atomic number contrast to differentiate between low and high atomic number elements, show that the fillers appear brighter (higher atomic number) than the surrounding epoxy (low atomic number). The fillers (white patches) are seen to be dispersed uniformly in the epoxy matrix with low filler loading (Fig. 4.3a–c). However, the dispersion of the fillers within the matrix becomes less uniform with the increment of filler loading, resulting in some agglomerations. These filler agglomerations can be seen in composites with $\geq$50 wt% of filler (Fig. 4.3d–g). To minimize the occurence of these agglomerations, higher shear forces through faster stirring are required to achieve a fine dispersion in the polymer matrix. Alternatively, the use of ultrasonication can be used to prevent or minimize filler agglomerations. These methods promote the "peeling off" of individual particles located at the outer part of the particle bundle, or agglomerates, and thus results in the separation of individualized particles from the bundles.

4.2.5 Mechanical Properties

Figure 4.4 shows the effect of filler loading on flexural strength, flexural modulus and Rockwell hardness of epoxy composites. The flexural strength has improved for composite with 10 wt% filler loading. For instance, the flexural strength of epoxy has improved by 48% in the composite with 10 wt% WO_3 loading. However, the addition of more filler ($\geq$30 wt%) caused a marked decrease in flexural strength due

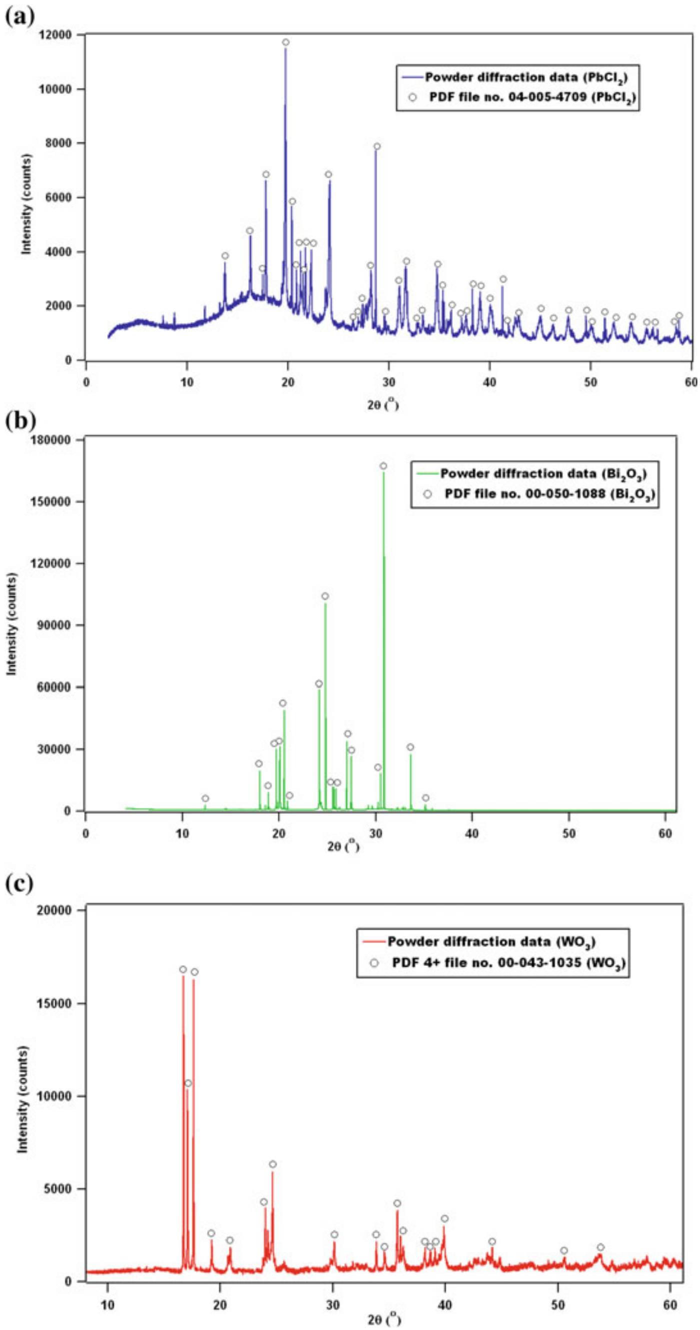

Fig. 4.2 Typical powder diffraction pattern of **a** $PbCl_2$-epoxy composite; **b** Bi_2O_3-epoxy composite and **c** WO_3-epoxy composite [23]

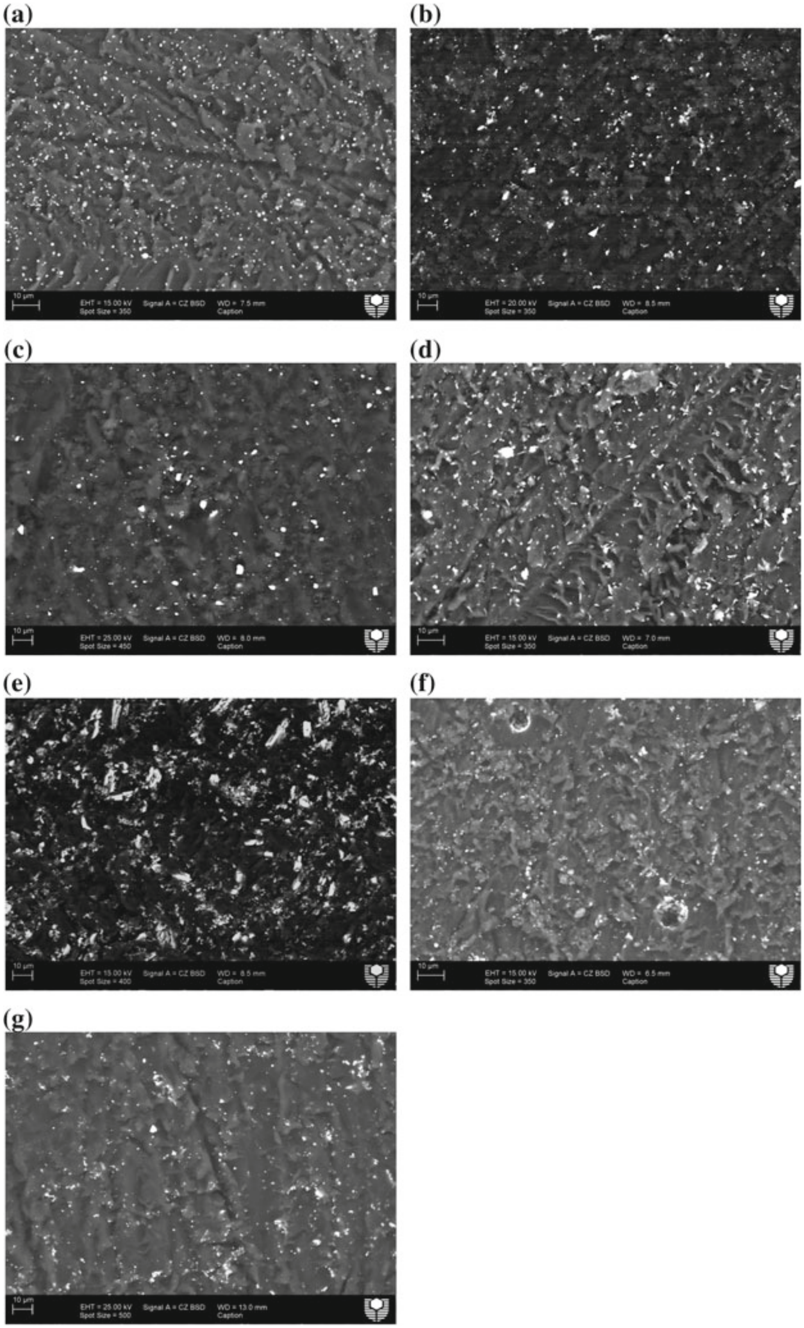

Fig. 4.3 Backscattered electron micrographs showing the dispersion of fillers in epoxy composites containing. **a** 10 wt% $PbCl_2$; **b** 30 wt% Bi_2O_3; **c** 30 wt% WO_3; **d** 50 wt% $PbCl_2$; **e** 50 wt% Bi_2O_3; **f** 70 wt% $PbCl_2$; and **g** 70 wt% WO_3 [23]

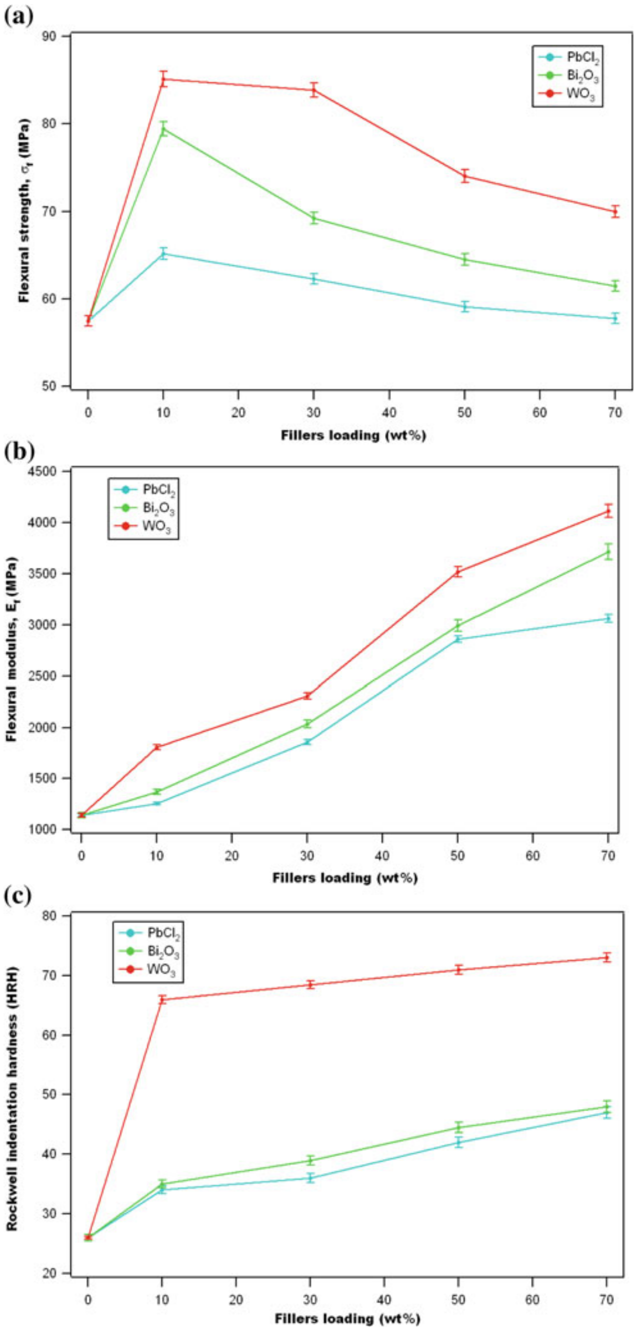

Fig. 4.4 The effect of filler loading on **a** flexural strength; **b** flexural modulus and **c** hardness of epoxy-composites [23]

to the filler not well dispersed within the epoxy matrix. In addition, the porosity for the samples was between 1 and 10% with more pores for filler $\geq$30 wt% because of air-bubbles trapped in the samples which act as stress-concentrators and thus the resultant weakening. On the other hand, the flexural modulus increased with an increase in filler loading which suggests that the stiffness of the composites obey the rule-of-mixtures. In comparison, the flexural strength and flexural modulus of lead glass are ~90 MPa and ~6500 MPa respectively, thus indicating that glass is still superior to epoxy. For the hardness results, they show that an increase in the filler loading resulted in a modest increase in hardness of the composite. In comparison, the Rockwell hardness of lead glass is ~HRC 043 [22].

The mechanical properties obtained in this work are adequate for the optimum sample (i.e. 70 wt% Bi_2O_3-epoxy composite) in X-ray shielding of radiological rooms since it is comparable with lead glass in terms of X-ray transmission although it shows lower flexural properties than lead glass. In particular, the mechanical properties of the composite did not change even after being repeatedly exposed to the X-ray beam of highest X-ray tube voltage. Although these flexural properties are inferior when compared to lead glass, this limitation can be overcome by increasing the thickness of the 70 wt% Bi_2O_3-epoxy composite.

4.3 Conclusions

It may be concluded that:

- $PbCl_2$, Bi_2O_3 or WO_3-epoxy composites have good X-ray shielding ability and hence they can be considered as candidate materials for X-ray shielding of radiological rooms.
- The 8 mm thick Bi_2O_3-epoxy composite with 70 wt% Bi_2O_3 is comparable with a 10 mm thick commercial lead glass which contains 56 wt% Pb.
- The 8 mm thick $PbCl_2$- and WO_3-epoxy composites were not comparable with the 10 mm thick lead glass unless they were prepared with a thickness greater than 10 mm.
- Both flexural modulus and hardness of composites increased with increasing filler loading but the flexural strength decreased markedly when the filler loading was equal or greater than 30 wt%.

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