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Characterisation of micro-sized and nano-sized tungsten oxide-epoxy composites for radiation shielding of diagnostic X-rays

Noor Azman N.Z^{a, b}, Siddiqui S.A^a, Low I.M^{a*}

^aDepartment of Imaging and Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845 Australia

^bSchool of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

*Corresponding author: j.low@curtin.edu.au; Tel: +618-9266 7544; Fax: +618-9266 2377

Abstract

Characteristics of X-ray transmissions were investigated for epoxy composites filled with 2-10 vol% WO₃ loadings using synchrotron X-ray Absorption Spectroscopy (XAS) at 10-40 keV. The results obtained were used to determine the equivalent X-ray energies for the operating X-ray tube voltages of mammography and radiology machines. The results confirmed the superior attenuation ability of nano-sized WO₃-epoxy composites in the energy range of 10-25 keV when compared to their micro-sized counterparts. However, at higher synchrotron radiation energies (i.e., 30-40 keV), the X-ray transmission characteristics were similar with no apparent size effect for both nano-sized and micro-sized WO₃-epoxy composites. The equivalent X-ray energies for the operating X-ray tube voltages of the mammography unit (25-49 kV) were in the range of 15-25 keV. Similarly, for a radiology unit operating at 40-60 kV, the equivalent energy range was 25-40 keV, and for operating voltages greater than 60 kV (i.e., 70-100 kV), the equivalent energy was in excess of 40 keV. The mechanical properties of epoxy composites increased initially with an increase in the filler loading but a further increase in the WO₃ loading resulted in deterioration of flexural strength, modulus and hardness.

Keywords: X-ray shielding, micro-sized WO₃-epoxy composites, nano-sized WO₃-epoxy composites, X-ray transmission, filler loading

1. Introduction

Hitherto, numerous analytical methods have been developed to investigate the effect of the particle size of a material on the X-ray attenuation for various incoming X-ray energies including scattered gamma-rays and X-rays [1-11]. It is widely believed that nano-sized particles are able to disperse more uniformly within the matrix with less agglomerations when compared to micro-sized particles, thus improving the X-ray attenuation ability of the material [6, 12, 13]. For instance, Holyńska (1969) found that the intensity of scattered radiations increased with increases in the grain size of a material. This size effect has been observed in a sand matrix and for samples containing heavy elements such as iron or barium [4].

Filler-reinforced polymers have gained increasing attention from X-ray technologists in radiation shielding since polymers have great potential in many important applications by virtue of their unique properties, such as low density, the ability to form intricate shapes, optical transparency, low manufacturing cost and toughness. One of the filler-reinforced polymers commonly used for radiation shielding is lead acrylic [14-16]. Moreover, some researchers have also tried to synthesise nano-sized filler-reinforced polymers for radiation shielding by virtue of the size effect in X-ray attenuation [2, 6, 17]. For instance, a recent study by Botelho et al. [13] revealed that the attenuation for X-ray beams generated from low tube voltages (i.e., 26-30kV) in nanostructured copper oxide (CuO) was better than microstructured CuO. However, no significant difference in attenuation was observed for X-rays generated from higher tube voltages (i.e., 60-102 kV). A similar conclusion on this size effect in X-ray attenuation was made by Kunzel et al. [18] for a nanostructured CuO-polymer system.

In a recent work on WO₃-filled epoxy composites [19], we investigated the effect of nano-sized and micro-sized WO₃ filler-epoxy composites on X-ray attenuation in the X-ray tube voltage range of 22-127 kV generated by a mammography unit and a general radiography unit. The equivalent X-ray energies for the various X-ray tube voltages used were in the range of 17.5-60 keV, which conformed to our expectation since the equivalent X-ray energies for a mammography unit were 17.5, 19.6, 20.2 and 22.7 keV which are the characteristic energies of molybdenum and rhodium; while the equivalent X-ray energy for a radiology unit is about one-third of the X-ray tube voltage used. The results showed that nano-sized WO₃ was more effective than micro-sized WO₃ in X-ray attenuation only in the low X-ray tube voltage range of 22-35 kV

but this size effect was not apparent at the higher X-ray operating tube voltage range of 40-120 kV [19]. Hence, the aim of this work was to verify our previous work on X-ray transmission in WO₃-filled epoxy composites by using synchrotron radiations as the X-ray source for the characteristic (monochromatic) X-ray energy range of 10-40 keV. The results obtained were compared with those of previous work [19] to determine the equivalent energy range of the previous machines used (a mammography unit and a radiology unit).

2. Experimental Procedure

2.1 Sample preparation

Nano-sized (<100 nm) tungsten oxide and micro-sized (~20 µm) tungsten oxide (WO₃) were used as the filler for synthesising WO₃-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 WO₃-epoxy composite samples are available in [19]. 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 WO₃ is shown in Table 1.

2.2 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 mm² and a photon flux of about 10¹¹ 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 (WO₃ vol%) for each synchrotron radiation energy. The X-ray transmission (I/I_o) was related to the linear attenuation coefficient (μ) and the thickness of the samples (t) through Equation (1):

$$(I/I_o) = \exp(-\mu t) \quad (1)$$

Next, all the samples were examined again with a mammography unit and a radiology unit according to previous experiments [19].

2.3 Powder diffraction

Powder diffraction (PD) measurements were conducted to identify the crystallite size of the WO₃. 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 2θ range of 0°-60° at a fixed wavelength of 1.13 Å. The crystallite size (*L*) of the nano-sized WO₃ was determined using the Scherrer equation as follows (Equation 2):

$$L = \frac{k\lambda}{(FWHM) \cos \theta} \quad (2)$$

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

2.4 Flexural tests

Three-point bending tests were used to determine the flexural strength and modulus of the WO₃-epoxy composites containing different loadings of nano-sized and micro-sized WO₃. Specimens with dimensions 60 mm × 10 mm × 2 mm were prepared for the test according to the ASTM D790-03 standard [20] 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.

2.5 Indentation hardness test

The hardness values of polished WO₃-epoxy composites were determined using a Rockwell hardness tester with scale H. The hardness measurements were conducted using an indentation load of 588.4 N and ball diameter of 0.3 cm. Five measurements were conducted for each sample in order to obtain an average value.

3. Results and Discussion

3.1 Characteristics of X-ray transmissions

Since the synchrotron radiations of the XAS beamline contain a large range of energies (i.e., 10-40 keV), the thickness of the samples was set at 2 mm to ensure that the detector was able to

obtain a meaningful X-ray transmission reading for the lower energy range without being totally absorbed by the samples. As shown in Fig. 1, there was an obvious difference in X-ray transmissions between the micro-sized WO₃-epoxy and nano-sized WO₃-epoxy composites of the same WO₃ vol% at the energy range of 10-20 keV. With a further increase of synchrotron energy to greater than 20 keV, there was no difference in X-ray transmissions between these two composites, thus indicating the absence of size effect at play. **The results show that for all the WO₃ loadings in an epoxy matrix, the ratio of the X-ray transmission of the micro-sized WO₃-epoxy composite (I/I_0)_m relative to the nano-sized WO₃-epoxy composite (I/I_0)_n, (I/I_0)_m/ (I/I_0) _n remained at ~1.0 for the synchrotron energy range of 25-40 keV. On the other hand, the ratio (I/I_0)_m/ (I/I_0) _n was 1.15-2.3 for all WO₃ loadings (see Fig. 2). The values determined for (I/I_0)_m/ (I/I_0) _n at these energy ranges indicate that the nano-sized WO₃-epoxy samples absorbed more low energy X-rays than their micro-sized WO₃-epoxy counterparts.**

Further investigations were conducted to verify our previous results [19] obtained from a mammography unit and a radiography unit. In this investigation, all the same measurements from the previous work were repeated with samples of 2 mm in thickness. Since a mammography unit generates characteristic X-ray energies of molybdenum (17.5 keV and 19.6 keV) or rhodium (20.2 keV and 22.7 keV), it is much easier to compare with the XAS results (see Fig. 3). In the results presented in Fig. 3, it is clearly shown that the X-ray transmission results for the mammography unit sat between the results of 15-25 keV for the XAS beam energies. In contrast, for the radiography unit, the operated X-ray tube voltages generated a broad spectrum (polychromatic X-ray beam). Thus, the equivalent energies for the X-ray tube voltages of the radiography unit were estimated from the XAS results by superimposing their data together (see Fig. 4). As can be seen in Fig. 4, the X-ray transmissions of samples for X-ray tube voltages of 40-60 kV were sitting between 25-40 keV while the others were sitting above 40 keV. Hence, the X-ray tube voltages of 40-60 kV operated by the radiography unit produced the equivalent X-ray energies in the range of 25-40 keV while the X-ray tube voltages of ≥ 60 kV had an equivalent energy of ≥ 40 keV.

Figure 5 shows the comparison of X-ray transmissions for samples with different thicknesses. Samples of 7 mm thickness were used in our previous study [19], whereas 2 mm thick samples were used in this study. Fig. 5a and Fig. 5b provide the results for the mammography unit only on samples with 4 vol% and 6 vol% loading of WO₃ respectively. As shown in these figures, the

differences in the X-ray transmission between the micro-sized and nano-sized WO₃-epoxy became larger for thicker samples (7 mm). In contrast, Fig. 5c shows insignificant differences in X-ray transmission between nano-sized and micro-sized WO₃-epoxy composites for radiography tube voltages only for samples with a loading of 4 vol% WO₃. This trend was also observed for all the other loadings (i.e., 2, 6, 8 and 10 vol% WO₃). These findings are in good agreement with the work by Künzel and Okuno (2012), which also showed that the grain size effect increased with the increase of the sample thickness at low energy X-ray beams (25 kV and 30 kV) but remained unchanged over the material thickness for higher energy X-ray beams (60 kV) [18].

In general, the photoelectric effect is the most likely interaction to occur within a matter at a lower photon (X-ray) energy range. In this interaction, a photon will transfer its entire energy to an electron in the material on which it impinges. The electron thereby acquires enough energies to free itself from the material to which it is bound and then may undergo single or multiple-scattering events with neighbouring atoms. In addition, there is also a slight fluctuation in the probability of emission of Auger electrons and fluorescent photons may form during this interaction. This phenomenon can contribute to the alteration of the mass attenuation coefficient of an element relative to the bulk material when considered over a small range of X-ray energies. The probability of photoelectric interaction is directly proportional to the cube of the atomic number of the absorbing material Z^3 and inversely proportional to the cube of the X-ray energy $(1/E)^3$.

Moreover, nano-sized WO₃-epoxy composites consist of a higher number of WO₃ particles/gram when compared to micro-sized WO₃-epoxy composites. Therefore, the distribution of the nano-sized WO₃ in the resin should also be different from that presented by micro-sized WO₃, thus resulting in a more uniform dispersion in the resin. As a consequence, the chances of an X-ray photon with lower energy to interact and be absorbed by WO₃ particles may be higher in nano-sized WO₃-epoxy composites than in micro-sized WO₃-epoxy composites. Figure 6 shows the back-scattered images of the same loading of WO₃ (4 vol%) within nano-sized WO₃-epoxy and micro-sized WO₃-epoxy composites using the Zeiss Evo 40XVP scanning electron microscope. The WO₃ particles were seen to be more closely dispersed in the nano-sized WO₃-epoxy composite (Fig. 6a) as compared to its micro-sized counterpart (Fig. 6b). Thus, the probability for the lower energy photons to interact with the WO₃ particles and be absorbed is higher for the nano-sized WO₃-epoxy composite.

As the photon energy increases, the photon (X-ray) penetration through the absorbing material without interaction increases and hence, less photoelectric effect relative to the Compton effect occurs. Thus, the X-ray attenuation by the absorbing material decreased since the Compton interaction was weakly dependent on Z and E and this interaction only took place between the incident photon and one of the outer shell electrons of an atom in the absorbing material.

In order to discover the X-ray shielding ability of the composites, the results were compared to commercial lead (Pb) sheets (model RAS20 Calibrated Absorber Set) of four different thicknesses (i.e., 0.81, 1.63, 3.18 and 6.35 mm) (see Fig. 7) using a radiography unit of tube voltages 40-100 kV. The results show that although the lead sheets gave the lowest X-ray transmissions at each tube voltage when compared to all compositions of WO₃-epoxy composites, the latter with 10 vol% of either micro-sized or nano-sized WO₃ can be a substitute for Pb in X-ray shielding by increasing the sample thickness to ≥ 7 mm. Hence, the usage of lead in X-ray shielding can be substituted by WO₃ whereby W is lighter and less toxic compared to Pb.

3.2 Crystallite size

The reference for fitting the peaks was taken from the International Centre for Diffraction Data 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 diffraction peaks shown in Fig. 8 belong to monoclinic WO₃ (PDF file 00-043-1035). These results indicate that both the micro-sized WO₃ and the nano-sized WO₃ were single-phase pure without impurities.

The diffraction patterns were plotted only in the 2θ range of 9-15° to clearly show the size difference of the peaks for each micro-sized and nano-sized WO₃. As shown in Fig. 8, the broad peaks belonged to nanometer-sized WO₃ crystallite whereas the well-defined crystalline peaks belonged to micrometer-sized WO₃. The crystallite size determined from the Scherrer equation for nano-sized WO₃ was 51.5 nm. These nano-crystallites were significantly smaller than the particle sizes provided by Sigma-Aldrich, thus indicating that at least 2 crystallites were present in each WO₃ particle of 100 nm in size.

3.3 Mechanical properties

Figure 9 shows the effect of filler loading on the flexural strength, flexural modulus and Rockwell hardness of the epoxy composites. The flexural strength was found to decrease with increased WO_3 filler size while it had little or no effect on flexural modulus. Similar results were reported by Park [21] who observed an increase in flexural strength with decreased particle size in silica-reinforced epoxy composites. However, Moloney et al. [22] reported a negligible effect of particle size on flexural modulus in their epoxy composites filled with silica.

From Fig. 9a, it can be seen that the flexural strength of pure epoxy was 49.9 MPa, but increased to a maximum value of 64 MPa for the composite containing 4 vol% nano-sized WO_3 . However, a further increase in the filler loading beyond 4 vol% resulted in a decrease in flexural strength whereby the composite containing 10 vol% nano-sized WO_3 exhibited the lowest flexural strength of 52.6 MPa. Similarly for micro-sized WO_3 -epoxy composites, the maximum flexural strength was obtained for a filler loading of 2 vol%. A reduction in flexural strength was again observed when the filler loading was increased beyond 2 vol% due to non-uniform dispersion of the filler within the matrix. The resultant agglomeration of the fillers acted as stress-concentrators which served to reduce the strength of the composites.

The flexural modulus of the composites increased with an increase in the filler loading for both the nano-sized and micro-sized WO_3 which may indicate that the stiffness of these composites obeyed the well-known rule-of-mixtures (Fig. 9b).

Finally, the hardness results presented in Fig. 9c indicate that an increase in the WO_3 filler loading resulted in an initial increase in the hardness of the composite, but a further increase in filler loading at 10 vol% caused a reduction in hardness probably due to the undesirable agglomeration of the fillers. The initial increase in the hardness of the composites observed for both the nano-fillers and the micro-fillers may be attributed to their uniform dispersion within the epoxy matrix, together with their strong interaction with the epoxy chains to form good interfacial bonding.

4. Conclusion

The size effect of WO_3 particles on the X-ray transmission in nano-sized and micro-sized WO_3 -epoxy composites has been investigated at various synchrotron radiation energies (i.e., 10-40 keV). The results presented in this work demonstrated that the size effect on X-ray attenuation was profoundly dependent on the energy of the synchrotron radiations. The particle size effect

was more pronounced at lower synchrotron radiation energies (10-20 keV) since the X-ray transmission in nano-sized WO₃-epoxy composites was less than in their micro-sized counterparts. However, this size effect became insignificant at higher energies of 20-40 keV because the X-ray transmissions in both nano-sized and micro-sized WO₃-epoxy composites were very similar. The X-ray transmission results for the mammography unit sat between the results of 15-25 keV for XAS beam energies. Meanwhile, the X-ray transmissions in samples for X-ray tube voltages of 40-60 kV of the radiography unit sat between 25-40 keV. In addition, for composites with the same filler loading, but with increasing sample thickness, the size effect in X-ray transmission was most prominent for X-ray tube voltages of 25-35 kV, but was negligible at 35-100 kV. As the filler loading of the WO₃ increased, the mechanical properties showed an initial optimum improvement, but a further increase in the filler loading caused these properties to deteriorate.

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Table 1: Compositions of WO₃-epoxy composites with different volume fractions of filler WO₃ and epoxy resin.

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

Figure captions:

1. Comparisons of X-ray transmission comparison in nano-sized and micro-sized WO₃-epoxy composites for synchrotron radiation generated by the XAS unit for energy of 10 – 40 keV.
2. The X-ray transmission ratio of micro-sized WO₃-epoxy composite $(I/I_o)_m$ to the X-ray transmission for nano-sized WO₃-epoxy composite $(I/I_o)_n$, $(I/I_o)_m/(I/I_o)_n$ for synchrotron energies (10-40 keV)
3. Comparisons of X-ray transmission in nano-sized and micro-sized WO₃-epoxy composites for synchrotron radiation generated by the XAS unit for energies of 10-25 keV and mammography unit tube voltages of 25-49 kV.
4. Comparisons of X-ray transmission in nano-sized and micro-sized WO₃-epoxy composites for synchrotron radiation generated by the XAS unit for energies of 25-40 keV and radiography unit tube voltages of 40-100 kV.
5. X-ray transmission comparison for different thickness of the sample for a) 4 vol% of WO₃ filler epoxy composites for mammography unit tube voltages of 30, 35 and 49 kV; b) 6 vol% of WO₃ filler epoxy composites for mammography unit tube voltages of 30, 35 and 49 kV; and c) 4 vol% of WO₃ filler epoxy composites for radiography unit tube voltages of 40, 60, 80 and 100 kV.
6. SEM images for epoxy composites filled with (a) 4 vol% nano-sized WO₃, and (b) 4 vol% of micro-sized WO₃.
7. X-ray transmission as a function of radiography unit X-ray tube voltage (40-100 kV) for all micro-sized and nano-sized WO₃-epoxy composites and commercial lead sheets.
8. Typical powder diffraction patterns for micro-sized and nano-sized WO₃ loading in epoxy composites.
9. Mechanical properties of epoxy composites showing : (a) flexural strength as a function of WO₃ filler loading; (b) flexural modulus as a function of WO₃ filler loading; and (c) Rockwell hardness as a function of WO₃ filler loading.