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From Gd2O3 suspension to nanocomposite: Synthesis, properties and radiation protection

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From Gd$_2$O$_3$ suspension to nanocomposite: synthesis, properties and radiation protection

This thesis is presented in fulfilment of the requirements for the degree of

Doctor of Philosophy

By

Ly Bao Truc La

Edith Cowan University

School of Engineering

2017
DISCLAIMER

I hereby declare that any ideas, analysis and discussion in this thesis are my own work, otherwise clearly referenced, and abide by University’s Plagiarism policy.

Signed: [Signature]

La, Bao Truc Ly

October 04th, 2017
USE OF THESIS

The Use of Thesis statement is not included in this version of the thesis.
ABSTRACT

This study provides details for the design, preparation of an environmentally friendly, clinically safe and lightweight radiation protective shield made of Gd$_2$O$_3$/epoxy nanocomposite (Gd-nanocomposite) which is proposed as an alternative to traditional toxic lead (Pb)-based aprons for diagnostic X-ray protection. In theory, this particulate nanocomposite can possess significant features of both inorganic particles and organic polymeric matrices. However, in practice, its performance does not simply depend on the sum of the individual contributions of characteristics of the constituent phases but on the interaction of their inner interfaces and the homogeneous dispersion of inorganic particles in the polymer matrix.

The miniaturization of inorganic particles to nanoscale before mixing with an organic matrix has been considered as an effective way to improve the interface of the dispersion phase. Unfortunately, homogeneous dispersion has still not yet been achieved in this type of material due to the coalescence of nanoparticles resulting from the large surface area of nanoparticles and their chemical incompatibility with the matrix. The effect of inter-particle forces arising from adsorbed typical cationic and anionic surfactants on the morphology of the ball milled gadolinium oxide (Gd$_2$O$_3$) is investigated to attain the optimal conditions for interface improvement between Gd$_2$O$_3$ particles and an epoxy matrix.

The experimental outcomes are interpreted in terms of the stabilization and interaction mechanisms of the fine washed Gd$_2$O$_3$ particles (size diameter <1µm) in an aqueous medium under the variation of the surface forces arising from adsorbed surfactants. The point of zero charge or isoelectric point (IEP) of ball milled Gd$_2$O$_3$ particles suspension is at pH 11. In the presence of adsorbed anionic SDS (Sodium dodecyl sulphate), the particles are refined together with numerous 2D nanowire or nano-rod particles at pH ~ 8. In contrast, the coarser particles are found when cationic CTAB (Cetyl trimethylammonium bromide) is used to modify the Gd$_2$O$_3$ surface. This is invoked from organic shell formed by the high adsorbability of negatively charged heads of SDS into the bare positive charge density of the particle. This capping agent acts as (i) a steric barrier preventing the agglomeration or rewelding of the powder during nanoparticle preparation and (ii) an intermediate adhesive that enhances the miscibility of the particle and liquid matrix, thereby improving the particle dispersion in the organic matrix.
Based on the above outcomes, an optimal geometric design of a non-lead based X-ray protective material with lightweight per volume unit is prepared. A plateau with 28-30% increments in the value of fracture toughness ($K_{IC}$ (Mpa.m$^{1/2}$)) is observed with a specific addition of 0.08 to 0.1 volume fraction ($\phi_s$) of SDS-encapsulated Gd$_2$O$_3$ particles in pure epoxy. The same quantity of particles also optimally raises the critical strain energy release rate ($G_{IC}$ (J.m$^{-2}$)) and Young’s modulus ($E$ (MPa)) of epoxy by approximately 22-24% and 18-25% respectively. A 16 mm thick sheet of fabricated filled composite at $\phi_s$ of 0.08 and 0.1 can shield greater than 95% (0.5 mm Pb-equivalence) and 99% (1 mm Pb-equivalence) respectively of a primary X-ray beam in the range of 60-120kVp. At the same X-ray attenuation (99% attenuation), the specimen is 7, 8.5, and 16 times lighter than wood, glass, and concrete respectively. At 0.5 mm Pb-equivalence, the composite also has 4.5-19.4% less weight per unit area than current commercial non-lead products.
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PUBLICATIONS BASED ON THE PRESENT WORK


LIST OF ABBREVIATIONS

AOT: sodium di-2ethylhexyl sulfosuccinate
CPP: critical packing parameter
CTAB: cetyl trimethyl ammonium bromide
CTAC: cetyltrimethylammonium chloride
DDAB: didodecylammonium bromide
DGEBA: diglycidyl ether of bisphenol A
FTIR: fourier transform infrared spectroscopy
Gd(AA)$_3$: gadolinium acrylate
Gd-nanocomposite: Gd$_2$O$_3$ particulate epoxy composite
HBL: hydrophilic-lipophilic balance
IDPI: isophoronediisocyanate
IEP: isoelectric point
NBR: Nitrile butadiene rubber
NPs: nanosized particles
NR: Natural rubber
O/W: oil in water emulsion
O-I composite: organic-inorganic composite
PEEK: poly ether ether ketone
PEG: polyethylene glycol
PVA: polyvinyl alcohol
SDS: Sodium ammonium dodecyl sulphate
SDS-Gd: milled Gd$_2$O$_3$ encapsulated in Sodium ammonium dodecyl sulphate surfactant
SEM: Scanning electron microscope
SPAN 80: sorbitan monooleate
TEM: Transmission electron microscopy
THF: Tetrahydrofuran
TX-100: p-tert octylphenylpolyoxyethylene ether
W/O: water in oil emulsion
XRD: X-ray powder diffraction
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LIST OF SYMBOLS

ϕs: volume fraction of solids (dimensionless)
τy: yield stress (dimensionless)
ζcrit: critical zeta potential (dimensionless)
ζ: zeta potential (dimensionless)
W: Width (m or mm)
T: X-ray transmission (dimensionless)
T: thickness (m or mm)
S: the value displaying on viscometer screen (%)
P: is the load applied (N)
L: Length (mm)
Ksv: vane constant (m³)
KIC: the plane strain critical stress concentration factor (Mpa.m¹/²)
K: the air kerma (kinetic energy released per unit mass of air) (Gy)
k: Debye parameter (dimensionless)
GIC: the critical strain energy release rate (J.m⁻²)
G: Gauge length (mm)
εw: permittivity of water (dimensionless)
E: Young’s modulus (MPa)
D₀: the surface distance between two particles (m)
d₁₀, d₅₀, d₉₀: the particle diameter (µm) in the cumulative distribution at 10 vol.%, 50 vol.%, 90 vol.%
D: surface separation distance between the interacting particles
A₁₂₁: Hamaker constant of the particle in water (zj)
A: X-ray absorbtion proficiency (dimensionless)
a: particle radius (m)
ν: Poisson's ratio
CHAPTER 1: INTRODUCTION

1.1. Research background

Hybrid organic and inorganic materials have been manufactured and in use since the 1950s. Their desirable properties result from combining some distinct characteristics of two or more components [1]. Individual types of inorganic and organic matters show typical properties that are a trade-off between their positive and negative characteristics. As can be seen from Table 1.1 for each characteristic, if one performs well, the other performs poorly and vice versa. The goal of combining both classes of these materials into hybrids is to develop new materials that have the advantages of both. One of the common ways to prepare a hybrid material is a dispersion of micron- or nanosized inorganic particles in an organic matrix. For example, instead of an expensive laminated structure of metallic compounds such as silver oxides or gold, only a small amount of the particles of these substances can be dispersed in polymers to generate O-I materials with the same functional characteristics [2].

<table>
<thead>
<tr>
<th>Property</th>
<th>Polymers or organic materials</th>
<th>Metals or inorganic substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Optical transparency</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Electric insulation ability</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Thermal insulation ability</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>Low(^+)</td>
<td>High</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Fire resistance</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Radiation resistance</td>
<td>Low(^+)</td>
<td>High</td>
</tr>
</tbody>
</table>

In the 1980s, the investigation of nanotechnologies led to the development of particulate hybrid organic-inorganic (O-I) nanocomposites in which the miniaturisation of the inorganic fillers in a polymer could improve the properties of hybrid products[3,4]. Particulate hybrid nanocomposites are divided into two main types, namely reinforced and functional polymer
nanocomposites. Reinforced nanocomposites involving the dispersion of inorganic nanosized particles of titanium compound, clay, calcium carbonate, carbon and glass fiber in different polymer matrices have been used in construction, cryogenic applications, defense, automobile and even in aircraft and aerospace areas [5,6]. Additionally, other metallic compounds with special properties are also combined with polymer matrices to create customized functional particulate nanocomposites. For example, a polyvinyl alcohol (PVA) polymer with fluorescent enhancement from the dispersion of gold nanoparticles provides a contrast in scanning probe microscopy and Raman spectroscopy or a molecular beacon for biomolecular recognition in sensing applications. Another example includes lead compounds/rubber composites that were synthesized to provide radiation shielding properties [7-9].

In this research, a new kind of functional particulate nanocomposite will be synthesized from dispersion of synthesized gadolinium oxide nanoparticles into an epoxy matrix. Because of a special electron configuration, this element can absorb X-ray radiation with high energy and a high degree of penetration. Although metallic lead material or lead/rubber hybrid composites conventionally were used as effective radiation shielding materials in medical practices, compared to gadolinium, it still has limitations on functional properties as well as being toxic [7-9]. Recently, there has been a recognition among manufacturers and users of a trade-off between the economic, health and environmental benefits of using Pb-free X-ray protection aprons that are composed of less toxic metallic powder than Pb imbedded into polymer. This recognition is reflected in an increasing demand for these “green” aprons despite the higher price of the products [10-12]. In this research, gadolinium is proposed as an element to replace Pb for “green” radiation protection. Combination Gd particles with a polymer can vary the mechanical performances of hybrid material from hard and stiffness to flexibility (rubber-like) for the multiple uses. Furthermore, this hopefully reduces the amount of gadolinium material required, and this reduces the weight of the product. Additionally, an effective and inexpensive method is proposed to decrease the cost of preparation.

The organic matrix of gadolinium/polymer nanocomposites may come from many kinds of polymer matrices such as rubber, polyvinyl alcohol (PVA), polyamide, and epoxy resin. In this work, epoxy resin, a kind of thermosetting polymer, will be used as a matrix of nanocomposite. Different kinds of epoxy polymers are effectively employed to disperse inorganic particles to create particulate composites for many applications. For example, nanosized particles such as Al₂O₃, SiO₂, ZnO and BeO, SiC, AlN, Si₃N₄ are dispersed in epoxy to prepare thermally conductive but electrically insulative adhesives or composites [13-
Silica, mica, and calcium carbonate were investigated and administered as fillers to improve the dielectric constant of epoxy thin film composites used in capacitor applications in the electronic packaging industry [16]. A silver/epoxy composite has been proposed as a potential electrical conductive adhesive [15]. Graphene platelet reinforced epoxy has been developed as a high thermal stability material [17-20].

Epoxy resins have valuable characteristics that make them an outstanding matrix such as low cost, low density, effective moisture resistance, chemical, corrosion and heat resistance, high electrical insulation, and good optic properties. More importantly, cured epoxy resin can vary from malleable, ductile, and tough to hard, strong, and brittle matrices. These performances are obtained by controlling the chemical structure of the epoxy oligomer and the curing agent [5,21,22]. Finally, it possesses exceptional processing characteristics such as an absence of byproducts or volatiles during curing reactions, slow shrinkage on cure, curing over a wide temperature range and the control of the degree of cross-linking [5,22]. As a result, epoxy formulations have been utilized in technical applications including protective coatings, adhesives, and as a matrix resins for high strength composites [23]. It is also used to replace metal, wood, and other traditional materials in industrial tooling applications to produce molds, master models, laminates, and castings. Due to improved manufacturing efficiency, the overall cost is lowered and the lead-time is shortened for many industrial processes [16,21,24]. Due to these properties, epoxy resin is chosen in this study as the matrix for an exploration of the properties of nanosized gadolinium oxide particle/epoxy composite.

1.2. Statement of research questions

1.2.1. Research problem

Nanocomposites are not simply physical mixtures which reflect the sum of the individual contributions of the performances of the constituent phases, but their important features are formed by the interaction between them [1,4,25]. Inhomogeneous dispersion can cause poor performance of the final product. The local aggregation and precipitation of the high loading content of the particle phase in continuous phases are usually found in poor disperse composite. Homogeneous dispersion is defined through two parameters: optimal internal interaction and chemical surface compatibility between two phases. To understand the research problem, some definitions and principles of phenomenon will be presented below.

Reducing the size of particles to nanoscale can theoretically increase homodispersion. However, it also increases the internal interaction surface area between the solid and liquid
phases and so increases the risk of particle agglomeration in fabrication process due to poor wettability and chemical compatibility between them [2].

The dispersability of the solid inorganic phase in a high viscous liquid organic phase is explained by wettability which may cause a thermodynamically stable or unstable solid-liquid suspension system. Wetting is the ability of a liquid to maintain contact with a solid surface resulting from intermolecular interactions when they are mixed together. It plays an important role in bonding or the adherence of two different phase materials in one heterogeneous mixture. The degree of wetting is determined by the chemical homogeneity between the particles in the solid phase and the matrix in the liquid phase[2].

A novel methodology of rare earth Gd\textsubscript{2}O\textsubscript{3}/polymer nanocomposites preparation is developed to address the disadvantages of the previous methods. Three main questions are covered:

1. How can nanoparticles of gadolinium oxide (Gd\textsubscript{2}O\textsubscript{3}) be synthesized using a convenient and inexpensive method?

2. How can the dispersion of synthesized particles in the epoxy matrix be improved?

3. How can the X-ray shielding and mechanical properties of the synthesized Gd/epoxy nano composite be characterized?

1.2.2 Research hypotheses

- Unlike current methods using available nanoparticle compounds, this research will start from the early stage of nanoparticle preparation before proceeding to the final stage of nanocomposite synthesis. Conducting these processes sequentially will allow better control of particle dispersion in the polymer matrix and reduce the cost of the process.

- The miniaturization of the dispersed phase to nanoscale improves the total interface area between the two phases leading to markedly improved mechanical and functional performance.

- The selection of suitable particle surfactant for particle surface-modification is expected to enhance chemical compatibility between two phases effectively.

1.3. The objectives of this research

The primary purpose of this research is to develop a novel methodology for the synthesis of a new type of organic/inorganic nanocomposite with high radiation shielding properties.
using Gadolinium compounds as nanosized fillers in an epoxy resin matrix. Other characteristics such as mechanical, chemical, and especially X-ray radiation attenuation properties are be investigated. The research has the following specific objectives:

1) Identify the relationship between synthesis conditions and the Gd$_2$O$_3$ particle size and geometry.

2) Determine the effect of interface compatibility and the dispersion of Gd compound particles in continues phase (water and epoxy) on material properties.

3) Investigate the relationship between X-ray protective properties and mechanical performance.

4) Evaluate the synthesized nanocomposite as a “green”, lightweight, Pb-free material for X-ray protection.

1.4 Scope of the research

To eliminate irrelevancies to the identified objectives and the problems, the scope of the research was limited as follows:

- The study was limited to using only a commercial epoxy system (d= 1.09g/ml) as a matrix of nanocomposite from Struers supplier. Cured material is synthesized from bisphenol A (epichlorhydrin) epoxy resin (number average molecular weight ≤ 700, d= 1.1g/ml) cured by Triethylenetetramine hardener (d= 0.98g/ml).

- The study used bulky gadolinium oxide (Gd$_2$O$_3$) available on the market as a precursor and for further processing.

- The strategy for blending two phases together including ex-situ and in-situ; however, this research just used ex-situ method to avoid unexpected reactions or side products during nanocomposite processing.

1.5. Research significance and innovation.

This research will advance knowledge in the area of hybrid nanocomposite preparation. The current methods are problematic due to inefficient process control, low yield of particle content, and the use of large amounts of organic solvents for interface improvement. By addressing the disadvantages of the existing approaches, a novel methodology this research is able to develop fundamental knowledge regarding ways to combine ideal functional properties with outstanding mechanical performance for particulate nanocomposites. As a
result, many new types of functional polymer/metal nanocomposites that might be used by the manufacturing, medical, mining, transport, and information and communications industries will be developed.

The study also provides essential information for developing an inexpensive and effective method to produce the nanosized gadolinium oxide particles which are employed in many practical applications, particularly in medical practice. More importantly, these consequent processes provide an effective and low cost approach for Gd-nanocomposite preparation that represents a new type of “green” radiation shielding material. These materials will be developed to protect people from dangerous radiation emanated from radioactive medical practices, mining, nuclear reactors, spatial and atomic research, and even the natural environment.

Being is one of 5 countries (China, USA, Brazil, India, Australia) occupying main mining with reserves annually the accumulative amount of 400 tones pure Gadolinium for industry and medical application, Australia takes obviously advantages in commercializing, developing and manufacturing this new “green” material [26-28].
CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

At the author’s request, Chapter 2 has been omitted from this version of the thesis.
CHAPTER 3: RESEARCH METHODOLOGY

3.1. Materials and experimental testing methods

3.1.1. Precursor gadolinium (III) oxide materials

Two precursor gadolinium (III) oxide (Gd$_2$O$_3$) powders with a purity of 99.99% at different diameter were used in this research. The first product purchased from Alfa Aesar (United Kingdom) had a size distribution of $d_{10}=0.28\,\mu m$, $d_{50}=4.34\,\mu m$ and $d_{90}=10.6\,\mu m$. The second one supplied by Sun Chemical Technology (Shanghai) Co., China had a size distribution of $d_{10}=0.26\,\mu m$, $d_{50}=5.50\,\mu m$ and $d_{90}=29.9\,\mu m$.

3.1.2. Size reduction and surface study

A high-energy SPEX8000 mixer/mill with hardened steel balls (12.5 mm diameter) at room temperature was used for Gd$_2$O$_3$ particle size reduction. Size distribution depends on the weight ratio between additives and powder, and milling time.

The zeta potential-pH behavior of mill Gd$_2$O$_3$ particles in water was characterized using a Colloidal Dynamic ZetaProbe operated in the potentiometric titration mode using 0.7 M KOH or 0.7 M HNO$_3$ solutions as the titrants.

The (static) yield stress-pH behavior was characterized using a Brookfield vane viscometer. At each step change of pH, the sample was agitated vigorously with a spatula for at least 15 minutes before pH and yield stress were measured. The maximum torque applied on a rotating (0.4 rpm) vane submerged in the colloid was transformed to the corresponding yield stress

$$\tau = \frac{S\% \times \text{Viscometer constant}}{100 \times K_{sv}}$$ (3.1)

$K_{sv}$ (m$^3$): vane constant Vane 74 KSV=7.5 x 10$^{-7}$m$^3$

Viscometer constant of LVDVII Pro= 6.73 10$^{-05}$NM

Viscometer constant of RVDV-II+ Pro= 0.7187 x 10$^{-3}$ NM

$\tau$(Pa): Yield stress

$S$ (%): the value displaying on viscometer screen

3.1.3. The morphology of synthesized nanoparticles, their dispersion in cured epoxy and fractography of Gd-nanocomposite

41
The size distribution of synthesized \( \text{Gd}_2\text{O}_3 \) particles was determined using a Malvern Mastersizer Microplus Particle Size Analyzer. Their morphology was also characterized by a scanning electron microscope (SEM) (a Zeiss 1555 VPSEM).

The diffuse map, geometry and size of dispersed particles and the fracture surface of synthesized nanocomposite were also observed through the above SEM. This provided information on the effect of homogeneous and mono dispersion on functional properties and mechanical performance.

3.1.4. Chemical characterization of encapsulated nanofillers

The chemical structure of synthesized Gd-nanoparticles was investigated using Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer) and X-ray diffraction (XRD) using a PANalytical EMPYREAN diffractometer with Co Ka radiation (\( \lambda = 0.1789\text{nm} \)).

3.1.5. Mechanical testing method

An Instron 5982 universal testing machine and its extensometer were employed to evaluate the mechanical properties of the \( \text{Gd}_2\text{O}_3 \) particulate composite at different solid volume fractions (\( \phi_s \)) of 0, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14.

Five dumb-bell specimens (Figure 3.1), based on the ASTM standard D638-02a specification of a gauge length of 50 mm and constant thickness of 5±1 mm, were prepared for each composite composition. The crosshead rate of 0.5 mm/min was used for tensile mechanical testing. The elastic deformation of the composite under load (Young’s modulus) was estimated from the gradient of the stress-strain curve. All the mechanical properties reported in this work were averaged from at least four individual tests.

\[
\begin{align*}
\text{W} & - \text{Width of narrow section} & 13 \text{ mm} \\
\text{L} & - \text{Length of narrow section} & 57 \text{ mm} \\
\text{WO} & - \text{Width overall, min} & 19 \text{ mm} \\
\text{LO} & - \text{Length overall, min} & 165 \text{ mm} \\
\text{G} & - \text{Gage length} & 50 \text{ mm} \\
\text{D} & - \text{Distance between grips} & 115 \text{ mm} \\
\text{R} & - \text{Radius of fillet} & 76 \text{ mm} \\
\text{T} & - \text{thickness} & 4 \text{ mm}
\end{align*}
\]

*Figure 3.1. Specimen geometry based on ASTM D638-99 for tensile testing of plastics.*
Five compact tension specimens (Figure 3.2) were also prepared for each composite composition to determine their fracture toughness. Again, a crosshead rate of 0.5 mm/min was employed. The fracture toughness characterizes the material’s resistance to brittle fracture in the presence of a crack. Two important parameters were calculated from the tests, i.e. the plane strain critical stress concentration factor (K_{IC}) and the critical strain energy release rate (G_{IC}), according to ASTM D 5045-99. The compact tension specimen configuration is shown in Figure 3.2. A pre-notch crack made by a band saw should be followed by tapping to create a pop up crack for fracture toughness measurement. The results should be validated by using stress-strain graphs as detailed by the standard. The razor crack length was in the range of 0.45 < a/W < 0.55. The K_{IC} is given by:

\[
K_{IC} = \frac{P \cdot F(x)}{T \cdot W}
\]

(3.2)

where P is the load applied, T, W are the thickness and the width of specimens. F(x) is a function of \( x = \frac{a}{W} \) and is defined as follows.

\[
F(x) = \frac{(2 + x) \cdot (0.866 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1-x)^{3/2}}
\]

(3.3)

The plane strain energy release rate (G_{IC}) can be calculated as follows:
\[ G_{kc} = \frac{(1-\nu^2) \cdot K_{kc}^2}{E} \]  

(3.4)

\( E \): Young’s modulus

\( \nu \): Poisson ratio

3.1.6. Radiation shielding property

The attenuation capacity of specimens was tested at Royal Perth Hospital with beams of six different energies from 60 to 120kVp, the common diagnostic radiographic region. The photon beams from an X-ray tube source of a Mobile DR X-ray unit (GE Optima XR220AMX) were emitted for 25 seconds at a current of 100 mA to suspensions as a radiation shielding screen. The radiation transmitted through samples was collected, recorded and analyzed using a free air chamber of a Non-invasive X-ray Beam Analyser (Unfors Xi R/F & MAM). In this study, the broad beam geometry of a DIN 6857 Standard test method was used: the distance from focal spot to chamber was one metre, and the sample sheets were located directly in front of this indicator. This geometry generates a more accurate attenuation measure because it is based on the total radiation reaching the chamber (contributed by penetrating primary and scattered radiation through materials), and the fluorescence generated by the sample itself [10,70]. The attenuation, \( A \), achieved by the constant thickness Gd-composite at different particle volume fractions at different X-ray energies was defined as follows:

\[ A(\phi_s) = \frac{K(0) - K(\phi_s)}{K(0)} \]  

(3.5)

Where \( K \) is a quantity parameter designed for X-ray shielding calculations called air kerma (kinetic energy released per unit mass of air (grays (Gy)). The values of \( K(0) \) and \( K(\phi_s) \) are the air kerma without shielding, and shielded by specimens with different particle volume fractions, at X-ray energy levels

3.2. Experimental structure:

Outlining the overall experimental structure of the research project was introduced in Figure 3.3. This part then briefly summarizes the works undertaken for each objective. All the
projects were recorded and discussed in journal articles, which are included in Chapters 4 to 7.

Task 1 was achieved in peer-reviewed journal articles included here as Chapters 4 and 5. Chapter 4 provided the relationship between particle size and milling time and the weight ratios of additive NaCl and Gd\(_2\)O\(_3\) precursors. The research also studied the surface characteristics of milled submicronized Gd\(_2\)O\(_3\) in aqueous solution. The dispersed-flocculated behavior of milled submicronized Gd\(_2\)O\(_3\) aqueous slurries was investigated via yield stress and zeta potential versus pH value techniques to stabilize the dispersion. Then well dispersed synthesized Gd aqueous suspensions at different volume fractions at a constant thickness were prepared for initial investigations of radiation attenuation performance. Based on the previous knowledge from Chapter 4, the effect of inter-particle forces arising from adsorbed typical cationic and anionic surfactants on the morphology of ball milled Gd\(_2\)O\(_3\) was researched in Chapter 5. The experimental outcomes were interpreted in terms of the stabilization and interaction mechanisms of fine washed Gd\(_2\)O\(_3\) particles (size diameter <1\(\mu\)m) in an aqueous medium under the variation of surface forces arising from adsorbed surfactant. Two different kinds of surfactants including anionic (sodium dodecyl sulfate (SDS)) and cationic (cetyl trimethyl ammonium bromide (CTAB)) capping agents were used for this study. The results recorded in Chapter 5 proved that the adsorbed organic SDS shell prevented the fine particles from re-welding during the dispersing, annealing route for both nanoparticle preparation and surface modification for particulate composite preparation.

Task 2 was achieved in peer-reviewed journal articles included here as Chapters 6 and 7. In these experiments, nanoscale SDS surface-modified Gd\(_2\)O\(_3\) particles were dispersed in epoxy matrix to produce particulate Gd\(_2\)O\(_3\) epoxy nanocomposite (Gd nanocomposite). The adsorption of sodium dodecyl sulphate (SDS) surfactant on the surface of ultrafine ball milled Gd\(_2\)O\(_3\) based on the effect of inter-particle forces reduces their agglomeration and aggregation in nanoparticle preparation and dispersion in the polymer matrix, thereby improving the radiation attenuation property of this material per unit area. The article included as Chapter 6 explored the relationship between solid volume fractions at a constant thickness of 8 mm and the X-ray protective performance of Gd\(_2\)O\(_3\)/epoxy nanocomposite. The X-ray protective performance versus weight per unit area of these specimens was also evaluated through different levels of X-ray protection in other materials such as concrete, glass, wood and especially other commercial lightweight “lead-free” products.
Work reported in Chapter 7 focused more on the dependence of the mechanical properties (fracture toughness, Young’s modulus and tensile stress) of particulate Gd-nanocomposite on different particle volume fractions. The amount of synthesized Gd$_2$O$_3$ particles (the optimal value of particle volume fraction ($\phi_{s(opt)}$)) in pure epoxy that was required to increase the fracture toughness ($K_{IC}$) value maximally was recorded. An examination of the microstructure of the fracture surface at this $\phi_{s(opt)}$ was employed to observe the dispersion of the filler in the matrix. This is a plausible mechanism for explaining the improved toughness. At a constant value of the volume fraction, the X-ray attenuation proficiency depends on the thickness of material. Based on the mechanical testing result, filled composite at $\phi_{s(opt)}$ at 8 mm thickness and 16 mm thickness was fabricated to investigate X-ray attenuation proficiency. Then, the X-ray protective performance versus weight per unit area of specimens with $\phi_{s(opt)}$ at different thicknesses was compared to that of wood, glass, concrete, and current commercial non-lead products.
Figure 3.3. Scheme of experimental structure with tasks and sub objectives

**Task 1:** Synthesis of nanoparticles and surface modification

- Identify relationship of additive, time and other conditions on sizes of milled Gd$_2$O$_3$ particles
- Research surface chemistry and rheology of ball milled Gd particle
- Study the influence of surfactants on the particle properties

**Task 2:** Synthesis of nanocomposites

- Analysis microstructure of nanocomposites
- Investigate mechanical properties of nanocomposites
- Evaluate X-ray protection properties of nanocomposites
Due to copyright reasons, Chapter 4 has been omitted from this version of the thesis.

Chapter 4 has been published as:


The green open access version of the journal article is available [here](https://doi.org/10.1016/j.colsurfa.2016.04.058).
CHAPTER 5: A NOVEL APPROACH FOR THE PREPARATION OF
NANOSIZED Gd2O3 STRUCTURE: THE INFLUENCE OF SURFACE FORCE ON
THE MORPHOLOGY OF BALL MILLED PARTICLES

Due to copyright reasons, Chapter 5 has been omitted from this version of the thesis.

Chapter 5 has been published as:


The green open access version of the journal article is available here.
At the author’s request, Chapter 6 has been omitted from this version of the thesis.
Due to copyright reasons, Chapter 7 has been omitted from this version of the thesis.

Chapter 7 has been published as:

doi: 10.1016/j.colsurfa.2017.09.038

The green open access version of the journal article is available here.
8.1. Thesis Summary

X-ray protective garments are typically comprised of lead-based materials, which are toxic to both people and the environment. Developing alternative lightweight radiation shielding materials is a priority for protecting people working with radiation. Gadolinium, with an electron configuration typical of radiation shielding elements, is proposed as a non-toxic replacement for lead. This study has provided new insights into the potential for a gadolinium suspension for replacing lead and proposes an effective preparation method. Inexpensive coarse Gd$_2$O$_3$ powder being 10-15 times less expensive than nano one is employed as a starting material. Additionally, cheap and simple ball milling method are employed then, so the total cost of processing reduce considerably.

Firstly, submicron Gd$_2$O$_3$ particles with a size distribution of $d_{10}$~0.23, $d_{50}$~0.38 and $d_{90}$~0.8µm are generated through a conventional and cost-effective ball milling method over 70 minutes with the mechanical support of a NaCl additive (1:1.5 Gd$_2$O$_3$:NaCl). The dispersed-flocculated behaviour of Gd$_2$O$_3$ and thus the uniformity of suspension is determined by pH and the solid volume fraction. Flocculation or domination of the attractive particle force of Gd$_2$O$_3$ in an aqueous medium is investigated in the pH range from 9 to 12.5, in which maximum flocculation occurred at pH of 11. The point of dispersed-flocculated transition or the balanced state of attractive and repulsive forces in the slurry, which determines the stable dispersion of Gd$_2$O$_3$ aqueous suspensions, is about pH 9. Flocculated performance of the given particles is also affected by the solid volume fraction ($\phi_s$) which strongly depends on its physical properties, such as the size, shape, and nature of the particles. Compared with other metal oxides at similar particle size, van der Waals attractive force of Gd$_2$O$_3$ particles in suspensions are unusually sensitive to the change of the volume fraction. This is due to the large variation in the shape and nature of the particles as characterized by the Hamaker constant. Based on the above information, the uniformly dispersed Gd$_2$O$_3$ aqueous suspensions prepared in the next stage provides the highly effective X-ray radiation shielding performance is required for a potential non-Pb based radiation attenuator.

This study also investigates the effect of inter-particle forces arising from adsorbed typical cationic and anionic surfactants on the morphology of ball milled gadolinium oxide (Gd$_2$O$_3$) for nano particle preparation and surface modification. The experimental outcomes are
interpreted in terms of the stabilization and interaction mechanisms of fine washed \( \text{Gd}_2\text{O}_3 \) particles (size diameter <1µm) in an aqueous medium under the variation of surface forces arising from adsorbed surfactant. After ball milling and washing, the point of zero charge or isoelectric point (IEP) of \( \text{Gd}_2\text{O}_3 \) particles suspension is at pH 11 where its maximum yield stress is observed. Because of hydrophobic interaction, the maximum yield stress of the Gd aqueous suspension increases by 30 times as the sodium dodecyl sulfate (SDS) is adsorbed on the particle surface and its IEP shifts slightly to a lower pH. Using cetyl trimethyl ammonium bromide (CTAB), the yield stress also increases by a much smaller extent (three times) and shifts to a higher pH of ~ 12.5. Without surfactants, the microstructure of dried \( \text{Gd}_2\text{O}_3 \) displays the coarse particles of various shapes, i.e. rod, spherical, and cubic shapes. This indicates that the milled particles remain agglomerated in dispersion. In the presence of adsorbed anionic SDS, the particles are refined together with numerous 2D nanowire or nano-rod particles at pH ~ 8. In contrast, coarser particles with absence of nano-rods are found when cationic CTAB is used to modify the \( \text{Gd}_2\text{O}_3 \) surface at a pH of about 12.5. The SDS-modified suspension exhibits a much higher yield stress, which results from finer particles in suspension. This is invoked from an organic shell formed by the high adsorbability of negatively charged heads of SDS into the bare positive charge density of the particle.

The adsorption of sodium dodecyl sulphate (SDS) surfactant on the surface of ultrafine ball milled \( \text{Gd}_2\text{O}_3 \) based on the effect of inter-particle forces reduces the agglomeration and aggregation in nanoparticle preparation and dispersion in the polymer matrix, thereby improving the attenuation property of this material per unit area. The relationship between X-ray attenuation of the synthesized particulate / epoxy composite and the particle volume fraction is investigated as follows: While a 8 mm thickness of Gd-nanocomposite with volume fractions \( (\phi_s) \) of 0.10, 0.12, and 0.14 can reduce transmitted X-ray intensity by about 93-99%, a 16 mm composite thickness \( (\phi_s=0.12) \) can achieve more than 99% protection in the energy range of 60-120kVp. These specimens show comparable attenuation efficiency with 0.25, 0.35, 0.5, and 1 mm thickness of pure lead sheets that are normally used for radiology protection. The weight per unit area of Gd-nanocomposite \( (\phi_s=0.14, \ 8 \ \text{mm thickness}) \) is 6-20 times lighter than concrete, glass, and wood at the same attenuation performance (97-99% attenuation). The X-ray protective performance vs weight per unit area of this specimen is also evaluated through other commercial lightweight “lead-free” products. This specimen, with 36-48% less weight, shows better attenuation proficiency than 3 other commercial non-Pb composite products in the energy range above 73kVp.
The relationship between the quantities of synthesized core shell Gd$_2$O$_3$ added to epoxy matrix and the mechanical and X-ray attenuation properties of particulate epoxy composite is studied in this research. As a result, an optimal geometric design of non-lead-based X-ray protective material with reasonable weight per volume unit was prepared. A plateau with a 28-30% increment of fracture toughness ($K_{IC}$) value was observed with the addition of 0.08 to 0.1 volume fraction ($\phi_s$) of Gd$_2$O$_3$ particles in pure epoxy. The same quantity of particles also optimally raises the critical strain energy release and the modulus of the epoxy about 22-24% and 18-25% respectively. An examination of the microstructure of the fracture surface shows relatively uniform nanoparticle dispersion, which is a plausible mechanism for explaining the improved toughness. The improved nanoparticle dispersion in the matrix enhanced both the mechanical and functional properties of the epoxy composite. A 1.6 cm thick sheet of fabricated filled composite at volume factions of 0.08 and 0.1 can shield more than 95% (0.5 mm Pb equivalence) and 99% (1 mm Pb equivalence) of irradiated X-ray beam. At the same X-ray attenuation (99% attenuation), the specimen is 7, 8.5, and 16 times lighter than wood, glass, and concrete respectively. The composite at 0.5 mm Pb-equivalence also has 4.5-19.4% less weight per unit area than current commercial non-lead products.

This research successfully provides an optimal design and preparation process for a new “green” material for radiation shielding.

8.2. Future work

A Gd atom is both a good X-ray shielding material and a thermal neutron absorption material. This research has now shown that Gd also possesses excellent X-ray shielding properties. The high-energy neutron shielding properties of this material will be evaluated in the future.

Additionally, depending upon the nature of the applications, it is possible to change the Gd-epoxy from being stiff to being elastomeric by tailoring the structure of the epoxy and the crosslinking agent [78-80]. The material in this research is rigid but it is just pre-commercial radiation shielding material, so the elasticity of the materials will be an area of future research to commercialize products.

For potential applications, the Gd-epoxy formulation can be used as a coating or an adhesive to improve the X-ray attenuation proficiency of permanent structures such as the walls, floors, and rooves of a radiographic x-ray room and other items in this room. It also can be used as a portable X-ray shielding screen or the shell structure of an X-ray radiator to
restrict undesirable radiation or radiation leakage. In addition, it can be used for wearable aprons or garments which require a flexible, tough, commercial epoxy formulation such as epiclon exa-4816 as the epoxy matrix. By the way, special epoxy formulations with Gd particles can be used as coated fabrics for, good wear resistance, good hydrolytic resistance, and good ultraviolet light resistance and X-ray attenuation in the textiles industry [230].
REFERENCES


[182] Y. K. Leong, "Yield stress and zeta potential of nanoparticulate silica dispersions under the influence of adsorbed hydrolysis products of metal ions—Cu (II), Al (III) and Th (IV)," J. Colloid Interface Sci., vol. 292, no. 2, pp. 557-566, 2005.


APPENDIX A: STANDARD OPERATION PROCEDURE OF ZETA POTENTIAL ANALYSIS

1. Preparing a slurry with particles concentration normally from 3% to 5%

\[
CP\% = \frac{m_{\text{particle}}}{m_{H_2O} + m_{\text{particle}}}
\]

\[
V_{\text{vessel}} = \frac{m_{\text{particle}}}{D_{\text{particle}}} + \frac{m_{H_2O}}{D_{H_2O}} \approx 260ml
\]

Density of Gadolinium oxide (\(D_{\text{particle}}\)) = 7.401 g/ml

Density of water (\(D_{H_2O}\)) = 1 g/ml

Weight \(m_{\text{particle}}\) (g) and then add \(m_{H_2O} = 260 - \frac{m_{\text{particle}}}{D_{\text{particle}}}\) (g). This slurry will be sonicated by Branson Digital B30 sonifier, 65-70% amplitude and then transferred into zeta probe clean container.

The zeta potential of around 2-5wt% suspensions was measured using Colloidal Dynamic Zeta Probe equipment at different pH condition. The pH of the suspension was changed by an addition of 0.7M KOH or 0.7M HNO3, via auto-control system.

2. Turn on ZetaProbe (Colloidal Dynamic) and calibrate if necessary. Put the slurry into the machine and turn on the stirrer with the speed from 200-250 rpm. Cleaning the pH probe and put it in the slurry and check the value of pH, conductivity (\(\mu\)s/cm).

3. Click on the icon (Zp polar) on computer desktop and then the zeta probe main panel will appear as follow ➔ press on “Data logging”
4. On main panel of “Data logging series”, the name of file will be put on “file name prefix” for example “LYLA-Gd-ball milling” → click on “Particle and Solvent Properties”

5. On main panel of “Particle and Solvent Properties”, click on “Look up” button of particle properties section. Then the Particle look up panel will be displayed → On “particle ID” choose one of suitable system from the list here we choose Fe₂O₃ → press Ok
6. After step 5 the panel of “Particle and Solvent Properties” will reappeared→ change the value of Particle density, Particles Dielectric Constant, Particle Concentration wt% as follow

Particle density=7.401g/ml

Particles Dielectric Constant= 11.4 [231]

Particle Concentration wt% (from step 1)
→ Press “Ok”

7. Go to “Data logging series” and press measure

8. After finish the measure stage, the value of pH, Volume and zetapotential will be recorded. If

- Zeta potential value is >0 → using NaOH or KOH 0.7M to titrate
- Zeta potential value is <0 → using HNO₃ 0.7M to titrate

9. Go back to main panel → click on “Titration”
10. The panel “Titration Input Panel” appears → click to choose “Potentiometric” → named the samples in “Filename Prefix” → press on “Particle and Solvent Properties” button to check information → click “Next” →

11. Put the pipette probe in slurry to prepare for titration process.

12. On “Potentiometric Series Titration” panel, put the name of titrated solvent in “Acid Id” and “Base Id” and value of Acid and Base concentration. From step 8 put the value of sample volume in the blank.

13. Check the pH value from machine put the “start pH” value in the blank → put the value of “End pH” as you plan → put “pH increment” value on the box (normally 0.5) → press “Titrate”
APPENDIX B: X-RAY ATTENUATION EFFICIENCY OF SPECIMENS

<table>
<thead>
<tr>
<th>Beam energy (kVp)</th>
<th>X-ray attenuation efficiency of 8 mm thickness at different volume fractions</th>
<th>X-ray attenuation efficiency of 16 mm thickness at different volume fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.18417 0.859 0.9281 0.9455 0.9679 0.9807 0.985</td>
<td>0.9633 0.9867 0.9922 0.9966 0.9984 0.9994</td>
</tr>
<tr>
<td>70</td>
<td>0.18208 0.8467 0.9215 0.9408 0.9634 0.9782 0.983</td>
<td>0.9586 0.9846 0.9913 0.9961 0.9981 0.9993</td>
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<td>0.17587 0.8314 0.9125 0.9344 0.9602 0.9759 0.981</td>
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</tr>
<tr>
<td>120</td>
<td>0.14892 0.7594 0.857 0.8874 0.9251 0.952 0.961</td>
<td>0.9179 0.9632 0.9767 0.9878 0.9929 0.9964</td>
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<td>70</td>
<td>0.18208 0.8467 0.9215 0.9408 0.9634 0.9782 0.983</td>
<td>0.9586 0.9846 0.9913 0.9961 0.9981 0.9993</td>
</tr>
<tr>
<td>80</td>
<td>0.17587 0.8314 0.9125 0.9344 0.9602 0.9759 0.981</td>
<td>0.9544 0.9832 0.9903 0.9959 0.9979 0.9992</td>
</tr>
<tr>
<td>90</td>
<td>0.16569 0.8154 0.9012 0.9267 0.9546 0.9738 0.979</td>
<td>0.9486 0.9807 0.9889 0.9951 0.9977 0.999</td>
</tr>
<tr>
<td>100</td>
<td>0.15932 0.7985 0.8885 0.9148 0.9464 0.9689 0.975</td>
<td>0.9405 0.9765 0.9862 0.9938 0.9968 0.9986</td>
</tr>
<tr>
<td>110</td>
<td>0.15935 0.7793 0.874 0.9023 0.9367 0.9609 0.969</td>
<td>0.9302 0.971 0.9821 0.9915 0.9953 0.9978</td>
</tr>
<tr>
<td>120</td>
<td>0.14892 0.7594 0.857 0.8874 0.9251 0.952 0.961</td>
<td>0.9179 0.9632 0.9767 0.9878 0.9929 0.9964</td>
</tr>
</tbody>
</table>
APPENDIX C: X-RAY ATTENUATION EFFICIENCY OF Pb SHEETS

<table>
<thead>
<tr>
<th>Beam energy (kVp)</th>
<th>X-ray attenuation efficiency of pure Pb at different thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>60</td>
<td>0.97403</td>
</tr>
<tr>
<td>65</td>
<td>0.962434</td>
</tr>
<tr>
<td>70</td>
<td>0.948651</td>
</tr>
<tr>
<td>75</td>
<td>0.93345</td>
</tr>
<tr>
<td>80</td>
<td>0.917615</td>
</tr>
<tr>
<td>85</td>
<td>0.901452</td>
</tr>
<tr>
<td>90</td>
<td>0.885307</td>
</tr>
<tr>
<td>95</td>
<td>0.869092</td>
</tr>
<tr>
<td>100</td>
<td>0.853315</td>
</tr>
<tr>
<td>105</td>
<td>0.837324</td>
</tr>
<tr>
<td>110</td>
<td>0.821643</td>
</tr>
<tr>
<td>115</td>
<td>0.806107</td>
</tr>
<tr>
<td>120</td>
<td>0.790595</td>
</tr>
</tbody>
</table>

Density of the materials (g/cm³)

<table>
<thead>
<tr>
<th>Gd₂O₃</th>
<th>dionized water</th>
<th>lead</th>
<th>wood</th>
<th>concrete</th>
<th>glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>1</td>
<td>11.34</td>
<td>0.64</td>
<td>2.4</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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### APPENDIX D: THE THICKNESS OF LEAD, WOOD, CONCRETE AND GLASS AT CORRESPONDING RADIATION ATTENUATION EFFICIENCY OF SPECIMENS

<table>
<thead>
<tr>
<th>Beam energy (kVp)</th>
<th>The thickness of other materials at corresponding radiation attenuation efficiency of 10 mm thick Gd$_2$O$_3$ aqueous suspension ($\phi_s = 0.082$) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lead</td>
</tr>
<tr>
<td>50</td>
<td>0.152</td>
</tr>
<tr>
<td>60</td>
<td>0.173</td>
</tr>
<tr>
<td>70</td>
<td>0.229</td>
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<tr>
<td>80</td>
<td>0.295</td>
</tr>
<tr>
<td>90</td>
<td>0.354</td>
</tr>
<tr>
<td>100</td>
<td>0.400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Beam energy (kVp)</th>
<th>The thickness of other materials at corresponding radiation attenuation efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lead</td>
</tr>
<tr>
<td>60</td>
<td>0.244768161</td>
</tr>
<tr>
<td>70</td>
<td>0.334323351</td>
</tr>
<tr>
<td>80</td>
<td>0.436952022</td>
</tr>
<tr>
<td>90</td>
<td>0.543922594</td>
</tr>
<tr>
<td>100</td>
<td>0.606920232</td>
</tr>
<tr>
<td>110</td>
<td>0.60884292</td>
</tr>
<tr>
<td>120</td>
<td>0.582032153</td>
</tr>
<tr>
<td>lead</td>
<td>wood</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>60</td>
<td>0.395031923</td>
</tr>
<tr>
<td>70</td>
<td>0.548337063</td>
</tr>
<tr>
<td>80</td>
<td>0.756265055</td>
</tr>
<tr>
<td>90</td>
<td>0.946322777</td>
</tr>
<tr>
<td>100</td>
<td>1.060136867</td>
</tr>
<tr>
<td>110</td>
<td>1.038701865</td>
</tr>
<tr>
<td>120</td>
<td>0.944095537</td>
</tr>
</tbody>
</table>
APPENDIX E: WEIGHT-THICKNESS Gd$_2$O$_3$/EPoxy Nanocomposite (g/cm$^2$) AT DIFFERENT PARTICLE VOLUME FRACTIONS

<table>
<thead>
<tr>
<th>Volume fraction $\phi_s$</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.14</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 mm</td>
<td>Weight-thickness Gd$_2$O$_3$ (g/cm$^2$)</td>
<td>0.231</td>
<td>0.346</td>
<td>0.462</td>
<td>0.578</td>
<td>0.693</td>
</tr>
<tr>
<td>Weight-thickness Epoxy (g/cm$^2$)</td>
<td>0.838</td>
<td>0.821</td>
<td>0.804</td>
<td>0.787</td>
<td>0.770</td>
<td>0.750</td>
</tr>
<tr>
<td>Weight-thickness Gd$_2$O$_3$/epoxy composite (g/cm$^2$)</td>
<td>1.069</td>
<td>1.167</td>
<td>1.265</td>
<td>1.365</td>
<td>1.463</td>
<td>1.577</td>
</tr>
<tr>
<td>16 mm</td>
<td>Weight-thickness Gd$_2$O$_3$ (g/cm$^2$)</td>
<td>0.461</td>
<td>0.693</td>
<td>0.923</td>
<td>1.155</td>
<td>1.386</td>
</tr>
<tr>
<td>Weight-thickness Epoxy (g/cm$^2$)</td>
<td>1.676</td>
<td>1.642</td>
<td>1.607</td>
<td>1.574</td>
<td>1.540</td>
<td>1.501</td>
</tr>
<tr>
<td>Weight-thickness Gd$_2$O$_3$/epoxy composite (g/cm$^2$)</td>
<td>2.137</td>
<td>2.334</td>
<td>2.530</td>
<td>2.729</td>
<td>2.926</td>
<td>3.153</td>
</tr>
</tbody>
</table>