




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Bio-EPDM/tungsten oxide nanocomposite foam with improved thermal storage and sea water resistance

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article

Abstract

Bio ethylene propylene diene monomer (EPDM) produced with sugarcane-derived ethylene is an eco-friendly alternative material that can perform similarly to an oil-based synthetic rubber while reducing dependence on fossil resources. In this study, bio-EPDM/tungsten oxide nanocomposite was prepared to improve thermal insulation properties of bio-EPDM foam for application in highly functional eco-friendly diving wetsuits. The synthesized tungsten bronze nanorods (TBNRs) were doped with sodium and added to the bio-EPDM compound, then foam was generated by molding at 155 °C under a high-pressure. After foam molding, the effects of TBNRs on the sea water resistance as well as the thermal and mechanical properties of bio-EPDM foam were investigated. As a result, TBNRs remarkably improved the softness and photothermal properties of bio-EPDM foam without a significant reduction of their mechanical properties. Especially, the excellent dimensional stability of the bio-EPDM foam with TBNRs under the sea water circumstance highlights its superiority as a material for marine sports. Overall results indicate that the bio-EPDM foam material containing TBNRs at the optimum ratio can be fully utilized for the development of eco-friendly and high-performance wetsuit materials with excellent elasticity, flexibility, and thermal insulation properties.

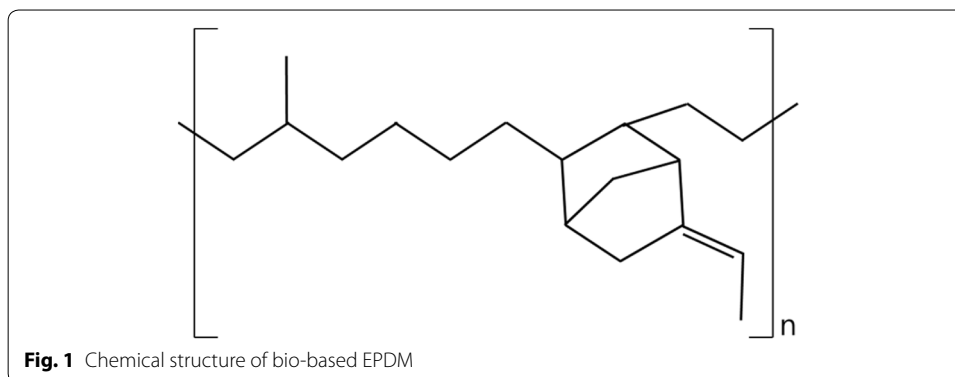
Keywords: Bio-EPDM, Tungsten bronze, Thermal storage, Seawater resistance, Nanorods

Introduction

With the recent increase in national income and the growing interest in quality of life, the popularization of marine sports has rapidly progressed. This has consequently led to a rapid growth of the marine sportswear market. Significant attention has focused on safe and functional marine sportswear products that enable the wearer to enjoy sports safely while providing protection from extreme environmental conditions. Wetsuits, a type of diving suit, are among the most popular items for marine sportswear and are designed to soak up water between the body and the suit while diving. They are manufactured by blowing synthetic rubber to form a foam, which is subsequently bonded with jersey fabric. Thermal insulation, strong elasticity, and high shock absorption are the required

material characteristics to produce safe and protective wetsuits (Her et al. 2017), and a range studies are being conducted to develop such high-performance materials for this application. In particular, studies on the material characteristics and thermal insulation of commercial wetsuits in terms of body part (Kim et al. 2016), mechanical properties (Naebe et al. 2013), and consumer recognition (Sang and Oh 2018) have mainly focused on the frequently used commercial material neoprene. However, while neoprene currently accounts for more than 40% of wetsuits materials, it is a chloroprene-based petroleum product that cannot be recycled or regenerated (Yoo and Park 2017), resulting in environmental pollution and a large CO₂ footprint during its disposal (Sang et al. 2019). In view of recent environmental concerns, there is a growing need to develop eco-friendly alternative materials. In addition, natural rubber and synthetic butadiene rubber exhibit weak durability against oxygen, ozone, heat, and gas, and can exhibit surface cracking and increasing compression set as a result aging. Thus, alternative materials must be developed to overcome these shortcomings. Ethylene propylene diene monomer (EPDM), a newly developed ethylene propylene-based rubber, is known to exhibit neoprene-like properties (e.g. excellent impact resistance) due to the presence of a diene in the copolymer of ethylene and propylene (Park and Hwang 2011). It is well-known as an excellent and economical elastomer with outstanding ozone resistance, heat resistance, and electrical insulation. Due to these properties, it has recently attracted attention as an industrial material for electrical, architectural, and automobile applications (Kim et al. 1999; Lee and Bae 2018; Min et al. 2004). The bio-based EPDM recently developed by Lanxess is an eco-friendly material that uses ethylene extracted from sugar cane as a raw material (Fig. 1). It is expected to resolve the environmental issues caused by neoprene by reducing the carbon footprint and fossil resource dependency. In addition, studies are being performed on bio-based elastomers, as environmentally friendly materials with a focus on the sustainable manufacturing of bio-based polyurethane and its compatibility (Kuranska et al. 2016; Li et al. 2018). In addition, studies on the manufacture of polyester elastomers using bio-based chemicals and elastomers based on vegetable oils such as rapeseed oil, linseed oil, soybean oil, peanut oil, and castor oil have been recently reported (Li et al. 2001; Wang et al. 2012, 2016).

Among the various functionalities required for wetsuit materials, thermal insulation is very important for maintaining body temperature in outside and underwater environment (Oh et al. 2019). For this reason, materials such as nano-zirconium neoprene



and heat flex neoprene have been applied in the manufacture of commercial wetsuits (Lee 2017). These materials are knitted using hollow aero-zirconium fibers or produced by bonding the thermal jersey material with a micro-brushed surface to neoprene for improved thermal insulation. In addition, various studies are being conducted to increase the thermal insulation by injecting an insulating gas into a closed cell of neoprene foam in order to lower the thermal conductivity; by synthesizing hybrid insulation materials; by preparing syntactic foams, and by preparing insulating aerogel blanket composites (Bardy et al. 2006; Moran et al. 2018). Recently, inorganic fillers with a photothermal effect have been investigated for improved thermal insulation (Bom et al. 2002; Gao et al. 2015; Velasco et al. 2002). Alkali metals including Cs, Rb, K, Na, Li, and Fr exhibit reflection absorption responses to electromagnetic waves by means of plasma vibration when they contain free electrons. In particular, tungsten bronze ($MxWO_3$), i.e. tungsten trioxide doped with an alkali metal, has been shown to exhibit a reflection absorption response in the near-infrared region with a high heating effect, leading to significant application potential in the automobile, construction, and biomedical industries (Choi 2015; Green and Hussain 1991; Liu et al. 2013).

Tungsten bronze is a non-stoichiometric compound that adopts various structures (e.g. the cubic, hexagonal, tetragonal, and pyrochlore structure), and displays a range of electrical and optical properties depending on its composition (Guo et al. 2012). When the alkali metal is intercalated into the framework formed by the corner-sharing WO_6 octahedra, the alkali metal contributes its electrons to the conduction band of WO_3 to form a surface plasmon polariton of free electrons. As a result, tungsten bronze nanorods (TBNRs) exhibit electrical properties that allow conduction to be controlled by varying the metal ion concentration. TBNRs also exhibit strong absorption in the near-infrared wavelength range based on sub-band energy levels (Choi 2015). Inorganic fillers on the other hand affect the behavior of the rubber products by interacting with the elastomeric matrix to form physical and chemical bonds (Milic et al. 2008). In particular, nanorod-shaped fillers are known to be effective mechanical reinforcers of polymer composite materials (Gao et al. 2014). Studies on the manufacture of safe and cost-effective TBNRs and film-like elastomer composites to improve the mechanical and photothermal properties of elastomers have been reported (Jeon et al. 2019). The application of TBNRs to rubber polymers can provide not only the required mechanical properties but also multiple functions such as photothermal properties. An in-depth study of highly functional wetsuit materials incorporating TBNRs was therefore proposed.

In the present study, the nanocomposite foams were prepared by adding TBNRs to bio-based EPDM. Their applicability as an eco-friendly and high-performance wetsuit material was confirmed by measuring the changes in mechanical, saltwater resistance, and photothermal properties. In addition, the optimum processing conditions were determined.

Experimental

Materials

Bio-EPDM (Keltan[®] Eco 6950C) as the base monomer was provided by LANXESS. Keltan[®] Eco 6950C (Mooney viscosity at 125 °C = 65 g/10 min; Cologne, Germany) consisting of 44 wt% ethylene and 9.0 wt% ethylene norbornene (ENB) was produced from

bio-based feedstock. Specifically, the ethylene content was derived from ethanol produced from sugarcane. The additives ZnO and stearic acid, which acts as accelerators, were purchased from PJ Chemtek (Yangsan-si, Gyeongsangnam-do, South Korea). The OBSH (4, 4'-oxybis (benzene sulfonyl hydrazide)) was purchased from Kumyang chemical (Yangsan-si, Gyeongsangnam-do, South Korea). Dicumyl peroxide (DCP) was purchased from Akzonobel (Amsterdam, Netherlands). In the present study, all the reagents were used as received.

Ammonium metatungstate hydrate (AMT, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$, MW = 2956.3 g/mol) and oleylamine (OA, >70% purity) were purchased from the Sigma-Aldrich Company (St. Louis, MO, USA). Toluene and acetone were purchased from DaeJung Chemicals (Siheung-si, Gyeonggi-do, South Korea). Sodium hydroxide (NaOH) was purchased from Samchun Chemicals (Seoul, South Korea).

Preparation of tungsten bronze nanoparticles

AMT (0.1 mmol, 0.296 g) and OA (16 mL) were added to a three-neck round-bottom flask and stirred for 1 h to create a slurry. Sodium hydroxide (NaOH, 0.40 mmol, 0.016 g) was then added and the mixture was stirred for an additional hour. After connecting the reflux condenser to the flask, nitrogen gas was injected for 1 h to create a nitrogen atmosphere inside the flask. Then, the mixture was gradually heated to 250 °C for 2 h with stirring. The mixture was then cooled to room temperature, excess acetone was added and the mixture was centrifuged at 8000 rpm for 15 min to remove the unreacted OA. After redistribution of the collected sediment with acetone and two rounds of centrifugation at room temperature, the tungsten bronze nanorods (TBNRs) were obtained in powder form.

A high-resolution penetrating electron microscope (HR-TEM, JEM3010, JEOL, Akishima, Japan) was used to identify the shape and structural features of the TBNRs. The size of the TBNRs was estimated by analyzing the TEM images using the Gartner micrograph program (Gatan Inc., Pleasanton, CA, USA). As shown in Fig. 2, TBNRs of 14.0 ± 2.4 nm length and 2.5 ± 0.5 nm diameter (aspect ratio 6:1) were obtained.

Preparation of foam composites with TBNRs

The Bio-EPDM was well mixed with a chemical blowing agent (10 parts per hundred (phr)), a substance which create a foam through bubble generation, crosslinking agent (0.5 phr), ZnO (3 phr), and stearic acid (1 phr) in a kneader (a closed mixer) at 100–110 °C for 20 min. The mixture was then transferred to an open mixer (a roll mill). The TBNRs were dissolved in 15 wt% toluene and gradually added to the bio-EPDM mixture to form a sheet at 60–80 °C for 5–10 min. Then, the sheets were left at room temperature for approximately 24 h to volatilize the toluene. The sheets were placed in a mold (2 mm in thickness) and molded at 155 °C under a high-pressure (150 kgf/cm²) for 20 min (Sang et al. 2019).

Photothermal and mechanical analysis of EPDM/ $\text{Na}_{0.33}\text{WO}_3$ composite foam

The effect of TBNRs additions on the microstructure of the bio-EPDM foam was evaluated with a field emission scanning electron microscope (FE-SEM, JSM6701, JEOL, Japan). Its specific gravity was measured according to the Korean Standard KS M

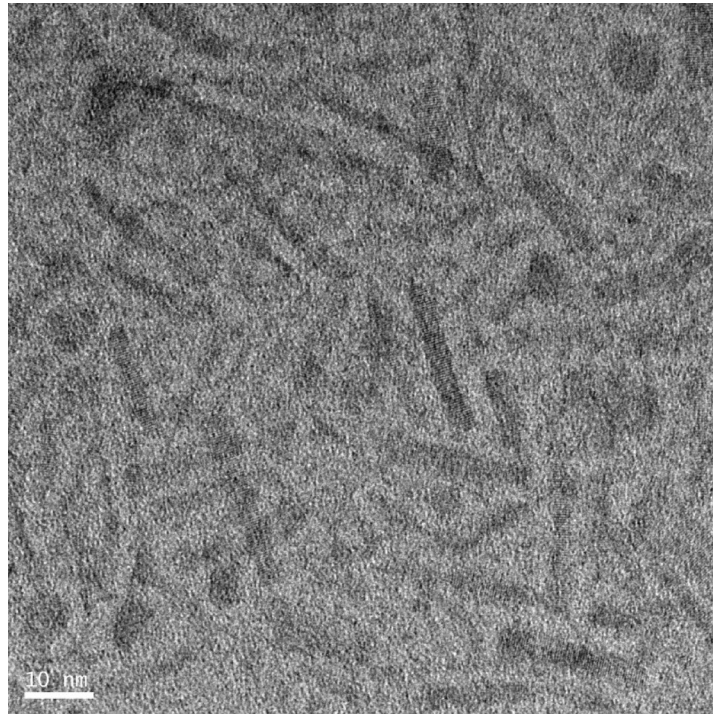


Fig. 2 HR-TEM images of tungsten bronze nanorods

6660:2016. Hardness tests (Asker C) were performed using a digital durometer according to the American Society for Testing and Materials (ASTM) D-2240 standard. Tensile strength and elongation were measured using a Universal Test Machine (UTM, MTDI UT-100F) according to the Korean Standard KS M ISO 1798:2012 to investigate the mechanical properties of the bio-EPDM foam. The tear strength (i.e. the resistance of foam to tearing) was measured using the unnicked angle tear strength method according to the Korean Standard KS M ISO 34-1:2014. The compression set, or resiliency of the compression deformation, was evaluated by measuring the thickness variation after compressing the specimen at a certain temperature for a certain amount of time, and calculating the residual decrease rate according to Eq. (1):

$$Cs = (L_0 - L_1)/(L_0 - L_2) \times 100 \quad (1)$$

where Cs (%) = the permanent compression reduction rate; L_0 (mm) = the original thickness of the test specimen; L_1 (mm) = the thickness of the test specimen after 30 min of compression, and L_2 (mm) = the thickness of the spacer.

The saltwater resistance of the bio-EPDM foam was measured using an accelerated immersion test in accordance with the Korean Standard KS M 6518:2016. The bio-EPDM foam was immersed in a 7% NaCl solution for 24 h at 4 °C. The volume changes of the foam specimens were recorded before and after immersion.

Thermogravimetric analysis (TGA) were used to measure the thermal properties of the bio-EPDM foam according to the addition ratio of TBNRs. The mass reduction of the bio-EPDM foam with TBNRs due to temperature was measured using TGA (TA1050, TA Instruments). After raising the temperature of the heater from room temperature to

700 °C at 10 °C/min and with an N₂ purging rate of 100 ml/min, the mass changes of the specimens were measured and analyzed.

To examine the photothermal properties of the EPDM foam with TBNRs, white light from a solar simulator (100 W, PEC-L01, Peccell Technologies Inc., Yokohama, Japan) was applied to the foam at a distance of 20 cm for 10 min. Near-infrared (NIR) images were captured every 20 s using an NIR camera (TG165, FLIR Systems, Wilsonville, OR, USA). The white light was then turned off and NIR images of the bio-EPDM foam with TBNRs were recorded every 20 s for a further 10 min to examine the thermal storage properties. The surface of the foam with 3 wt% TBNRs was also irradiated for 10 min, and remained lights-out for another 10 min. The process was repeated five times to observe the changes of photothermal performance due to heating by repeated irradiation.

Results and discussion

Cross-linking and blowing characteristics of bio-EPDM foam with TBNRs

In contrast to pure poly (ethylene) and poly (propylene), EPDM rubbers produced by co-polymerization of ethylene and propylene do not crystallize well and exhibit rubbery properties. However, polymers of ethylene or propylene cannot be vulcanized because they do not contain double bonds. Therefore, ethylene norbornene is applied as a third monomer to create a three-membered copolymer that facilitates vulcanization of the double-bonds by sulfur, thereby creating a synthetic EPDM rubber with a network structure that offers elasticity. The characteristics of the vulcanized rubber are greatly affected by various additives and reaction conditions. The cure curve, blowing pressure, and blowing speed of the bio-EPDM composite specimens were measured using a flat die rheometry (VR-3110 FDR, Ueshima Seisakusho Co. Ltd., Tokyo, Japan) at 155 °C to examine the vulcanization behavior of bio-EPDM composite blended with various TBNRs rates during the kneading and roll milling process. As shown in Fig. 3a, the viscosity of specimen injected at room temperature decreased as the temperature rose to 155 °C, which was the initially set temperature. The specimen showed a minimum torque value at approximately 39 s. Afterwards, heat-induced cross-linking was performed, and the torque values gradually increased over time, indicating that the cross-linking density increased as vulcanization progressed. When the TBNRs were added, the torque value decreased more rapidly. This is attributed to the higher thermal conductivity of the TBNRs, which caused the viscosity of EPDM to decrease more quickly, thus resulting in a lower torque value. In additions, it can be inferred that TBNRs reduced the degree of cross-linking, since the difference between the maximum and minimum torque values indicates the degree of cross-linking. Consequently, the TBNRs seem to delay the cross-linking speed of the unsaturated double-bonds of EPDM (Cha et al. 2001). The well-distributed inorganic TBNRs particles also provide the core sites of the bubbles during foaming, thereby promoting uniform generation of multiple bubbles while maintaining a stable cross-linking speed (Fig. 3b, c) (Lee et al. 2018). This stable foaming process induces sufficient growth of the bubble cells and can increase the relative foaming ratio (Kim et al. 2001), as confirmed by specific gravity measurements (Table 1) and SEM images (Fig. 4).

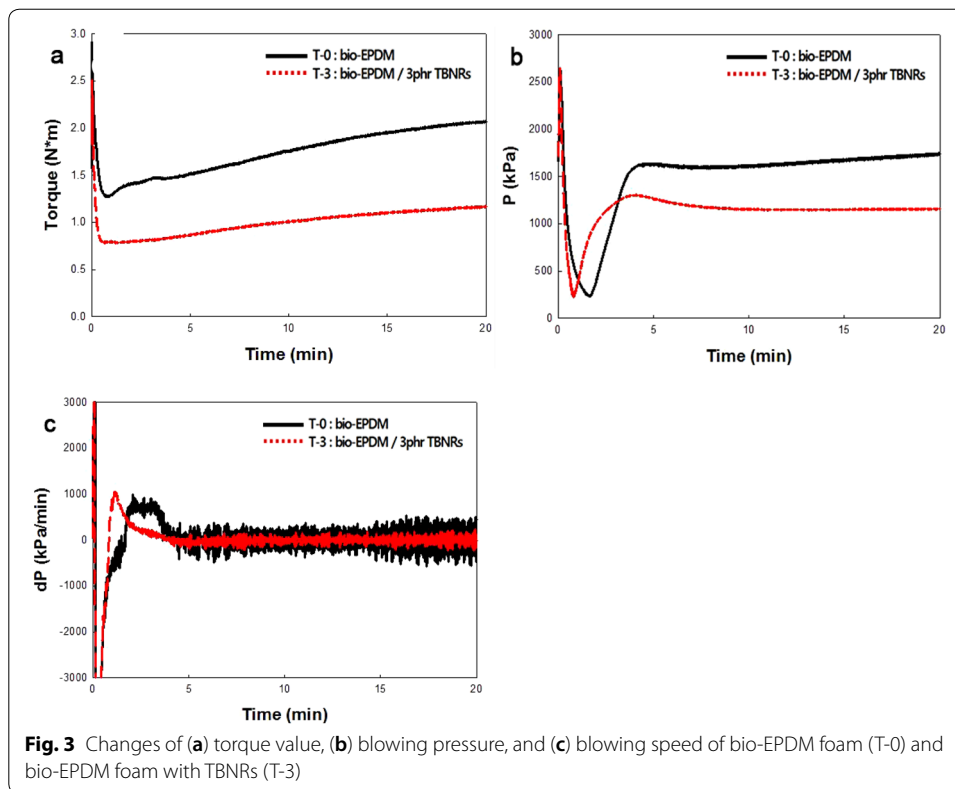


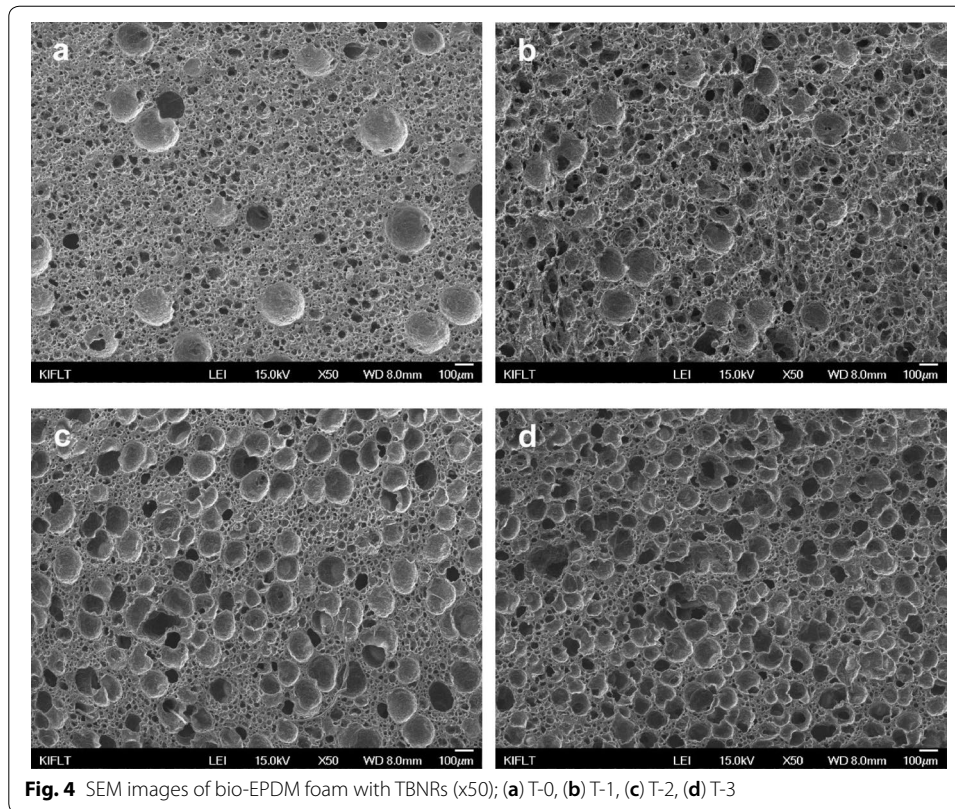
Table 1 Physical and mechanical properties of bio-EPDM foam with TBNRs

Properties	Specimens			
	T-0	T-1	T-2	T-3
Sp. Gr.	0.154	0.148	0.150	0.151
Hardness (Asker C)	24 ± 1	21 ± 1	21 ± 1	20 ± 1
Tensile strength (kg/cm ²)	6.20	7.15	5.60	4.20
Elongation (%)	977	935	850	690
Tear strength (kg/cm)	3.15	2.75	2.95	2.25
Compression set (%)	67.5	66.7	67.6	69.8

T-0: bio-EPDM foam, T-1: bio-EPDM foam with 1 phr TBNRs, T-2: bio-EPDM foam with 2 phr TBNRs, T-3: bio-EPDM foam with 3 phr TBNRs

Cell morphology

Factors that influence the foam cell shape include the degree of cross-linking, foaming conditions, foaming agent components, and the content and the size of the filler (Ahn 2011). The microstructural changes of the bio-EPDM foam according to the ratio of added TBNRs (0 phr, 1 phr, 2 phr, 3 phr) were analyzed via FE-SEM imaging. The analyses showed that the cell sizes in the bio-EPDM foam without TBNRs were small and irregular, with uneven distribution (Fig. 4a). It seemed that the cells generated by the blowing agent were unable to merge with nearby cells due to the increased viscosity and cross-linking density, resulting in low foaming ratios and the formation of very dense closed cells (Cha et al. 2001). Large bubble cells found in



small quantities are interpreted as reduced foam stability, as they were generated by the merger and collapse of bubble cells in a short period of time due to intense reactions that rapidly generated large quantities of bubble cells. In contrast, higher ratios of TBNRs resulted in more uniform cell sizes and distributions with a larger average cell size (Fig. 4b–d). Even using a small amount of tungsten with good thermal conductivity improves the decomposition properties of the blowing agent by promoting heat transfer in the composite, and cell size appears to increase uniformly with a good foaming ratio under a low cross-linking density. As described above, it seems that the cross-linking delay and stabilization of blowing speed upon addition of TBNRs controls bubble growth and induces the formation of cells with a uniform size and distribution (Bashir et al. 2014).

Mechanical properties of bio-EPDM foam with TBNRs

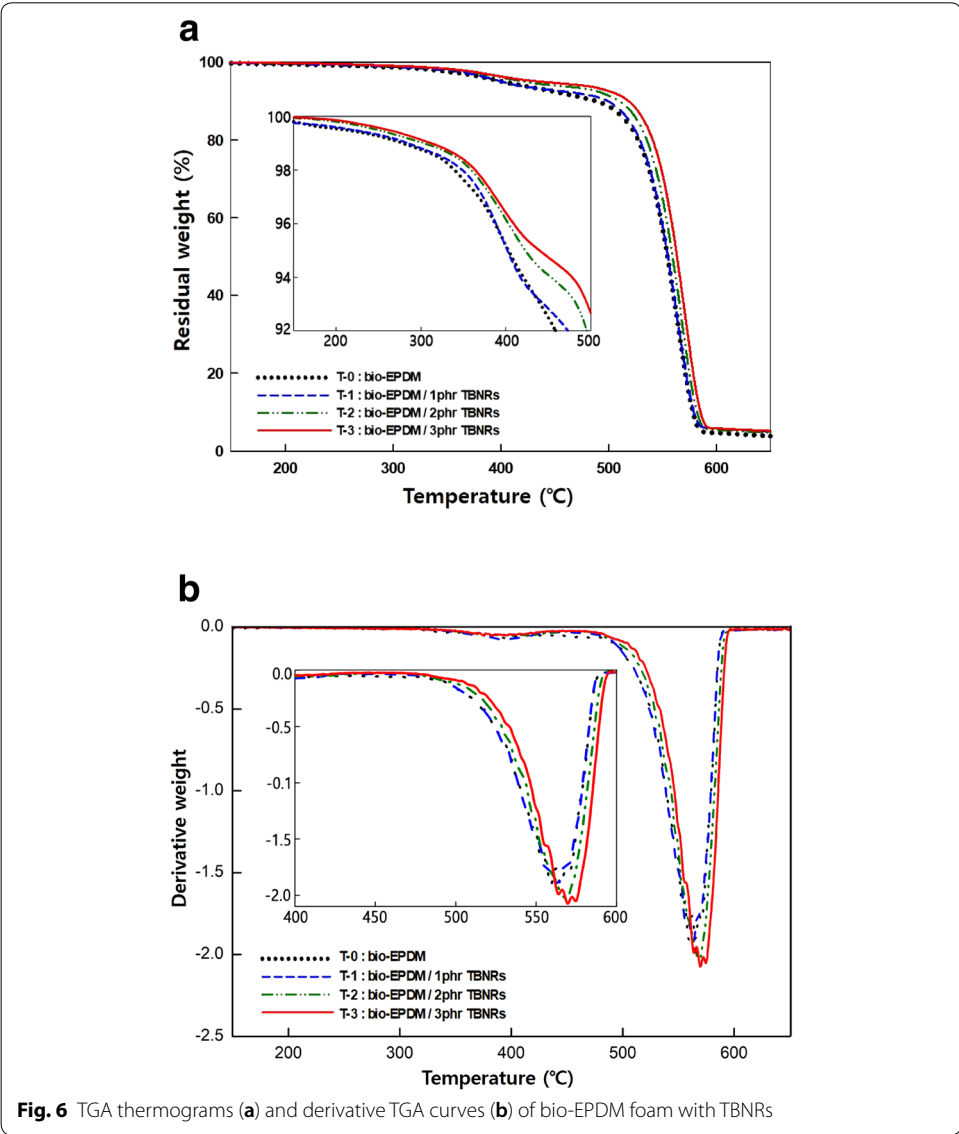
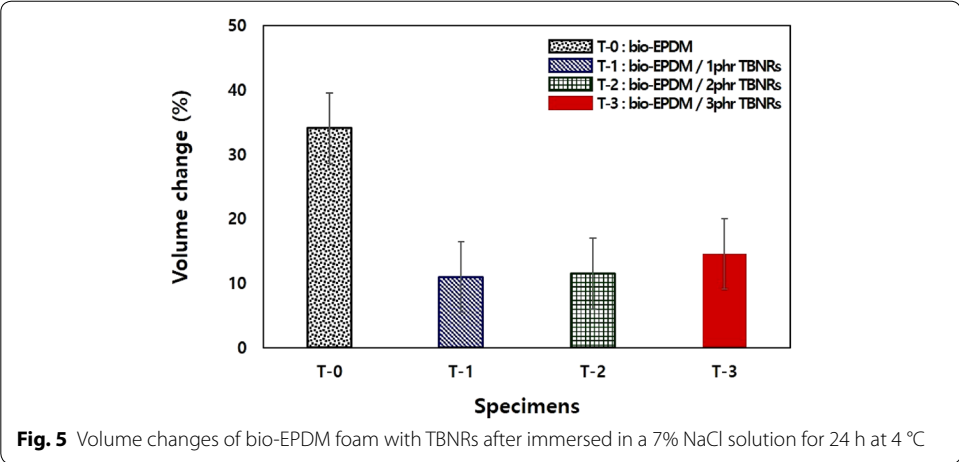
Generally, the mechanical properties of the foam are greatly influenced by the degree of cross-linking, the specific gravity, and the structural properties of the cell as well as the mechanical properties of the base polymer (Cha et al. 2001). The effect of TBNRs on the physical and mechanical properties of bio-EPDM foam were measured and shown in Table 1. The specific gravity values of specimens was generally similar at the 0.150 level, but it was slightly reduced with the addition of TBNRs. This seems to be due to the reduced density of the matrix and the improved foaming ratio resulting from the reduction of cross-linking density. However, the addition of a small amount of TBNRs did not seem to have a significantly impact on their mechanical properties. The hardness values

decreased slightly from 24 ± 1 in the absence of TBNRs to 21 ± 1 with the addition of 1 phr and 2 phr TBNRs, and 20 ± 1 with the addition of 3 phr TBNRs. As reported in a previous study (Jeon et al. 2019), the addition of TBNRs appears to increase the cell size and reduce cell wall thickness, thereby reducing the overall foam hardness.

In the absence of TBNRs, the tensile strength, elongation, and tear strength of bio-EPDM foam are 6.2 kg/cm^2 , 977% and 3.15 kg/cm , respectively. When 1, 2 and 3 phr of TBNRs were blended with bio-EPDM foam, the corresponding tensile strengths were 7.15 kg/cm^2 , 5.6 kg/cm^2 and 4.2 kg/cm^2 , the corresponding elongations were 935%, 850% and 690%, and the corresponding tear strengths were 2.75 kg/cm , 2.95 kg/cm and 2.25 kg/cm . It indicated that the overall mechanical properties decreased slightly as the addition ratio of TBNRs increased. It can be explained by the fact that the addition of TBNRs increased the foaming ratio and produced relatively large bubble cells, resulting in fewer cell ribs. Therefore, the total area of the cell ribs that can withstand external stress appears to have been reduced, and consequently, the mechanical properties of the foam also appear to have been reduced. As a result, it seems that the formation of the bubble cells reduced the polymer content, which influenced the mechanical properties of the matrix. Meanwhile, when TBNRs are added, a uniform cell structure is formed, and stress is dispersed to improve the form stability and prevent excessive degradation of the mechanical properties. Therefore, it can be concluded that the mechanical properties of bio-EPDM foam with TBNRs are maintained at 70% or higher compared to the foam without TBNRs.

The elastic properties of the foam with and without TBNRs were investigated by measuring the compression set. The specimen without TBNRs displayed a compression set of 67.5%, while the addition of 1, 2, and 3 phr of TBNRs resulted in values of 66.7%, 67.6%, and 69.8%, respectively. No significant changes were observed up to a loading of 2 phr TBNRs. Even with 3 phr TBNRs, a slight (2–3%) decrease in the compression set was observed. These results can be due to the fact that the resistance against the compressional force could be maintained by the regularly formed network structure of cell ribs which lead compressive forces more evenly distributed, even though the addition of TBNRs slightly reduced the cross-linking density of the cell walls. This improved the support for restoring the cell structure and increased the structural stability of the cell walls, allowing the materials to maintain its recovery from compressional force. Furthermore, interfacial interactions between the oleylamine (OA) chain on the surface of TBNRs and EPDM matrix increased the binding force between the cell wall and the cell ribs, which likely increased the overall cell stabilization.

Marine environments are very complex regarding their effects on the deterioration of elastomers. The results of saltwater resistance tests (Fig. 5), an important indicator of wetsuit durability for marine use, showed that the specimen containing TBNRs had excellent dimensional stability and, consequently high salt resistance. This may also be due to the interface interactions between the OA chain on the surface of TBNRs and the EPDM matrix, increasing the binding force between the cell wall and the cell ribs, thereby increasing the cell's morphological stability. As a result, it is judged that the saltwater resistance, determined by the dimensional stability of foam, could be improved by improving processing stability of the polymer as well as cell stabilization.

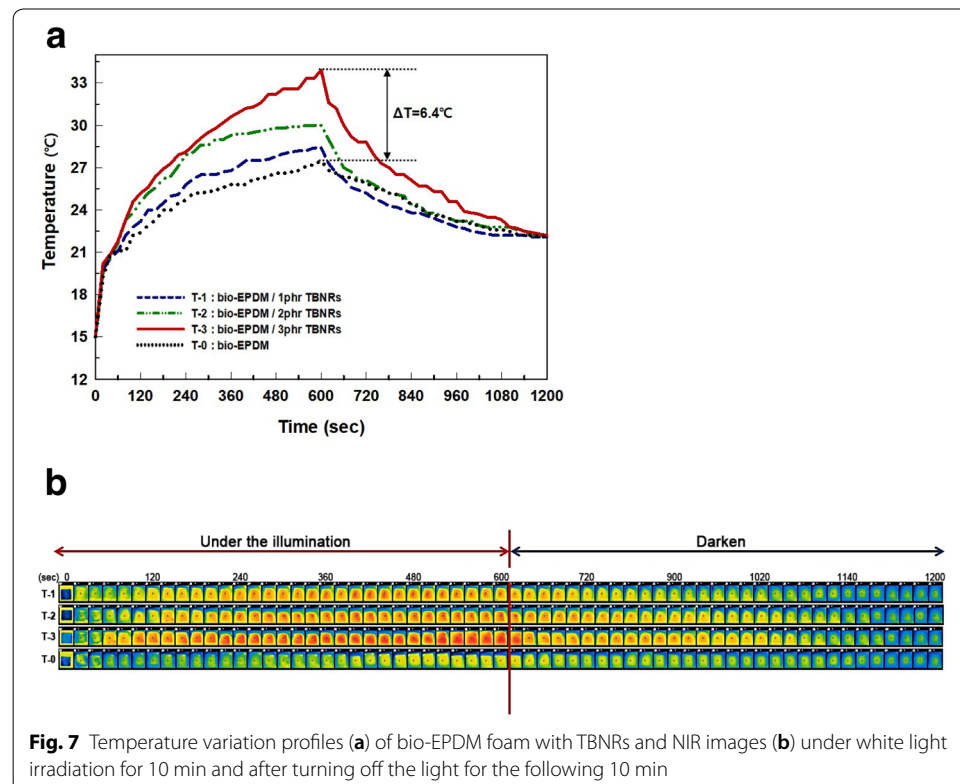


Thermal properties of bio-EPDM foam with TBNRs

The thermal properties of bio-EPDM foams with various mass ratios of TBNRs are shown in Fig. 6. The TGA thermogram in Fig. 6a indicates that the first mass-loss about 2% occurred in the temperature range of 150–350 °C, which is due to the decomposition of the OA hydrocarbon chain. Decomposition of the EPDM polymer began at 430 °C and was complete at 590 °C, leaving a small amount of tungsten. Figure 6b is an enlarged image of the section 200–500 °C, representing the derivative TGA curve in Fig. 6a. It was observed that the decomposition temperature of the bio-EPDM foams moved to higher temperature as the amount of TBNRs increased. These results indicate that the interfacial interaction between the OA chain on the surface of the TBNRs and the bio-EPDM matrix improved the chemical stability of the bio-EPDM foam and improved the thermal stability of the composite foam consequently (Jeon et al. 2019).

Photothermal properties of bio-EPDM foam with TBNRs

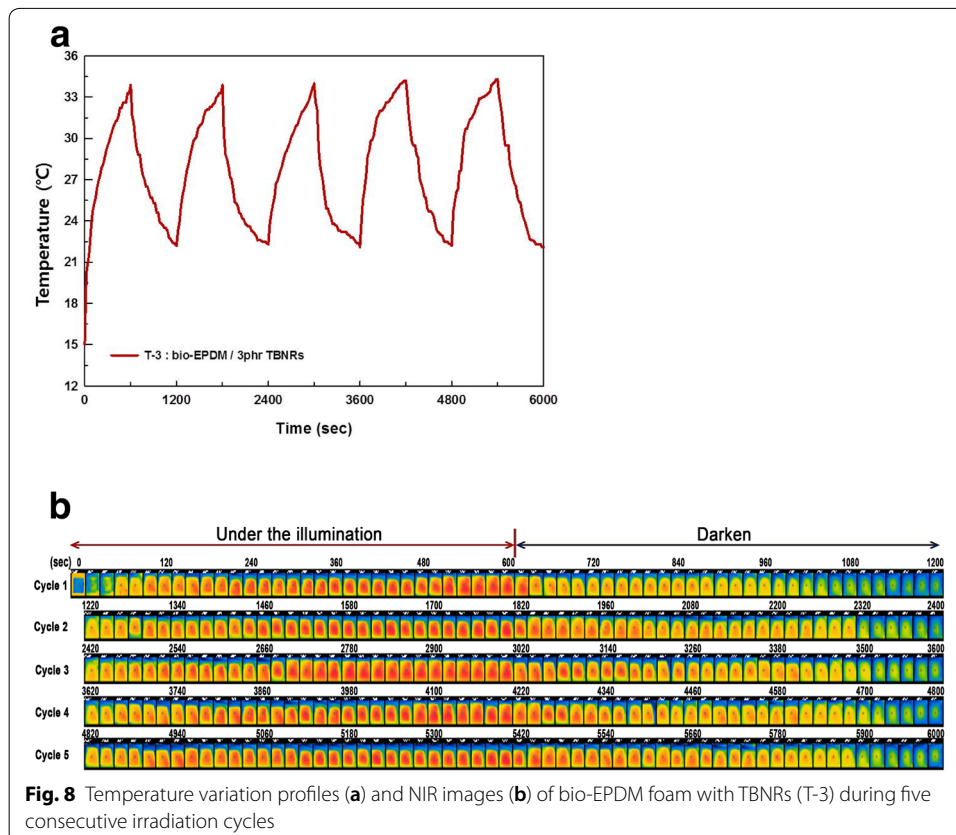
To determine the effect of TBNRs on the foam's photothermal function, the surface temperature change upon irradiation with a solar simulator was measured. The surface temperature of the specimen was measured using an NIR camera under white light irradiation produced by a solar simulator for 10 min at room temperature of 22 °C, followed by another measurement for 10 min after turning off the light. The surface temperature was measured every 20 s and the NIR images were captured as presented in Fig. 7. Before white light irradiation, the surface temperature of all specimens were 15 °C. As irradiation time increased, the surface temperature of all specimens increased, and the



maximum surface temperature of the specimen after 10 min of light irradiation was 27.5 °C, 28.4 °C, 30.0 °C, and 33.9 °C with 0, 1, 2, and 3 phr TBNRs, respectively. With 3 phr TBNRs, the surface temperature of the specimen was 6.4 °C higher than that of the specimen without TBNRs, indicating an excellent photothermal effect. Tungsten bronze (MxWO_3) has a heat generating effect due to its strong heat absorption ability by plasmon polariton of free electrons in the range of NIR wavelength. Therefore, these results clearly show that the tungsten bronze demonstrates a photothermal effect even when it was mixed into a 2 mm thick foam as fillers in the bio-EPDM matrix.

Effect of multiple light exposures

The change in the photothermal performance of the specimen containing 3 phr TBNRs (which was found to exhibit the best photothermal effect) was observed after multiple exposure to 10 min/cm² of white light (100 W) and 10 min of no light on the specimen surface. A representative NIR image is presented in Fig. 8. The maximum surface temperature of the specimen after each cycle of repeated irradiation was 33.9 °C, 33.9 °C, 34.0 °C, 34.2 °C, and 34.3 °C. No significant changes in the photothermal performance of the specimen were observed after multiple exposure, indicating that a continuous photothermal performance can be maintained with bio-EPDM-TBNRs composite foam.



Conclusions

Bio-EPDM composite foams were prepared with various ratio of TBNRs to develop an eco-friendly wetsuit material for marine sports. The changes in the mechanical properties, elastic properties, saltwater resistance, and photothermal properties were examined. Overall, when TBNRs were added, the cross-linking and blowing speed of the foams were well-balanced, and smooth nucleation and cell growth were achieved internally. As a result, the processing stability of the foam was improved, forming a foam elastomer with excellent thermal insulation, flexibility, elastic properties, and foam stability without significant changes in mechanical properties. In particular, the excellent foam stability of the bio-EPDM foam with TBNRs in sea water highlights its superiority as a material for marine sports. Moreover, the excellent photothermal effect after light irradiation indicated that the material developed in this study is suitable for use as a thermo-functional wetsuit material for water sports and activities. Therefore, the bio-EPDM foam material containing TBNRs at the optimum ratio can be fully utilized for the development of eco-friendly and high-performance wetsuit materials with excellent elasticity, flexibility, and thermal insulation.

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Authors' contributions

KWO and JP are principal investigators who designed the research plan and experiments. JSS, EYP, TK, and YE carried out the experiments, analyzed the data, and drafted the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The data sets used and analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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