

# Chapter 2

## Materials and Methodology



**Abstract** Various composite samples were prepared by mixing lead oxide, bismuth oxide or tungsten oxide of either nano-sized or micro-sized with epoxy resin, acrylic, PLA and PVA polymers using three different methods i.e melt-mixing, ion-implantation and electrospinning. Meanwhile, there were various samples characterization tests were done such as X-ray attenuation measurement, density measurement and morphology studies in order to characterize the properties of the prepared samples so that they were applicable and suitable to be the X-ray shielding material candidate.

### 2.1 Lead Oxide–Epoxy Composites

#### 2.1.1 Samples Preparation

Micron-sized of PbO and Pb<sub>3</sub>O<sub>4</sub> powder (Chem Supply, Gillman, South Australia, product number LL021) were used as the filler to prepare lead oxide–epoxy composite samples. Initially, the filler powder was added into the FR251 epoxy resin (Bisphenol-Adiglycidyl ether polymer) before the FR251 hardener (isophoronediamine) was mixed into it. The ratio of epoxy resin to hardener used was 2:1. The mixing of filler powder in epoxy resin was done through gentle stirring with a wooden stick within a beaker with constant speed for 10 min to ensure uniform dispersion of the powder in epoxy matrix. The well-mixed mixture was then cast in a 4 × 6 cm<sup>2</sup> rectangular silicon rubber mold with a thickness of 5 mm and could set overnight at room temperature. The list of samples with different weight percentages of PbO and Pb<sub>3</sub>O<sub>4</sub> fillers are shown in Table 2.1.

**Table 2.1** List of composites prepared with different weight fractions of filler and epoxy system and corresponding designations used in this study

Composite by weight fraction (wt%)			Composite designation
Filler	Epoxy system		
PbO	10	90	A1
	30	70	A2
	50	50	A3
	70	30	A4
Pb <sub>3</sub> O <sub>4</sub>	10	90	B1
	30	70	B2
	50	50	B3
	70	30	B4

### 2.1.2 Density Measurements

The apparent density  $\rho$  of prepared samples was measured using the Archimedes method and calculated using Eq. (2.1) [1]. A calibrated single pan electrical balance, ethanol, and toluene were used for this purpose.

$$\rho = \frac{m_1}{m_2 - m_3}(\rho_l) \quad (2.1)$$

where  $m_1$ ,  $m_2$  and  $m_3$  are the mass of the sample weighted on the balance, the mass of the sample hanging on balance arm in the air and the mass of the sample hanging on the balance arm immersed in ethanol respectively while  $\rho_l$  is the density of the immersion liquid (ethanol and toluene).

The measured densities were compared with the theoretical values,  $\rho_c$  (with an assumption that the samples were free from voids) which are determined according to Eq. (2.2) [2]:

$$\rho_c = \frac{100}{\left[ \frac{F}{\rho_f} + \frac{E}{\rho_e} \right]} \quad (2.2)$$

where  $F$  is the wt% of the filler,  $E$  is the wt% of epoxy,  $\rho_f$  is the density of filler,  $\rho_e$  is the density of epoxy system.

### 2.1.3 Measurement of X-Ray Mass Attenuation Coefficients ( $\mu_m$ )

To determine the initial dose (Do), the generated X-rays were directly exposed to the DIADOS diagnostic detector connected to DIADOS diagnostic dosimeter (PTW-Freiburg, Germany) without having passed through any sample. The distance between the X-ray tube and the detector was set to 100 cm, and the X-ray beam was well collimated according to the size of the sample. This experiment was done using a calibrated X-ray machine in Royal Perth Hospital, Western Australia. The final dose (D) was taken with the sample placed on the detector. The exposure was set at 10 mA s, where the X-ray tube voltage was started at 40 kVp with 10 kVp increment up to 100 kVp. Next, the linear attenuation coefficient ( $\mu$ ) for each sample was determined by Eq. (2.3), where  $x$  is the thickness of the sample. This  $\mu$  is divided by the calculated  $\rho_{comp}$  according to Archimedes' method [1] to determine  $\mu_m$  (Eq. 2.4).

$$\mu = \frac{(\ln \frac{D_o}{D})}{x} \quad (2.3)$$

The observed results of  $\mu_m$  were compared with the theoretical values evaluated from Hubbell's database, NIST XCOM.

$$\mu_m = \frac{\mu}{\rho_{comp}} \quad (2.4)$$

### 2.1.4 Powder Diffraction

Powder diffraction measurements were performed at the Australian Synchrotron in Melbourne to identify the crystalline phases present in the samples. This work was conducted on the Powder Diffraction beamline, and the diffraction patterns were recorded in the  $2\theta$  range of 10–60° at a fixed wavelength of 1.37 Å.

### 2.1.5 Optical Microscopy

Optical microscopy was done using Nikon ME600 optical microscope. The samples were polished using diamond pastes from 15 to 1.0  $\mu\text{m}$  to obtain mirror-like surface finish.

**Table 2.2** List of prepared samples with different weight fractions of filler ( $\text{WO}_3$ ) and epoxy resin

Composite by volume fraction (vol%)	
Filler ( $\text{WO}_3$ )	Epoxy resin
5	95
10	90
20	80
30	70
35	65

### 2.1.6 Scanning Electron Microscopy (SEM)

The surface of the samples was also examined using a Zeiss Evo 40XVP scanning electron microscope. Samples were Pt-coated to prevent any charging on the samples during the imaging process. The backscattered electron technique was chosen to gain better contrast because of different atomic number between epoxy and lead. A pure epoxy sample was also examined as a control.

## 2.2 Tungsten Oxide—Epoxy Composites

### 2.2.1 Samples Preparation

Nano-sized (<100 nm) and micro-sized (~20  $\mu\text{m}$ ) tungsten oxide ( $\text{WO}_3$ ) were used as filler for synthesizing  $\text{WO}_3$ -epoxy composites. The former was obtained from Sigma-Aldrich and the latter (FR251) from Fibreglass and Resin Sales.

To prepare  $\text{WO}_3$ -epoxy composite samples,  $\text{WO}_3$  powder was added into the FR251 epoxy resin (Bisphenol-A diglycidyl ether polymer) before the FR251 hardener (Isophoronediamine) was mixed into it. The ratio of epoxy resin to hardener used was 2:1. The mixing of  $\text{WO}_3$  powder in epoxy resin was done through gentle stirring using a stirring machine at constant speed for 15 min to ensure uniform dispersion of the powder in epoxy matrix. The well-mixed mixture was then cast in a 4 cm  $\times$  6 cm rectangular silicon rubber mould with a thickness of 7 mm and could set overnight at room temperature. The list of prepared samples with different weight percentages of  $\text{WO}_3$  are shown in Table 2.2.

### 2.2.2 Measurement of X-Ray Mass Attenuation Coefficient ( $\mu_m$ )

This work was done using two different sets of equipment. For the lower X-ray energy range, a mammography unit (brand: Siemens AG, model: 2403951-4 G.E

Health Care) was used while a general diagnostic X-ray machine (brand: Shimadzu, model: Circlex 0.6/1.2 P364DK-100SF) was used for the higher X-ray energy range. The initial X-ray intensity ( $I_0$ ) was determined by directly measuring X-rays with the DIADOS diagnostic detector connected to DIADOS diagnostic dosimeter (PTW-Freiburg, Germany) in the absence of the sample. The dosimeter is a universal dosimeter for measuring simultaneous dose and dose rate for radiography, fluoroscopy, mammography, dental X-ray and CT with a sensitivity of 0.01 microRoentgen ( $\mu\text{R}$ ). Meanwhile the transmitted X-ray intensity ( $I$ ) was taken with the sample placed on the detector. The distance between the X-rays' tube and the detector was set to 86 cm since this is the maximum distance that can be adjusted for the mammography unit, and the X-ray beam was well collimated to the size of the sample.

The exposure was set at 10 mAs to obtain meaningful readings for this type of detector. The range 22–49 kV of X-ray tube voltage was selected from mammography unit since the machine can go only within this range for lower X-ray energy. On the other hand, the range of X-ray tube voltage (40–120 kV) was chosen from the general diagnostic X-ray machine because this range is the normal range of X-ray tube voltage used in general diagnostic imaging purposes. The transmitted X-ray beam intensity ( $I$ ) for each sample at each X-ray tube voltage was determined directly from the dosimeter reading. For each composite, the measurements were performed three times to obtain an average value. The performance of micro-sized and nano-sized  $\text{WO}_3$ -epoxy composite was compared from the graph of  $I$  as a function of filler loading for each X-ray tube voltage.

## 2.3 Ion-Implanted Epoxy

### 2.3.1 Samples Preparation

Pure epoxy samples were prepared by mixing one part of FR251 hardener (Isophoronediamine) with two parts of FR251 epoxy resin (Bisphenol-A diglycidyl ether polymer). The mixing of epoxy resin and hardener was done through gentle stirring using a stirring machine (2 level of speed) within a beaker with constant level 1 speed for 10 min to ensure the uniformity of the mixture. Then, the mixture was cast in cylindrical Fixiform moulds (diameter of 25 mm) with a thickness of 2 mm and allowed to set overnight. The cured epoxy samples were polished using diamond pastes from 15 to 1.0  $\mu\text{m}$  to obtain flat and mirror-like surface finishes.

### 2.3.2 Ion-Implantation

For this preliminary investigation of the X-ray attenuation characteristics of ion-implanted composites, we started with lower implanted dose in order to prevent

possible melting and/or decomposition of the epoxy samples during ion implantation. Polished epoxy samples were implanted with tungsten (W), gold (Au) and lead (Pb), produced by a metal evaporation and direct extraction ion source. For this type of ion source, the charge distribution of positive ions was measured previously by RBS and they are:  $W^{+1} = 1\%$ ,  $W^{+2} = 16\%$ ,  $W^{+3} = 58\%$ ,  $W^{+4} = 25\%$ ,  $Au^{+1} = 12\%$ ,  $Au^{+2} = 78\%$ ,  $Au^{+3} = 9\%$ ,  $Au^{+4} = 1\%$  and  $Pb^{+1} = 35\%$ ,  $Pb^{+2} = 64\%$ ,  $Pb^{+3} = 1\%$ . These values are close to the theoretical prediction using the Debye–Huckel approximation of non-ideal plasma [3]. The RBS measured values of charge distribution result in an average charge of  $W + 3.07$ ,  $Au^{+1.99}$  and  $Pb^{+1.66}$ . Thus, the ion acceleration of 40 kV used in this work afforded an average implantation energy of  $W = 122.8$  keV,  $Au = 79.6$  keV and  $Pb = 66.4$  keV, and a projected range in epoxy of 80 nm, 59 nm and 54 nm, respectively. The beam size was close to  $20\text{ cm}^2$ , and the beam current used in this experiment was around 30 IA. The ion fluence was monitored by converting the ion target current into pulses using a current-to-frequency convertor. In this work all three ions were implanted at nominal doses between  $7 \times 10^{14}$  ions/cm<sup>2</sup> and  $1.4 \times 10^{15}$  ions/cm<sup>2</sup>, measured by RBS, after the implantation process, and converted in [at. %] for ease of comparison.

### ***2.3.3 Ion Beam Analysis and Rutherford Backscattering Spectroscopy (RBS)***

The near surface composition depth profiling of ion-implanted epoxy samples was characterized by ion beam analysis and RBS using a beam of 1.8 MeV He<sup>1+</sup> ions beam at the Australian Nuclear Science and Technology Organisation. The information obtained was processed using SIMNRA code [4] which allowed calculation of depth distribution of implanted species and the implanted dose, which was converted in concentration. For these particular samples, a depth resolution of the order of 10 nm was achieved for the implanted heavy element.

### ***2.3.4 Measurement of X-Ray Mass Attenuation Coefficients ( $\mu_m$ )***

This work was done using a general diagnostic X-ray machine (brand: Shimadzu, model: Circlex 0.6/1.2 P364DK-100SF). The initial X-ray dose ( $D_0$ ) was determined by directly measuring X-rays with the DIADOS diagnostic detector connected to DIADOS diagnostic dosimeter (PTW-Freiburg, Germany) in the absence of the sample. The dosimeter is a universal dosimeter for measuring simultaneous dose and dose rate for radiography, fluoroscopy, mammography, dental X-ray and CT. Meanwhile the exit dose (D) was taken with the sample placed on the detector. The distance between the X-rays tube and the detector was set to 100 cm and the X-ray

beam was well collimated to the size of the sample. The exposure was set at 10 mAs to obtain meaningful reading for this type of detector while the tube voltage was increased from 40 to 100 kV in step of 10 kV for each dose measurement. The range of X-ray tube voltage (40–100 kV) was selected because this diagnostic imaging purposes. The mass attenuation coefficient, ( $\mu_m = 1/\rho_{\text{comp}}$ ) for each sample was determined from Eqs. (2.3) and (2.4).

## 2.4 Ion-Implanted Acrylic and Glass

### 2.4.1 Samples Preparation

Commercial samples of acrylic and glass were used for this work.

### 2.4.2 Ion-Implantation

As a starting study of X-ray shielding capability on different ion-implanted matrices, the sample matrixes were implanted with tungsten (W) of a nominal dose ( $7 \times 10^{14}$  ions/cm<sup>2</sup>) and lead (Pb) of the nominal dose ( $7 \times 10^{14}$  ions/cm<sup>2</sup>) and ( $1.4 \times 10^{14}$  ions/cm<sup>2</sup>) respectively. These lower nominal doses were chosen as the preface investigation in order to prevent possible melting and/or decomposition of the sample matrix during high energy implantation and then will be converted in [at. %] for ease of comparison. The ions were produced by a metal evaporation and the direct extraction ion source. The charge distribution of positive ions of W and Pb as measured previously by RBS are:  $W^{+1} = 1\%$ ,  $W^{+2} = 16\%$ ,  $W^{+3} = 58\%$ ,  $W^{+4} = 25\%$ , and  $Pb^{+1} = 35\%$ ,  $Pb^{+2} = 64\%$ ,  $Pb^{+3} = 1\%$  which are nearly the same as the theoretical prediction by the Debye–Huckel approximation of non-ideal plasma [3]. The RBS measured values of the charge distribution provided an average charge of  $W^{+3.07}$  and  $Pb^{+1.66}$ . Meanwhile, an average implantation energy of W = 122.8 keV and Pb = 66.4 keV was afforded with the ion acceleration of 40 kV used in this study. The beam size was close to 20 cm<sup>2</sup>, and the beam current used in this experiment was around 30  $\mu$ A. The ion fluence was monitored by converting the ion target current into pulses using a current-to-frequency convertor.

### 2.4.3 Ion Beam Analysis and Rutherford Backscattering Spectroscopy (RBS)

Characterization of the near surface composition depth profiling of all ion-implanted samples was performed using an ion beam analysis and RBS with a beam of 1.8 MeV

He<sup>1+</sup> ions beam at the Australian Nuclear Science and Technology Organization. Next, the information gathered was processed with SIMNRA code [4] to get the calculation of the depth distribution of implanted species and then was converted in concentration [at.%]. These results were compared with the previous results on ion-implanted epoxy samples [5].

#### **2.4.4 Measurement of X-Ray Linear Attenuation Coefficients ( $\mu_m$ )**

A general diagnostic X-ray machine (Make: Shimadzu, Model: Circlex 0.6/1.2 P364DK-100SF), a DIADOS diagnostic detector and a DIADOS diagnostic dosimeter (PTW-Freiburg, Germany) were used to study the X-ray shielding capability of these implanted sample matrixes. The DIADOS dosimeter is a universal dosimeter for measuring simultaneous dose and dose rate for radiography, fluoroscopy, mammography, dental X-ray and CT. The incident X-ray dose was measured by placing the detector directly below the X-ray tube at a distance of 100 cm. The exit dose (D) was measured by placing the sample on the detector. The X-ray beam was well collimated to the size of the sample and the exposure was set at 10 mAs to receive significant readings for this type of detector. The range of X-ray tube voltage (40–100 kV) was selected for this investigation since this range is the normal range of X-ray tube voltage used in the general diagnostic imaging purposes. The linear attenuation coefficient,  $\mu$  (unit:  $\text{cm}^{-1}$ ) for each sample was determined from Eq. (2.3).

### **2.5 Electrospun Bismuth Oxide/Poly-lactic Acid Nanofibre-Mats**

#### **2.5.1 Materials**

Bismuth (III) oxide ( $\text{Bi}_2\text{O}_3$ ) particles of sizes 90–210 nm and 10  $\mu\text{m}$  were used as filler for synthesizing electrospun  $\text{Bi}_2\text{O}_3$ /poly lactic acid (PLA) nanofibre mats and  $\text{Bi}_2\text{O}_3$ /PLA thin films.  $\text{Bi}_2\text{O}_3$ , chloroform and methanol were obtained from Sigma-Aldrich. Meanwhile, PLA (3051D) pellets with the molecular weight  $M_n = 93.500$  g mol and glass transition temperature  $T_g = 65.50$  °C were supplied by NatureWorks USA.

**Table 2.3** Prepared electrospun Bi<sub>2</sub>O<sub>3</sub>/PLA nanofibre mats with different weight fractions (wt%) of filler (Bi<sub>2</sub>O<sub>3</sub>) and PLA

Filler (Bi <sub>2</sub> O <sub>3</sub> ) (wt%)	PLA (wt%)
24	76
28	72
34	66
38	62

### 2.5.2 Samples Preparation

Electrospinning was carried out using 9% wt/v PLA solution by mixing with 8 mL of chloroform and 2 mL methanol as the solvents. The micro(m)-Bi<sub>2</sub>O<sub>3</sub> and nano(n)-Bi<sub>2</sub>O<sub>3</sub> suspension was added at 24–38 wt% to the polymer solution and was homogenized for 45 min under ultrasonication. For electrospinning process, the solutions were transferred to a 10-mL syringe pump with 25-G needles. The flow rate of polymer solution was 1 mL/h, and the applied positive voltage used was in the range of 18–20 kV. The distance between the needle tip and the target was set at 12 cm. The resulting nanofibre mats were collected on a flat aluminium foil for about 2 h to get an acceptable thickness for X-ray transmission experiment. The nanofibre mat was removed from the aluminium foil and was cut to a dimension of 2.0 × 1.5 cm<sup>2</sup> or was folded together before cutting so that the nanofibre mat has an acceptable thickness for a reliable X-ray transmission experiment. Three sets of the same nanofibre mats were prepared. The list of prepared electrospun Bi<sub>2</sub>O<sub>3</sub>/PLA nanofibre mats with different weight percentages of Bi<sub>2</sub>O<sub>3</sub> are shown in Table 2.3.

The solution casting method was performed to prepare Bi<sub>2</sub>O<sub>3</sub>/PLA thin films for verifying the X-ray transmission results obtained for electrospun Bi<sub>2</sub>O<sub>3</sub>/PLA fibre mats. In this method, PLA was mixed with the chloroform without methanol (since methanol was only used in the electrospinning process to increase the conduction of the solution and will totally evaporate during the process) of the same amount as in the electrospinning process and was homogenized for 45 min under ultrasonication. Then, the solution was poured into a beaker of 5 cm diameter and left in the fume cupboard for 24 h to dry. Next, the thin film was removed from the beaker and three sets of the same thin film were cut to pieces of 2.0 × 1.5 cm<sup>2</sup> for X-ray transmission experiments. The list of prepared Bi<sub>2</sub>O<sub>3</sub>/PLA thin films with different weight percentages of Bi<sub>2</sub>O<sub>3</sub> are the same as shown in Table 2.3.

### 2.5.3 Measurements of Sample Thickness and Porosity

Since it is difficult to produce all the electrospun Bi<sub>2</sub>O<sub>3</sub>/PLA fibre mats to have a constant thickness which is an important factor in X-ray transmission comparison, the average thickness of nanofibre mat was measured by weighing and carefully

determining the area of the nanofibre mat. The average thickness ( $t_{ave}$ ) of the nanofibre mat was determined from Eq. (2.5) where  $m$  is the mass,  $A$  is the surface area; and  $\rho$  is the apparent density of the electrospun  $\text{Bi}_2\text{O}_3/\text{PLA}$  nanofibre mat.

$$t_{ave} = \frac{m}{A\rho} \quad (2.5)$$

The apparent density ( $\rho$ ) of the electrospun  $\text{Bi}_2\text{O}_3/\text{PLA}$  fibre mat was accurately measured using the density bottle method (ASTM D854). An average of three measurements was taken for each electrospun  $\text{Bi}_2\text{O}_3/\text{PLA}$  fibre mat. The porosity of the electrospun nanofibre mat was calculated by using the following Eq. (2.6). A calibrated single pan electrical balance and distilled water were used for this purpose.

$$Porosity(\%) = \left(1 - \frac{\rho}{\rho_{theory}}\right) \quad (2.6)$$

where,  $\rho_{theory}$  is the bulk density of the  $\text{Bi}_2\text{O}_3/\text{PLA}$  composite.

The average thickness  $t_{ave}$  of individual ( $2.0 \times 1.5 \text{ cm}^2$ ) thin films was measured using vernier caliper. Meanwhile, the apparent density ( $\rho$ ) of thin films was measured using Eq. (2.7) where  $m$  is the weighted sample's mass and  $A$  is the surface area of  $\text{Bi}_2\text{O}_3/\text{PLA}$  thin film.

$$\rho = \frac{m}{t_{ave} \times A} \quad (2.7)$$

#### 2.5.4 Measurement of X-Ray Transmission

Two separate instruments were used to characterize the X-ray transmission of prepared samples. The first involved the use of X-ray absorption Spectroscopy (XAS) beamline at the Australian Synchrotron. Experiments were carried out in the energy range of 7–20 keV using a Si (311) monochromator and a beam size on the sample of about 0.25 by 0.25 mm<sup>2</sup> and a photon flux of about 10<sup>11</sup> ph/s. Transmission data were collected in an ionization chamber after the sample, and compared to the incident beam flux. For each sample 20 readings were recorded at each energy. To normalize the data collected readings were also recorded for an empty sample holder.

The second instrument used was a mammography unit (brand: Siemens AG, model: 2403951-4 G.E Health Care) at Royal Perth Hospital, Western Australia. For the work with this mammography unit, the exposure was set at 10 mAs to obtain meaningful readings for DIADOS diagnostic detector connected to the DIADOS diagnostic dosimeter (PTW-Freiburg, Germany) and the range 22–49 kV of X-ray tube voltage was selected. The dosimeter is a universal dosimeter for measuring

**Table 2.4** Anode/filter combination operated by the mammography machine

X-ray tube voltage (kV)	Anode/filter combination
22	Mo/Mo <sup>a</sup>
25	
30	
35	Mo/Rh <sup>b</sup>
40	
45	Rh/Rh <sup>c</sup>
49	

<sup>a</sup>Molybdenum anode/molybdenum filter. <sup>b</sup>Molybdenum anode/rhodium filter. <sup>c</sup>Rhodium anode/rhodium filter

simultaneous dose and dose rate for radiography, fluoroscopy, mammography, dental X-ray and CT with a sensitivity of 0.01 microRoentgen ( $\mu\text{R}$ ). Three different anode/filter combinations (Table 2.4) were used for filtering the X-ray beam produced by the chosen X-ray tube voltages used for the mammography machine, since the combination was controlled by the machine itself. The X-ray beams generated by these anode/filter combinations composed mainly of the characteristic X-ray energies of molybdenum (17.5 and 19.6 keV) or rhodium (20.2 and 22.7 keV). For each sample, the measurements were performed three times. The detector was placed 86 cm under the X-ray tube since this is the maximum distance that can be adjusted for the mammography unit, and the X-ray beam was well collimated to the size of the sample size to minimize the scattered X-ray produced by the sample.

An average value for the incident intensity  $I_o$  (determined by directly measuring X-rays passed through the detector in the absence of the sample) and transmitted intensity  $I$  (determined by a sample placed in front of the detector) were calculated and a graph of the X-ray transmission ( $T = I/I_o$ ) as a function of wt% was plotted for each of the X-ray tube voltage chosen with ( $T$ ) was related to Eq. (2.8).

$$T = \left( \frac{I}{I_o} \right) = e^{-\mu t_{ave}} \quad (2.8)$$

### 2.5.5 Scanning Electron Microscopy (SEM)

The depth profile of the samples was examined using Zeiss Evo 40XVP scanning electron microscope at the voltage of 15 kV with the working distance between 8.0 and 9.0 mm. Both secondary electrons (SE) and backscattered electron (BSE) techniques coupled with an energy dispersive X-ray spectroscopy (EDS) were done after standard coating with platinum to minimize charging to show the different of the image due to the different atomic number of PLA and bismuth. A pure electrospun PLA nanofibre mat was also examined as a benchmark.

**Table 2.5** Compositions of WO<sub>3</sub>-epoxy composites with different volume fractions of filler WO<sub>3</sub> and epoxy resin

Composite by volume fraction (vol%)	
Filler (WO <sub>3</sub> )	Epoxy resin
2	98
4	96
6	94
8	92
10	90

## 2.6 Micro-sized and Nano-sized Tungsten Oxide-Epoxy Composites

### 2.6.1 Samples Preparation

Nano-sized (<100 nm) tungsten oxide and micro-sized (~20 μm) tungsten oxide (WO<sub>3</sub>) were used as the filler for synthesising WO<sub>3</sub>-epoxy composites. The former was obtained from Sigma-Aldrich and the latter (FR251) from Fibreglass and Resin Sales. The particle sizes were provided by Sigma-Aldrich.

Details about the preparation of the WO<sub>3</sub>-epoxy composite samples are available in [6]. For the current work, the thickness of the samples was set at 2.0 mm. The list of the prepared samples with the different volume percentages of WO<sub>3</sub> is shown in Table 2.5.

### 2.6.2 Measurements of X-Ray Transmission

This work was done using the X-ray Absorption Spectroscopy (XAS) beamline at the Australian Synchrotron located in Melbourne. Experiments were carried out in the energy range of 10–40 keV using an Si (311) monochromator and a beam size on the sample of about 0.25 × 0.25 mm<sup>2</sup> and a photon flux of about 10<sup>11</sup> ph/s. Data on X-ray transmission ( $I/I_o$ ) were collected in an ionisation chamber after the sample, and compared to the incident beam flux. For each sample, 20 readings were recorded at each energy level. To normalise the data collected, readings were also recorded for an empty sample holder. The average  $I/I_o$  was calculated and plotted as a function of filler loadings (WO<sub>3</sub> vol%) for each synchrotron radiation energy. The X-ray transmission ( $I/I_o$ ) was related to the linear attenuation coefficient ( $\mu$ ) and the thickness of the samples ( $t$ ) through Eq. (2.8).

Next, all the samples were examined again with a mammography unit and a radiology unit according to previous experiments [6].

### 2.6.3 Powder Diffraction

Powder diffraction (PD) measurements were conducted to identify the crystallite size of the  $\text{WO}_3$ . This was done at the Australian Synchrotron in Melbourne, on the Powder Diffraction beamline. Mythen detectors were used to record the diffraction patterns in the  $2\theta$  range of  $0^\circ$ – $60^\circ$  at a fixed wavelength of  $1.13 \text{ \AA}$ . The crystallite size ( $L$ ) of the nano sized  $\text{WO}_3$  was determined using the Scherrer equation as follows (Eq. 2.9):

$$L = \frac{k\lambda}{(FWHM) \cos \theta} \quad (2.9)$$

where  $k$  is a constant depending upon the crystal shape and size ( $k = 0.90$ ),  $\lambda$  is the wavelength, FWHM is the full-width half maximum of the peak and  $2\theta$  is the diffraction angle of the strongest peak.

### 2.6.4 Flexural Tests

Three-point bending tests were used to determine the flexural strength and modulus of the  $\text{WO}_3$ -epoxy composites containing different loadings of nano-sized and micro-sized  $\text{WO}_3$ . Specimens with dimensions  $60 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$  were prepared for the test according to the ASTM D790-03 standard [7] on a universal testing machine (LLOYD Instruments). A minimum of three samples was tested for each composite and the average results were taken. In these measurements, the samples were tested to the applied load with the results calculated by the NEXYGEN Plus software.

### 2.6.5 Indentation Hardness Test

The hardness values of polished  $\text{WO}_3$ -epoxy composites were determined using a Rockwell hardness tester with scale H. The hardness measurements were conducted using an indentation load of  $588.4 \text{ N}$  and ball diameter of  $0.3 \text{ cm}$ . Five measurements were conducted for each sample in order to obtain an average value.

## 2.7 Starch Filled Bi<sub>2</sub>O<sub>3</sub>–PVA Composites

### 2.7.1 Materials

Bismuth (III) oxide, Bi<sub>2</sub>O<sub>3</sub>, with a density of 8.9 g/cm<sup>3</sup>, (10–100 nm, Sigma-Aldrich) and (20 lm, Alfa Aesar), polyvinyl alcohol, PVA [molecular weight: 89,000–98,000; hydrolysis rate: 99? %; density: 1.3 g/cm<sup>3</sup> (Sigma-Aldrich)], and starch (potato starch, Sigma-Aldrich) were used in the present study.

### 2.7.2 Samples Preparation

PVA powder was dissolved in double distilled water at 90 °C and stirred for 6 h in order to ensure that the powders dispersed uniformly. The micro-sized and the nanosized Bi<sub>2</sub>O<sub>3</sub>–PVA composites were added with different weight percentages (wt%), as depicted in Table 2.6.

The PVA solution was prepared by mixing the PVA powder with distilled water in a beaker. Then, Bi<sub>2</sub>O<sub>3</sub> powder was added and heated at a constant temperature (90–100 °C). The solution was stirred at a constant speed for 6 h in order to ensure that the powders dispersed uniformly. The micro-sized and the nano-sized Bi<sub>2</sub>O<sub>3</sub>–PVA composites were prepared with different weight percentages (wt%), as depicted in Table 2.6. The steps were repeated with the addition of different amounts of starch, as listed in Table 2.7. For the initial investigation, the addition of starch into the composite was prepared only for the Bi<sub>2</sub>O<sub>3</sub> filler with wt% of 8, 12, and 15. This procedure was performed to gain better dispersion of both micro-sized and nano-sized Bi<sub>2</sub>O<sub>3</sub> particles within the PVA matrix, as well as to assist in enhancing the effect of Bi<sub>2</sub>O<sub>3</sub> particle sizes on the X-ray transmission readings. This preliminary approach was done due to the supporting evidence provided by Hejri et al. [8], who claimed that uniform dispersion of TiO<sub>2</sub> nanoparticles was found within the

**Table 2.6** Weight percentage of Bi<sub>2</sub>O<sub>3</sub> and PVA

Element	Weight percentage (wt%)				
Bi <sub>2</sub> O <sub>3</sub>	8	12	15	18	21
PVA	92	88	85	82	79

**Table 2.7** Weight percentage of Bi<sub>2</sub>O<sub>3</sub>, PVA and starch

Element	Weight percentage (wt%)					
Bi <sub>2</sub> O <sub>3</sub>	8	8	12	12	15	15
PVA	91	89	87	85	84	82
Starch	1	3	1	3	1	3

starch–PVA matrix. Finally, the mixture was cast in a rectangular glass plate with a dimension of 11.6 cm × 9.56 cm. The sample was left to dry for a week in a closed container within a fume cupboard. After drying, the polymer composite was peeled off from the casting plate, stored, and ready for transmission measurement. The average thickness of the polymer composite was found to be about 0.25 mm.

### **2.7.3 Density Measurements**

The density,  $\rho$ , of the samples was determined by using the Archimedes principle with ethanol as the immersion medium, based on the relation provided in Eq. (2.1).

### **2.7.4 Measurement of X-Ray Transmission**

The X-ray transmission was performed by using two modalities, i.e., X-ray fluorescence spectroscopy (XRF) and mammography units (brand: Philips, model: MammoDiagnost AR). In addition, several metal targets, such as niobium, molybdenum, palladium, silver, and tin, were used to measure the X-ray transmission by the samples via XRF unit. These metal targets produced the characteristic of X-ray with energy values of 16.59, 17.46, 21.21, 22.20, and 25.2 keV, respectively. Meanwhile, the mammography unit was used to measure the energy of the X-ray photons produced by tube voltages that ranged from 23 to 35 kV. As for the X-ray transmission measurement of the samples by using XRF unit, the composite sample was placed in front of the germanium detector and it was exposed with the selected energy. On the other hand, for the mammography unit, the source to surface (SSD) distance was arranged at 66 cm and the exposure was set at 10 mAs. The X-ray transmission was obtained by measuring the dose received via Raysafe Xi MAM detector system. The dosimeter is well known as a universal dosimeter for measuring simultaneous dose and dose rate for radiography, CT, mammography, and fluoroscopy. Moreover, the X-ray beam was collimated to a dimension of 3 cm × 9.3 cm in order to minimize any scattered radiation. The initial X-ray beam intensity ( $I_0$ ) was obtained by directly measuring the dose received by the detector in the absence of sample. Other than that, the final X-ray beams' intensity ( $I$ ) was taken by measuring the dose received with the sample placed on the detector. Initial investigations of starch–composite mixture related to Bi<sub>2</sub>O<sub>3</sub> particle size and its effect on the X-ray transmissions had been carried out by using the XRF unit.

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