

EFFECTS OF PROCESSING ON MECHANICAL, MORPHOLOGICAL, AND NEUTRON-SHIELDING PROPERTIES OF B₂O₃/UHMWPE COMPOSITES

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Abstract

Sufficient and high-quality neutron-shielding materials are necessary for safety of radiation-related workers from the risk of excessive neutron exposure. As a result, This work investigated effects of two different processes, namely a combination of extrusion and compression molding (two-step method) and a compression molding (one-step method), used to produce neutron-shielding sheets from Ultra High Molecular Weight Polyethylene (UHMWPE) with the addition of 50 wt% boron oxide (B₂O₃) on mechanical, morphological, and neutron-shielding properties. The results indicated that, for a pristine UHMWPE, the neutron-shielding properties from both processes were not noticeably different. However, with the addition of 50 wt% B₂O₃, neutron-shielding properties were significantly enhanced, with the values obtained from the two-step method considerably higher than the ones from the one-step method. The improvement in the neutron-shielding properties in samples processed with the two-step method, which was also the case in overall mechanical properties, were mostly due to better dispersion of the B₂O₃ particles from the additional extrusion step. Furthermore, morphological images obtained using SEM revealed that less agglomeration of B₂O₃ particles was found in the UHMWPE composites processed using the two-step method. This contributed in part to better phase continuity of the UHMWPE matrix and, consequently, higher mechanical and neutron-shielding properties.

Keywords: UHMWPE, boron oxide, mechanical properties, extrusion, compression, morphology

Introduction

Neutron radiation has been widely used in several applications, as follows: neutron radiography, which is a non-destructive technique for analyzing structures of a sample (Witkowska *et al.*, 2005), Boron Neutron Capture Therapy (BNCT) technique, which is based

on a neutron absorption mechanism between boron-10 (¹⁰B) and irradiated thermal neutrons that produces high-energy alpha particles capable of curing tumor and cancer cells (Barth *et al.*, 1992), and energy generation in nuclear power plants, which relies on

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the released energy from a fission reaction involving thermal neutrons and nuclear fuels (Uranium-235 or ²³⁵U) (Bakr *et al.*, 2019). Despite having considerable benefits, neutron exposure has greater negative biological effects on organs and tissues than charged particles and energetic photons do since neutrons could interact and severely damage functionality of living cells that have high water contents by negatively altering DNA, resulting in both acute and chronic symptoms (ICRP, 2003). Examples of the effects from neutrons in human include the reduction in production of blood cells, severe skin burn, and increases in risks of cancer and death (National Research Council, 2006). Hence, in order to increase and to promote safety of radiation-related personnel and the general public, the utilization of adequate and efficient neutron-shielding materials, which is one of the three main radiation safety principles named “As Low As Reasonably Achievable” or “ALARA” along with time and distance management, is mandatory in all nuclear facilities.

As mentioned, the utilization of neutron-shielding materials is a necessary tool to reduce the risk of health hazards associated with excessive neutron exposure. A common neutron-shielding material usually contains high contents of light elements/compounds such as hydrogen atoms in water (H₂O), concrete, and polymers (polyethylene (PE) and natural rubber (NR)). In principle, the reduction of neutron energy in these hydrogen-rich materials primarily relies on a cascaded elastic scattering between incoming fast neutrons and light elements in the materials, which results in the energy of neutrons being continuously transferred to light elements until their energy becomes negligible. Specifically, materials based on high-density polyethylene (HDPE) is widely utilized in neutron-shielding applications at the present, with its preferable properties in exceptional strength, high durability, wide availability, and relatively low cost. Additionally, another type of PE, namely ultra high molecular weight polyethylene (UHMWPE), is gaining great interest from global radiation users to be developed as advanced neutron-shielding materials due to its distinguishing properties including high toughness, high impact strength, great resistance to corrosive chemicals, being nontoxic, low moisture absorption, and high hydrogen content. As a result, UHMWPE consequently presents itself as a potential state-of-the-art neutron-shielding candidate for specific applications requiring extra properties beyond the usual HDPE products (Manley, 2016).

Despite being able to reduce neutron energies, UHMWPE alone is not the most effective neutron shielding material since considerably large numbers

of scattering interaction are required to reduce substantial amount of neutron energies. This drawback of UHMWPE is that total neutron cross section of hydrogen nuclei in UHMWPE is relatively low (~0.33 barns for the neutron absorption cross section and ~82.02 barns for the total neutron scattering cross section), leading to a low probability of interaction with neutrons and, hence, requiring greater thickness of materials to thermalize and shield all neutrons. To enhance the neutron-shielding properties, a compound containing high neutron-absorption cross-section elements such as boron oxide (B₂O₃) and samarium oxide (Sm₂O₃) could be added to UHMWPE such that the initiation of neutron-absorption mechanism could be formed. Since neutron absorption is far more effective in neutron attenuation than scattering, less numbers of neutron interaction are needed and the shielding ability is consequently improved (Toyen and Saenboonruang, 2017).

However, despite the high potential of B₂O₃/UHMWPE composites in neutron-shielding applications, the process of forming the composites becomes another challenge in producing high-qualified and well-dispersed neutron shields as the process of UHMWPE is usually limited to only dry-mixing (a one-step method) due to the extremely high viscosity of UHMWPE that prevents the use of conventional melt-mixing method (Wood *et al.*, 2011). This limitation in the process could result in poor interfacial compatibility and poor filler dispersion, which subsequently lead to lower mechanical strength of the material when B₂O₃ is added to the matrix. To overcome this constraint, an extrusion step with the help of paraffin oil as a plasticizer to reduce the viscosity of UHMWPE could be introduced in the mixing processes before being compression molded (a two-step method) to form final test specimens. This additional extrusion step would increase the mobility of the long UHMWPE molecular chains and allowing better penetration of B₂O₃ particles into UHMWPE grains, resulting in a potential improvement in the dispersion of filler and overall mechanical strength of the composites (Toyen *et al.*, 2019).

As previously mentioned, it is clear that the development of high quality neutron-shielding material is important and the processes to form the materials play crucial roles in defining properties of the materials, this work aimed to explore the potential of utilizing B₂O₃ as a neutron-absorbing filler in the UHMWPE composites by thorough investigation on mechanical, morphological, and neutron-shielding properties of B₂O₃/UHMWPE composites that were processes/formed using two different methods (one-step vs. two-step methods). The results obtained from this work would be useful

not only to academic researchers who are interested in scientific information but also to industrial partners who seek suitable processing methods for UHMWPE based products.

Materials and Methods

UHMWPE (U310 grade) was kindly supplied by IRPC Public Co., Ltd., Thailand, with an average molecular weight of 3×10^6 g/mol, a density of 0.94 g/cm^3 , and an average particle size of $170 \text{ }\mu\text{m}$. B_2O_3 (99.99%) was purchased from Richest Group, Shanghai, China, with an average particle size of $\sim 88.2 \text{ }\mu\text{m}$, measured using a scanning electron microscope (SEM) (TM4000 Plus; Hitachi; Japan) and the particle size was determined using the ImageJ software version 1.50i as shown in Figure 1. Paraffin oil (commercial grade) was used as a plasticizer to reduce the viscosity of the UHMWPE during processing and was purchased from Facobis Co., Ltd., Thailand, Commercial grade n-hexane (100% w/w) was purchased from Chemipan Corporation, Thailand, and was used as the extraction solvent to limit the degradation in the mechanical properties by the paraffin oil in the composites.

Preparation of Pristine UHMWPE and B_2O_3 /UHMWPE Composites

For a two-step method, UHMWPE, B_2O_3 (50%wt.), and paraffin oil (10 wt% of UHMWPE) were initially hand-mixed and, later pre-mixed in a high-speed mixer (LMXS; Lab Tech Engineering; Thailand) for 1 min. The mixture was compounded using a twin-screw extruder (CTW 1000C; HAAKE Rheomax; Germany) with a barrel temperature of 170°C - 185°C from the feed zone to die zone and a screw speed of 40 rpm. Then, the extrudate was pelletized into granules and the remaining paraffin oil was extracted in n-hexane solvent for 24 h. Extracted extrudates were dried in a hot oven (GT-7017-L; Gotech Testing Machines Inc.; Taiwan)

at 80°C for 14 h to remove the volatile n-hexane. Finally, the extrudate was molded to form testing specimens at 185°C and a pressure of 15 MPa for 14 min using a hot press (LP-20M LMXS; Lab Tech Engineering; Thailand). For a one-step method, UHMWPE and B_2O_3 were initially hand-mixed and pre-mixed in the high-speed mixer and immediately fabricated in the hot press. The overall experimental design is shown in the experimental flow diagram (Figure 2).

Neutron Shielding Properties

Composite samples ($18 \text{ cm} \times 18 \text{ cm} \times 0.5 \text{ cm}$) were used to investigate the neutron shielding ability using a 300 mCi $^{241}\text{Am/Be}$ neutron source enclosed in a paraffin cylinder. A stack of 5 cm high density polyethylene (HDPE) sheets was used as a moderator to thermalize fast neutrons to thermal neutrons. A ^3He -filled neutron detector having 60% thermal neutron detection efficiency was used to detect thermal neutron intensity before the shielding sample (I_0) and after the shielding sample (I). Equation 1-4 were used to calculate important neutron properties of the samples, which included the neutron transmission ratios (I/I_0), linear attenuation coefficient (μ), half-value layer (HVL), and tenth-value layer (TVL), respectively. The reported values were calculated by averaging the measurements of three samples.

$$I = I_0 e^{-\mu x} \quad (1)$$

$$\mu = \frac{-\ln(I/I_0)}{x} \quad (2)$$

$$\text{HVL} = \frac{\ln(2)}{\mu} \quad (3)$$

$$\text{TVL} = \frac{\ln(10)}{\mu} \quad (4)$$

where μ is the linear attenuation coefficient and x is the thickness of the composites. It should be noted the thickness of all samples was fixed at 5 mm for

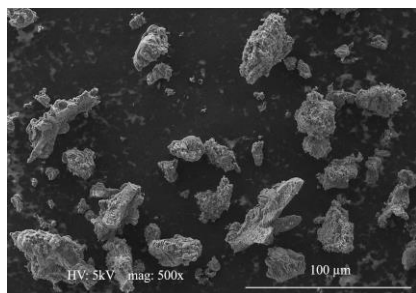


Figure 1. SEM image of B_2O_3 powder ($\times 500$ magnification)

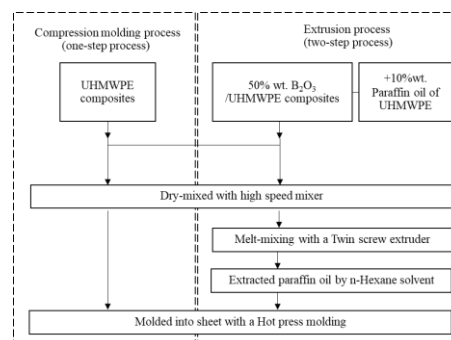


Figure 2. Experimental flow diagram for the preparation of B_2O_3 /UHMWPE composites using two different methods

all neutron-shielding measurement and the tests were carried out at the Thailand Institute of Nuclear Technology (TINT) using the experimental set-up shown in Figure 3.

Mechanical Properties

The tensile properties were determined using a universal testing machine (Autograph AG-I 5 kN; Shimadzu, Japan) with a cross-head speed of 100 mm/min following the ASTM D638-14 standard testing. The testing specimens had a gauge length of 25 mm and a thickness of 1 mm. Hardness (Shore D) was tested according to the ASTM D2240-03 standard testing using a hardness durometer (Teclock GS-719G; Japan). The reported mechanical properties were calculated by averaging the measurements of five samples.

Scanning Electron Microscopy (SEM) Studies

All samples were fractured in a brittle manner using liquid nitrogen before using scanning electron microscopy (SEM) at 5-10 kV accelerating voltage to evaluate the dispersion and distribution of the filler in the UHMWPE composites.

Results and Discussion

Neutrons Shielding Properties

As shown in Table 1, which shows the neutron-shielding properties of pristine UHMWPE and 50 wt% B_2O_3 /UHMWPE composites, the results indicated that the pristine UHMWPE from both processing methods had similar neutron attenuation properties. These behaviors were observed because the shielding mechanism of the pristine UHMWPE mostly relies on the inefficient elastic scattering between neutrons and hydrogen atoms in UHMWPE, making both samples poor neutron absorbers with only 2% reduction in the initial neutron intensity for 5 mm samples as the samples required large numbers of scattering to sufficiently reduce neutron energy (Toyen *et al.*, 2019). However, with the addition of 50 wt% B_2O_3 into UHMWPE, the neutron shielding ability of the composites was significantly improved in both samples as seen by much larger reduction of more than 58-60% in I/I_0 , and subsequently the decreases (increase) in HVL and TVL (μ) values. This observed improvement was due to the addition of B_2O_3 , which contains ^{10}B atoms having high neutron absorption cross-section of 3,840 barns in comparison of only 82 barns in hydrogen atoms (Lee *et al.*, 2014), that significantly increased probability of neutrons being absorbed and attenuated by the composites (Poltabtim *et al.*, 2019). The scheme representing different shielding

mechanisms of pristine UHMWPE and B_2O_3 /UHMWPE composites are shown in Figure 4, which illustrated more neutrons transmitted through a pristine UHMWPE (Figure 4(a)) than through B_2O_3 /UHMWPE composites (Figures 4(b) and 4(c)).

Another interesting result of neutron shielding properties shown in Table 1 is that the B_2O_3 /UHMWPE composites processed using the two-step method had a slightly higher ability in neutron attenuation than the samples using the one-step method as seen by higher (lower) values of μ (I/I_0 , HVL , and TVL) in B_2O_3 /UHMWPE composites. The differences in neutron attenuation abilities between the two samples were due to obvious

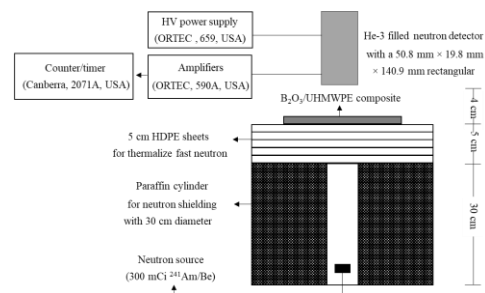


Figure 3. Set-up for thermal neutron shielding test of B_2O_3 /UHMWPE composites

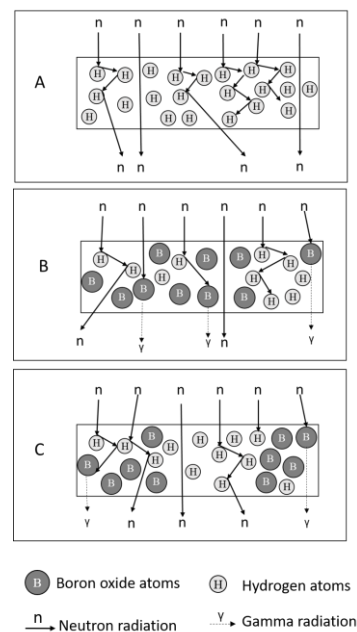
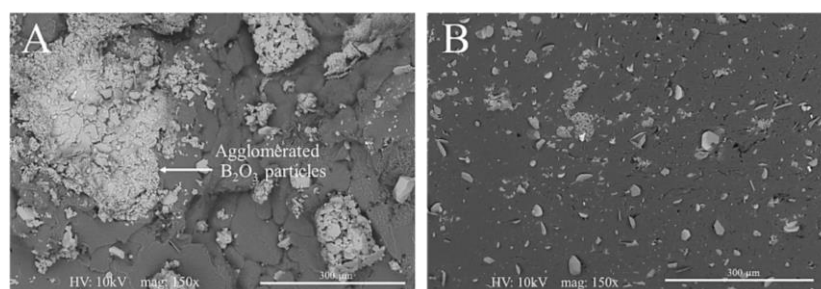


Figure 4. Schematic diagrams of neutron interaction for (A) pristine UHMWPE, (B) 50 wt% B_2O_3 /UHMWPE composites processed using a two-step method, and (C) 50 wt% B_2O_3 /UHMWPE composites processed using a one-step method

Table 1. Neutron shielding and mechanical properties of pristine UHMWPE and 50 wt% B₂O₃/UHMWPE composites

Specimen	Neutron shielding properties			
	I/I_0	μ (cm ⁻¹)	HVL (cm)	TVL (cm)
UHMWPE (one-step)	0.98±0.01	0.03±0.01	24.72±8.47	82.14±28.14
UHMWPE (two-step)	0.98±0.01	0.04±0.01	21.31±7.20	70.78±23.90
B ₂ O ₃ /UHMWPE (one-step)	0.42±0.01	1.71±0.01	0.40±0.23	1.34±0.01
B ₂ O ₃ /UHMWPE (two-step)	0.40±0.01	1.81±0.03	0.39±0.06	1.28±0.02
Specimen	Mechanical properties			
	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore D)
B ₂ O ₃ /UHMWPE (one-step)	588.26±127.07	3.47±1.09	1.7±0.4	60±1
B ₂ O ₃ /UHMWPE (two-step)	887.28±95.28	8.09±0.70	2.8±0.9	62±2

**Figure 5. SEM image (150×) of B₂O₃/UHMWPE composite processed using (A) one-step process and (B) two-step process**

differences in the dispersion of the B₂O₃ particles in UHMWPE matrix, of which the sample processed using the two-step method had much better particle dispersion (Figure 5(b)) than the sample with the one-step method that had high agglomeration of B₂O₃ particles (Figure 5(a)). The better dispersion and distribution of B₂O₃ particles led to the increase in the probability of neutrons being interacted and absorbed by the well-dispersed ¹⁰B atoms in the composites, making the sample with the two-step method a better neutron-shielding material in comparison with the sample with the one-step method. The schemes showing the effect of particle dispersion on radiation-shielding ability are shown in Figure 4, in which Figure 4(b) has better particle dispersion and less neutrons being transmitted than in Figure 4(c). Similar reports of the effects of particle dispersion could also be found in other reports (Li *et al.*, 2017). In summary, the overall results implied that the addition of B₂O₃ could greatly enhance neutron-shielding ability of the composites, whereas the two-step processing method led to better dispersion of B₂O₃ particles and, subsequently, higher neutron attenuation of the materials.

Mechanical Properties

The mechanical properties of the B₂O₃/UHMWPE composites are also shown in Table 1,

which indicated that the samples processed using the two-step method had higher mechanical properties than the sample processed using the one-step method as seen by higher values in tensile modulus at 100% elongation, tensile strength, elongation at break, and hardness (Shore D) found in two-step samples. These behaviors were observed because the samples using the one-step method had worse dispersion of B₂O₃ particles in UHMWPE matrix, with clear particle agglomeration and voids due to the high filler-filler interaction of B₂O₃ particles and poor interfacial compatibility between B₂O₃ and UHMWPE, respectively. These effects led to more pronounced phase discontinuity in UHMWPE matrix and, consequently, lower mechanical strength. The SEM images revealing the agglomeration of B₂O₃ particles and voids inside the UHMWPE composites are shown in Figures 5(a) and 6(a), respectively.

On the other hand, B₂O₃/UHMWPE composites processed using the two-step method had better particle dispersion (Figure 6(b)) from the additional extrusion step during the mixing process with the help of paraffin oil as a plasticizer in improving the processability by reducing the overall viscosity of UHMWPE that led to better movement of UHMWPE molecular chains, allowing B₂O₃ particles to better penetrate and disperse inside the matrix (Fang *et al.*, 2006; Wood *et al.*, 2011).

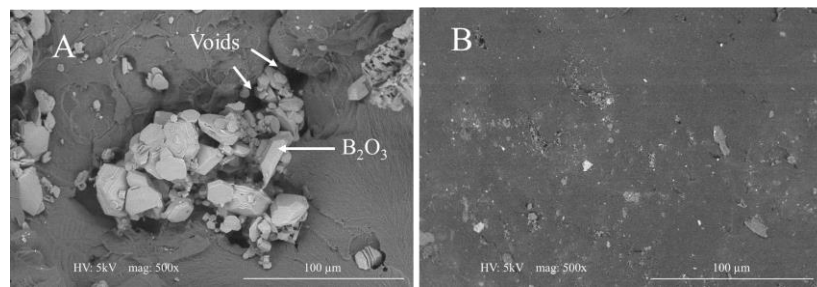


Figure 6. SEM image (500×) of B₂O₃/UHMWPE composites processed (A) one-step process and (B) two-step process

Furthermore, the improvement in filler dispersion also led to better phase continuity of UHMWPE matrix, of which UHMWPE had exceptional strength and was the main material to withstand external force, making the sample tougher and stronger.

Conclusions

Since utilizing adequate and efficient neutron-shielding materials are mandatory in all nuclear facilities for the safety of both personnel and general public, the development of novel shielding materials, with preferably higher mechanical strength, is needed. This work compared neutron-shielding, mechanical, and morphological properties of the UHMWPE composites with the addition of 50 wt% B₂O₃ processed using either a one-step or two-step method. The results indicated that the addition of B₂O₃ in the composites and the introduction of extrusion step in the two-step processing method considerably enhanced neutron-shielding abilities of the composites as seen by higher (lower) μ (I/I_0 , HVL , and TVL) values. The results also indicated that the two-step processing method led to improve mechanical properties of the composites as seen by higher tensile modulus, tensile strength, elongation at break, and hardness (Shore D) values. In conclusion, based on the overall results from this work, the addition of B₂O₃ in UHMWPE and the introduction of extrusion step presented very promising formula and procedure in producing novel and high quality neutron-shielding materials that would be useful for both academic and industrial purposes.

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