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Manufacturing process and properties of lead-free natural rubber sponge for use in X-ray and gamma ray shielding applications

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Abstract. In this work, light-weighted, flexible, and lead-free X-ray/gamma-ray shielding natural rubber (NR) sponges were developed with the help of a blowing agent, namely Oxybis (benzene sulfonyl) hydrazide (OBSh) (its contents varied from 0, 8 to 16 parts per hundred parts of rubber; phr), and an X-ray/gamma protective filler, namely bismuth oxide (Bi_2O_3) (its content varied from 0, 100, 300, to 500 phr) in natural rubber (NR) composites. The results suggested that the densities and overall mechanical properties decreased with increasing contents of OBSh, while the increases in Bi_2O_3 resulted in the increases in tensile strength and hardness (Shore A), however, initially increases tensile strength and elongation at break but later decreases at 300 and 500 phr. In terms of radiation shielding properties, it was found that the ability to attenuate X-rays and gamma rays improved with increasing Bi_2O_3 contents. Hence, the overall properties investigated in this work suggested that the developed NR sponges could be used to attenuate X-rays and gamma rays efficiently with additional properties of being light-weighted and highly flexible, which are crucial for safety of radiation-related personnel and users.

1. Introduction

X-ray and gamma rays are two types of relatively high-energy electromagnetic waves that currently play important roles in various applications including cancer therapy [1], material imaging [2], and medical sterilization [3]. Despite the mentioned benefits, risks of exposure to both X-ray and gamma rays could potentially lead to fatal health hazards in radiation workers and users [4]. In order to prevent excessive X-ray and gamma exposure, sufficient shielding materials that could attenuate incoming intensities to safe levels must be introduced and used in all radiation-related workplaces. In principle, materials composing of high-atomic-number (Z) and high-density elements are normally used as shielding materials in order to prevent such risks. This is because high- Z materials such as lead (Pb) had relatively high probability of interactions with incoming X-ray and gamma rays, leading to higher energy transfer and larger attenuations [5].

However, Pb-containing materials could inversely pose environmental and health risks to product users as Pb is hazardous and lacks chemical stability [6]. As a result, Pb-free X-ray/gamma ray shielding



materials have drawn special attention from researchers. In order to achieve similar shielding properties as Pb-containing materials, other high-Z and high-density elements such as bismuth (Bi) could also act as effective radiation protective fillers. In particular, for applications that require flexibility with good mechanical properties, natural rubber (NR) and synthetic rubbers such as EPDM could be used as the main matrices with the addition of Bi compound [7, 8]. Furthermore, in order to reduce weight/density of the materials, blowing agents could be added to the composites [9]. As a result, this work developed NR composites with the addition of bismuth oxide (Bi_2O_3) and Oxybis (benzene sulfonyl) hydrazide (OBSH), of which X-ray and gamma ray shielding, density, mechanical, and morphological properties of the composites were thoroughly investigated and reported.

2. Experimental

2.1 Materials and chemicals

Natural rubber (grade STR 5L) was used as the main matrix for this work. The vulcanizing formulations and their roles are given in Table 1.

Table 1. Material formulations of NR composites including chemicals and their roles.

Ingredient	Content (phr*)	Function
Natural rubber (STR 5L)	100 (part)	Matrix
ZnO	5.0	Activator
Stearic acid	3.0	Activator
Mercaptobenzothiazole; MBT	1.0	Accelerator
6PPD	1.0	Anti-oxidant
Silica	40.0	Reinforcement
Polyethylene glycol; PEG	5wt% added of silica	Activator
Paraffinic oil	10.0	Processing aid
Sulphur	2.0	Crosslinker
Bismuth oxide; Bi_2O_3	0, 100, 300, 500	X-ray & gamma protective filler
Oxybis (benzene sulfonyl) hydrazide; OBSH	0, 8 and 16	Blowing agent

* phr: parts per hundred parts of rubber by weight

2.2 Preparation of NR composites

The NR was masticated on a laboratory two-roll mill (Yong Fong Machinery Co., Ltd., Thailand) for 3 min. The masticated NR was then compounded with the chemicals given in Table 1 using the two-roll mill for further 17 min. To prepare the NR sheets, hot compression molding at the temperature of 165°C with a hydraulic pressure at 170 kg/cm² was used for every individual compound.

2.3 Mechanical properties

The tensile properties including tensile modulus at 100% elongation, tensile strength, and elongation at break of the NR composites were investigated using a universal testing machine (Autograph AG-I 5kN, Japan) following ASTM D412-06 standard testing. For hardness measurement, all the samples were tested using a hardness durometer, Shore A, (Teclock GS-719G, Japan) according to ASTM D2240-05.

2.4 Density and morphology studies

Densities of the all NR sponges were determined using Archimedes water replacement technique according to ASTM D792-00. For the study of morphology and the distribution of fillers, the samples were investigated using a scanning electron microscope (SEM), JEOL (JSM-6610LV), at 10-kV accelerating voltage with back-scattered electrons (BSE). It should be noted that the samples were coated with gold using an ion sputtering device for 60 sec before performing SEM.

2.5 X-ray and gamma ray shielding properties

The X-ray shielding properties were tested using a 100-kV X-ray generator, which produced an X-ray beam with the Half-Value Layer (HVL) of 1.1 mmCu. The results of the X-ray attenuation were reported as equivalent to standard Pb (mmPb) and percentage of attenuation. For gamma ray shielding properties, the tests were performed using a ⁶⁰Co point source, which emits gamma rays with the average energy of

1.25 MeV. Linear attenuation coefficient (μ), percentage of gamma transmission, and HVL were reported for all samples.

3. Results and discussion

3.1 Mechanical properties of NR sponges

Table 2 Mechanical properties and densities of NR sponges with/without OBSH and Bi₂O₃. The values are presented as mean \pm standard deviations of the mean.

Properties	NR composites											
	No OBSH / Bi ₂ O ₃ (phr)				8-phr OBSH / Bi ₂ O ₃ (phr)				16-phr OBSH / Bi ₂ O ₃ (phr)			
	0	100	300	500	0	100	300	500	0	100	300	500
Tensile modulus (MPa)	1.3 \pm 0.1	2.9 \pm 0.1	3.6 \pm 0.2	3.3 \pm 0.2	1.2 \pm 0.1	1.7 \pm 0	1.7 \pm 0.2	0.9 \pm 0.1	1.0 \pm 0.1	1.4 \pm 0	1.2 \pm 0.1	1.5 \pm 0.1
Tensile strength (MPa)	10.5 \pm 1.2	15.6 \pm 0.9	10.4 \pm 1.1	7.6 \pm 0.8	4.6 \pm 0.3	8.3 \pm 1.1	5.0 \pm 0.6	3.4 \pm 0.3	3.9 \pm 0.3	4.8 \pm 0.7	3.3 \pm 0.2	2.3 \pm 0.3
% Elongation at break	489 \pm 19	396 \pm 14	296 \pm 30	250 \pm 17	289 \pm 12	324 \pm 21	249 \pm 16	385 \pm 28	306 \pm 14	255 \pm 16	227 \pm 10	168 \pm 11
Hardness (shore A)	46 \pm 1	60 \pm 1	69 \pm 1	71 \pm 1	22 \pm 1	34 \pm 1	35 \pm 1	39 \pm 2	19 \pm 2	27 \pm 2	31 \pm 3	48 \pm 3
Density (g/cm ³)	1.09	1.65	2.52	3.07	0.73	1.17	1.79	2.34	0.59	1.05	1.19	2.18

As shown in Table 2, it was found that, at the same Bi₂O₃ content, tensile properties and hardness (shore A) decreased with increasing OBSH content. This was due to OBSH produced small closed-cell structures inside NR matrix as shown in Fig. 1, reducing the ability to resist tensile forces from the presence of gas phases. On the other hand, at the same OBSH content, increasing Bi₂O₃ contents led to the increases in tensile modulus and hardness (shore A), probably due to the high rigidity of Bi₂O₃, while tensile strength and elongation at break initially increased when its content increased to 100 phr but later decreases as more Bi₂O₃ was added to the composites. This was due to the fact that Bi₂O₃, which is a metal oxide that could act as a co-activator, helped in chemical crosslinking, leading to higher crosslink density and higher values of tensile strength and elongation at break. However, as more Bi₂O₃ was added, filler-filler interactions occurred, leading to the agglomeration of Bi₂O₃ and resulting in worse particle dispersion and lower tensile strength/elongation at break [8].

In terms of the densities of NR composites, the values decreased with increasing OBSH contents due to small closed-cell structures that were produced from the addition of OBSH as shown in Fig.1. Furthermore, it was found that the densities of NR composites increased with increasing contents of Bi₂O₃, mainly due to the much higher density of Bi₂O₃ particles (density of Bi₂O₃ is 8.9 g/cm³).

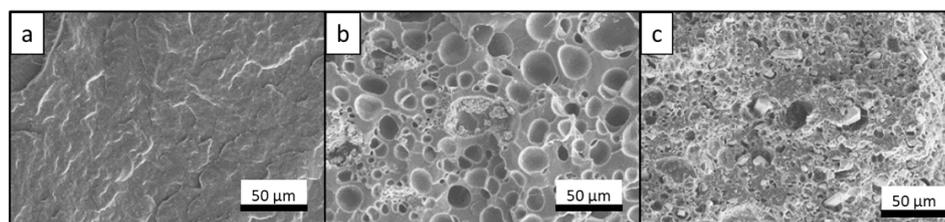


Fig. 1. Cross-sectional morphology of (a) NR composites, (b) NR composites with 8-phr OBSH, and (c) NR composites with 8-phr OBSH and 500-phr Bi₂O₃.

3.2 Gamma and X-ray shielding properties

Gamma ray and X-ray shielding properties of both NR solids and sponges with varying contents of Bi₂O₃ and OBSH are shown in Fig. 2 and Table 3, respectively. The results showed that increasing contents of Bi₂O₃ improved radiation shielding properties as seen by the increase in μ and the decreases in % gamma transmission and HVL. The improvement in gamma ray/X-ray shielding properties was mainly due to the increase of Bi elements in the NR composites that could interact and attenuate gamma

rays/X-rays. However, the addition of OBSH led to the decrease in gamma shielding properties due to empty spaces in the NR matrix diluted effects of Bi element. Nonetheless, the values of linear attenuation coefficient at 500-phr Bi_2O_3 were in an acceptable range as they were similar to the values reported in ref. [7] and ref. [8], however, with smaller density and weight.

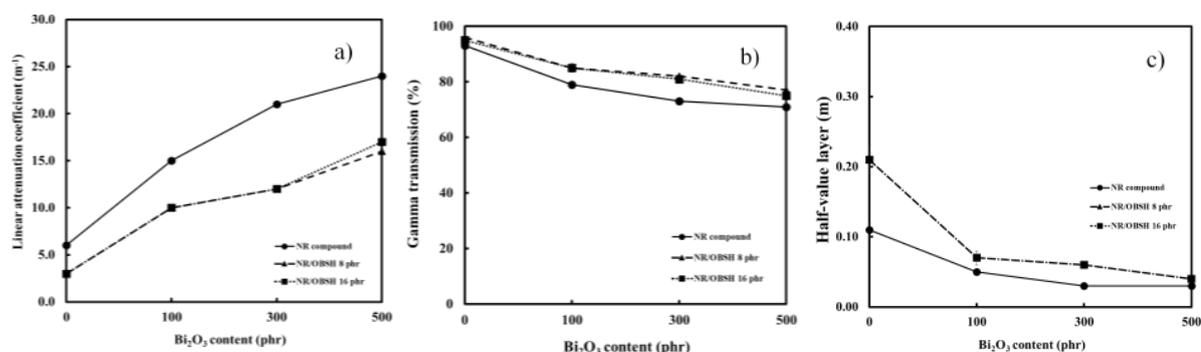


Fig. 2. Results of (a) linear attenuation coefficient, (b) gamma transmission, and (c) HVL of NR and 8-phr OBSH/NR composites with varying contents of Bi_2O_3 .

Table 3. X-ray shielding properties of NR sponges

X-ray shielding properties	8-phr OBSH/NR sponges	
	0-phr Bi_2O_3	500-phr Bi_2O_3
Equivalent to Pb (mmPb)	0.01	0.34
% Attenuation	4.1	75.0

4. Conclusion

The results indicated that the addition of the blowing agent, OBSH, led to the decreases in overall mechanical, density, and gamma/X-ray shielding properties of NR sponges. Furthermore, the addition of Bi_2O_3 led to the increases in tensile modulus, hardness (shore A), density, and gamma ray/X-ray shielding properties, while initially increased tensile strength and elongation at break at the Bi_2O_3 content up to 100 phr but later decreased as more Bi_2O_3 was added to the NR composites. The overall results suggested that NR sponges with the addition of OBSH and Bi_2O_3 could be used as light-weighted, lead-free, and flexible gamma ray/X-ray shielding materials.

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