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RESEARCH PAPER

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Physical Properties of Biodegradable Fishing Net in Accordance with Heat-Treatment Conditions for Reducing Ghost Fishing

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Abstract

This study aims to improve the physical properties of biodegradable fishing nets in the sea after a certain period to reduce ghost fishing and protect the marine ecosystem. The net, made of biodegradable resin, has a low melting point, which makes it difficult to be heat-treated. Furthermore, the performance of the net varies depending on the manufacturer. The physical properties of a series of biodegradable nets from PBS and PBAT resin blend heat-treated for 20 min at 55-75 °C with 5 °C intervals were investigated. No significant difference in the breaking strength of the net was observed from 55 °C to 70 °C, but it was considerable between 75 °C and 55 °C. As the heat treatment temperature increased, the pore size inside the knot decreased, and the binding strength increased. The shape of the biodegradable net became uniform as heat treatment temperature increased. The net heat-treated at 75 °C for 20 min was most preferable based on shape, physical properties of the net. In addition, biodegradable nets, which are still in development stage, should be improved in accordance with the needs of fishermen, and must be distributed in the future for the protection of marine environment and life.

Introduction

Until the early 1960s, most nets for fishing were made from natural fibers such as cotton and Manila hemp. However, since World War II, the development and distribution of synthetic fibers such as nylon made of polyamide (PA) has rapidly replaced natural fibers (Andres & Garrother, 1964). Synthetic fibers exhibit excellent strength and flexibility, resulting in good fishing performance and durability. Moreover, it could be applied to a wide range of products owing to their low cost and good processability. They have greatly contributed to the improvement in performance of small fishing gears such as gill nets (Anonymous, 1990; Wright & Doulman, 1991; Richards, 1994).

However, when left in the sea or swept away, these synthetic nets do not degrade and retain functionality for a long period of time, causing "ghost fishing" which leads to loss of fishery resources. In addition, the abandoned fishing gears affect marine environment by entangling and killing marine animals (Erzini *et al.*, 1997; Smolowitz, 1978; Santos, Saldanha, Gaspar, & Monteiro, 2003a, 2003b; Tschernij & Larsson, 2003; Ayaz *et al.*, 2006; Kim, Kim, Lim, An, & Suurronen, 2016). Countries around the world are promoting a systematic program to manage the derelict fishing gears in an integrated manner to prevent ghost fishing and derelict fishing gears.

Recently, Korea has developed nets using biodegradable resins that are degraded by microorganisms (bacteria or fungi) in sea water after a certain period to prevent ghost fishing and protect the marine ecosystem (Park *et al.*, 2007a, Park, Park, Bae, & Lim, 2007b, Park, Kim, Choi, & Cho, 2010;). Polybutylene succinate (PBS) and Polybutylene adipate-*co*-terephthalate (PBAT) are blended with the resins for these biodegradable fishing gears. The resins harden because of their poor flexibility when spun as netting twines. Generally, after mesh weaving, the nets are finished by the steam heat treatment process which spreads the nettings evenly and strengthens the knots. The biodegradable resin blend of PBS and PBAT has a melting temperature of 114 °C, which is difficult to control the heat treatment temperature in the steam heat-treatment system. Thus, either the knot condition is poor, or the mesh shape is irregular, leading to significant variance in the physical performances of the nets. In addition, net without proper heat treatment was reported to be easily torn due to the external force resulting from the imbalance of the force. Its bad shape was also observed to affect fishing performance. Biodegradable nets cannot be loaded on board of the fishing boat properly because they are bulkier than the nylon net. This swelling phenomenon encourages the net to be caught by the feet of the fisherman during work or be entangled in the net hauler. This problem was reported to be due to the imbalance of heat treatment (Park & Kim, 2012).

The physical performances (breaking strength, elongation, mesh shape etc.) of the biodegradable net depend on the heat treatment method after net weaving. Quantitative data collection is necessary through experimentation because of affecting fishing performance. And it is necessary to standardize the net making process for manufacturer.

This study aims to evaluate the physical properties of biodegradable nets at varying heat treatment temperature. The results will be used as fundamental data for improving the quality and fishing performance of biodegradable fishing gears, effectively promoting the use of biodegradable fishing gears.

Materials and Methods

Characteristics of Biodegradable Netting Twine

The biodegradable netting twine was made monofilament type with the biodegradable resin blended of PBS 82 wt% (weight percentage) and PBAT 18 wt%, which were chosen for its excellent strength and flexibility, respectively.

PBS is an aliphatic polyester that is composed through esterification and condensation polymerization of 1,4-butanediol as fatty group glycol with succinic acid as fatty group dicarboxylic acids. It has high flexibility, excellent structural strength, and high crystalline properties. But has a low extension coefficient due to its high crystalline properties. Its specific gravity is 1.26, melting point is 114 °C (Fujimaki, 1998).

PBAT resin according to the present embodiment corresponds to a fatty group/aromatic group co-polyester that is formed of 1,4-butanediol as fatty group glycols, and adipic acids that are fatty group components and dimethyl terephthalate (DMT) that are aromatic group components, as dicarboxylic acids. The PBAT resin has the same property as that of elastomer, and thus has an excellent extension coefficient, and simultaneously has a low strength and a low solidification speed compared to the PBS resin as a homopolymer. By using the different physical properties of the PBS resin and the PBAT resin, a structural strength required for a fishing gear was ensured, and simultaneously the flexibility, elastic recovery and impact resistance of the fishing gear was ensured (Park *et al.*, 2007a).

The monofilament spun by polymerizing PBS and PBAT is degraded by microorganisms such as bacteria or fungi within two years (Ishii *et al.*, 2008), resulting in low-molecular weight oligomers. The performance of the biodegradable monofilament used in this study was compared with a conventional nylon (polyamide, PA) monofilament with same thickness.

Heat Treatment Method After Net Weaving

The test net composed of 82% PBS and 18% PBAT was produced by spinning netting twines with 0.296±0.002 mm diameters (Denier, 783.88 Td). The mesh size was 52 mm (stretched inner size). The number of horizontal and vertical stiches was 1,000 and 280, respectively, and mesh weaving was performed with double knot. The heat treatment was performed by applying steam to a sealed flat plate chamber. The heat setter was rectangular (12 m × 2 m × 0.5 m, L×B×D), installed inside with a cradle to fix the net. The cradle was hydraulically driven for the interval to be adjusted according to net length and mesh size. The test nets were fixed to a cradle installed at both ends of the heat treatment chamber. Traction of 245±10 N was applied for the meshes to be completely extended. The heat treatment was performed by installing the net, closing and sealing the chamber lid, and injecting steam at 100 °C to the connected piping (Figure 1). The test fishing gears were prepared by heat treatment for 20 min between 55 and 75 °C (chamber temperature) at 5 °C interval. The amount of steam injected was adjusted using a valve to keep the temperature within ±2 °C during the heat treatment. The initial temperature in the chamber during the heat treatment was set at 25±2 °C, and the average internal pressure was 4.12 $N\cdot cm^{-2}$.

The biodegradable resin used in this study has a thermal property at a melting temperature of 114 ° C and is occurred the glass transition at 80-85 °C. In addition, this resin has the thermal property of heat distortion at about 97 °C. In these temperatures, resin or

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monofilament for net was large change physical properties (Xu and Guo, 2010). Therefore, the maximum heat treatment temperature was determined to 75 °C considering the glass transition temperature. Table 1 shows the heat-treatment conditions for each sample.

Analysis of Physical Properties of Netting Twine and Net

To determine the physical properties of the monofilament used for the test fishing gear, its breaking strength (=tensile strength at break), elongation at break, and elasticity were measured. To measure the breaking strength and elongation at break, tensile testing was performed in compliance with the ASTM D638 material test method using a universal testing machine (Instron3365, Instron Corp., Norwood, USA) with a 5-kN load cell and the minimum displacement rate is 0.01 mm min^{-1}. The measurement results were stored to the 0.1mN every 0.1S in a computer database prior to analysis. The clamps were set 400 mm apart to hold the filament during the tensile test. The ultimate tensile strength (break strength) and elongation at break were measured for 20 specimens.

The nets were measured by fixing five stiches horizontally and vertically on the grips following the KS K0412 (2005) test using a universal testing machine. The results were averaged for 20 nets per temperature. The breaking strength and elongation were measured at breaking point and were expressed as the breaking strength and elongation of one strand of the netting twine.

The temperature of testing room at time of test was 24±2°C and relative humidity was 64±2%.

The heat-treatment condition was determined and analyzed by observing the shape of the knots and measuring the bar distance using an optical microscope (SV-35, Sometech Co. LTD, Korea).

Distance between bars of a mesh was measured after drying the heat-treated samples for 24 h. As shown in Figure 2, the distance was measured between bars on the upper part of a mesh. The X-shaped specimens were obtained for measuring distance between bars by cutting the lower part of a mesh and the upper part of a mesh. Specimens were placed naturally on the measuring plate of an optical microscope and measured. This was performed 20 times, and the values were averaged. The image was magnified 40 times using an optical microscope and that was analyzed with image analysis software (ITplus 4.0, Sometech Co. LTD, Korea).

Results

Physical Properties of Netting Twine

To investigate the physical properties of the netting twine used in the fishing gear, breaking strength, knot strength, and elongation of each netting twine were

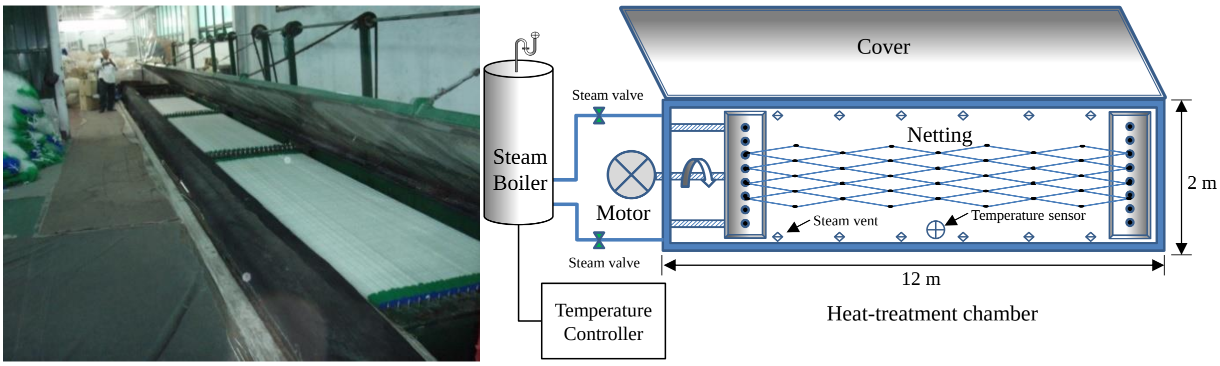

Figure 1. Schematic diagram of steam heat-treatment chamber for fishing net.

Table 1. Heat-treatment conditions of experimental fishing nets

Material	Temperature (°C)		Steady time (min) 3)
	Setting Temp. 1)	Avg2). Temp.	
Bio-netting	55	54±2	20
	60	61±2	
	65	67±1	
	70	72±1	
	75	77±1	

1) Temp. : Temperature
2) Avg. : Average
3) Heat treatment for 20 min upon reaching the set temperature

measured in both dry and wet conditions.

The breaking strength and elongation from the experiments were compared with those from commercial nylon netting twine of the same standard. The results are shown in Table 2 and Figure 3.

For breaking strength measurements, the nylon monofilament was 58,361 N·cm^{-2} when dry and 47,508 N·cm^{-2} when wet. The strength in wet condition decreased by 18.8% compared with that in dry condition. The elongation was 25.1% in dry condition and 31.7% in wet condition, an increase of 26.0%.

On the other hand, the bio-monofilament of the biodegradable net had strength of 47,508 N·cm^{-2} in dry condition and 47,005 N·cm^{-2} in wet condition, equivalent to 99.1% of the wet nylon strength. The elongation was 25.7% in dry condition and 26.0% in wet condition, showing minimal difference. The elongation of bio-monofilament was 82.1% that of the nylon, both in wet condition.

The tensile strength and elongation test of knotted monofilament results for each sample are shown in Table 3 and Figure 4. The tensile strength of knotted nylon monofilament was 43,040 N·cm^{-2} in dry condition and 38,331 N·cm^{-2} in wet condition. The tensile strength in wet condition was 11.0% less than that in dry condition. The elongation was 15.6% in the dry condition and 23.2% in wet condition, a significant increase of 48.2%.

On the other hand, the biodegradable netting twine used in the test fishing gear showed the tensile strength of knotted bio monofilament of 31,696 N·cm^{-2} in dry conditions and 32,523 N·cm^{-2} in wet conditions, equivalent to 84.9% of the wet nylon tensile strength. The elongation was 19.5% in dry conditions and 20.0% in wet conditions, showing little difference. The elongation of the knotted bio-monofilament was about 86.4% that of knotted nylon monofilament in wet condition. As reported in Kim, Park, Lee, & Lim (2013), nylon netting twine absorbs water, which leads to a significant increase in its elongation when wet.

Physical Properties of Biodegradable Net with Different Heat Treatment Temperatures

The breaking strength and elongation of the biodegradable net with different heat-treatment temperatures are shown in Table 4. In addition, their variations are illustrated in Figure 5. The temperature

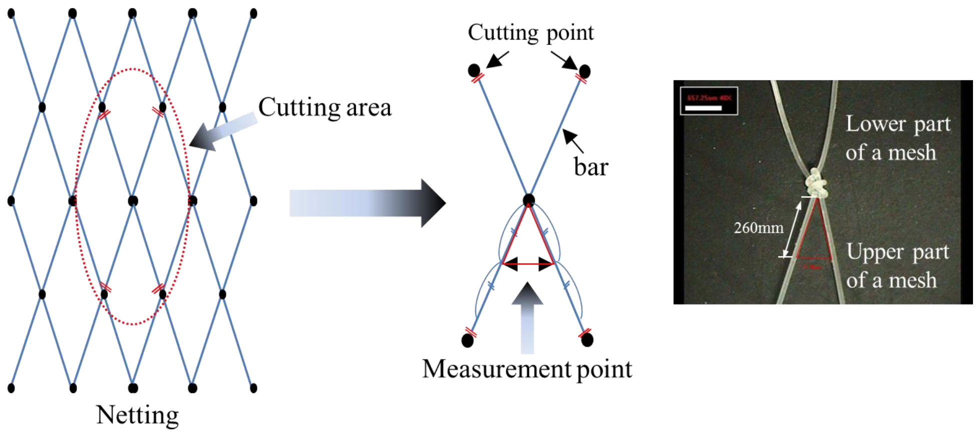

Figure 2. The measuring point the distance between bars in a mesh.

Table 2. Strength and elongation of Bio and Conventional (Nylon) monofilaments in dry and wet conditions

Material (Diameter, mm)	Denier (Td)	Weight (g·m^{-1} ± S.D.[1)])	Breaking strength		Elongation	
			Dry (N·cm^{-2} ± S.D.)	Wet (N·cm^{-2} ± S.D.)	Dry (% ± S.D.)	Wet (% ± S.D.)
Nylon[2)] (Ø0.293)	690.92	0.077 ± 0.0001	58,361 ± 10.93	47,409 ± 19.28	25.12 ± 1.61	31.65 ± 2.34
Bio[3)] (Ø0.296)	783.88	0.087 ± 0.0010	47,508 ± 4.25	47,005 ±4.75	25.73 ± 0.66	25.97 ± 0.49

1) Standard deviation
2) Conventional monofilament for gill net

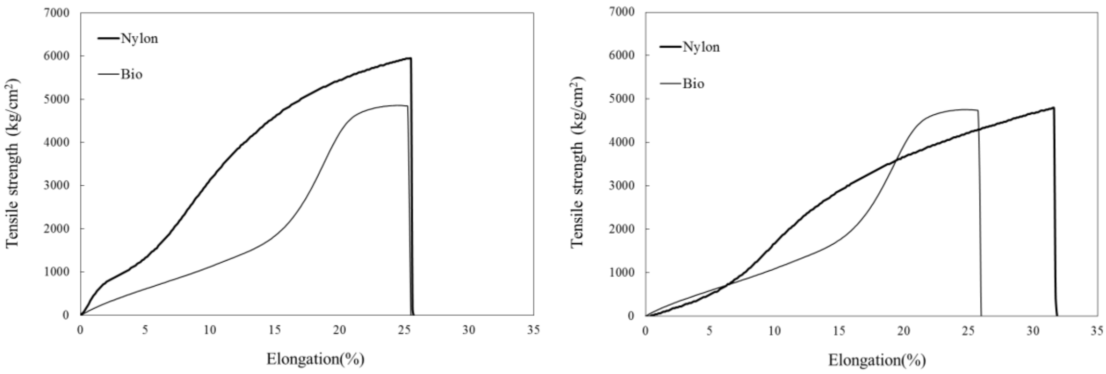

Figure 3. Strength and elongation curves of each monofilament.
*Dry condition (Dry) denotes without soaking in sea water;
Wet condition (Wet) denotes that involved soaking the monofilament in distilled water for 24 h

Table 3. Strength and elongation of Bio and Nylon (PA) knotted monofilaments used in experimental netting in dry and wet conditions

Material (Diameter, mm)	Denier (Td)	Weight ($g·m^{-1}$ ± S.D.[1])	Breaking strength		Elongation	
			Dry ($N·cm^{-2}$ ± S.D.)	Wet ($N·cm^{-2}$ ± S.D.)	Dry (% ± S.D.)	Wet (% ± S.D.)
Nylon[2] (Ø0.293)	690.92	0.077 ± 0.0001	43,040 ± 51.65	38,331 ± 44.17	15.63 ± 2.18	23.16 ± 4.22
Bio[3] (Ø0.296)	783.88	0.087 ± 0.0010	31,696 ± 21.32	32,523 ±21.06	19.54 ± 0.22	20.02 ± 0.23

[1] Standard deviation
[2] Conventional monofilament for gill net
[3] Bio was fabricated by blending PBS and PBAT resins

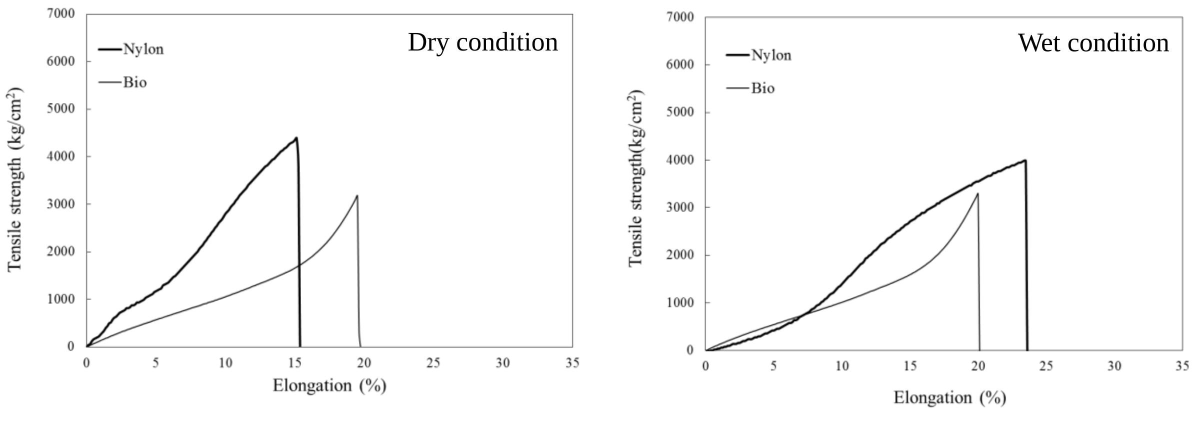

Figure 4. Strength and elongation curves of each knotted monofilament.
*Dry denotes the dry condition that did not involve immersion in sea water;
Wet denotes the wet condition that involved immersing the monofilament in distilled water for 24 h

was controlled by manually adjusting the steam valve, which presented inaccuracy in maintaining the set temperature leading to a deviation of ±2°C. As it increased, the breaking strength of the biodegradable net decreased gradually. For samples from the heat-treatment at 55°C, the breaking strength was 25,754 $N·cm^{-2}$ in dry condition and 23,099 $N·cm^{-2}$ in wet condition. For samples from the heat-treatment at 70 °C, it was 21,854 $N·cm^{-2}$ when dry and 21,736 $N·cm^{-2}$ when wet, showing insignificant change. However, at 75°C, it was 20,002 $N·cm^{-2}$ and 20,511 $N·cm^{-2}$, respectively, showing a remarkable change. Elongation is generally inversely proportional to the breaking strength of the netting twine. However, in this study, it also decreased with increasing heat-treatment temperature. The elongation in dry condition showed significant

Table 4. Strength and elongation of bio nettings in dry and wet conditions

Heat-treatment Temperature (°C)	Breaking strength			
	Dry (N·cm^{-2} ± S.D.)	Wet (N·cm^{-2} ± S.D.)	Dry (% ± S.D.)	Wet (% ± S.D.)
Raw netting[1)]	25,754 ± 1.37	23,608 ± 2.74	21.93 ± 2.34	19.25 ± 7.91
55 (54)[2)]	22,912 ± 1.08	23,099 ± 0.39	21.16 ± 2.99	20.56 ± 1.16
60 (61)	22,422 ± 1.96	22,677 ± 0.98	22.44 ± 5.01	21.32 ± 2.32
65 (67)	22,148 ± 1.57	22,364 ± 1.76	20.73 ± 4.09	21.47 ± 7.00
70 (72)	21,854 ± 1.18	21,736 ± 1.08	21.62 ± 3.66	20.77 ± 3.29
75 (77)	20,002 ± 0.98	20,511 ± 1.37	19.79 ± 3.47	19.60 ± 5.97

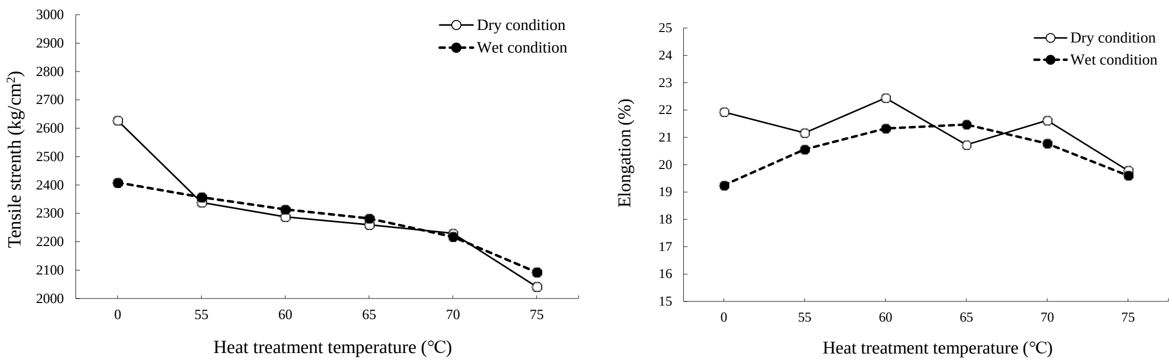

Figure 5. Changes in strength and elongation of biodegradable with varying heat treatment temperatures *0 °C represents no heat treatment.

fluctuations and decreased starting from samples heat-treated at 65°C in wet condition (Figure 5).

As the heat-treatment temperature increased, the knot binding strengthened. At 55°C, the heat-treatment of netting was not complete, leading to bending of the bars, and insufficient bonding of the knots. However, as adequate heat-treatment temperature increased, the knot bonding improved and knot size diminished. The heat-treated mesh at 75°C showed uniform bar spreading, firmly bonded knot, and reduced knot size.

In the mesh, the distance between bars was significantly farther at lower heat-treatment temperature. The distance decreased as temperature increased. The mesh bars at the lowest heat-treatment temperature of 55°C showed were 3.85 mm apart, 2.02 times greater than that for the specimen heat-treated at 75°C with only 1.91 mm. The distances were similar for sample heat-treated at 55°C (3.85 mm) and 60°C (3.34 mm), which suggests incomplete heat-treatment. Subsequently, the bar distance significantly decreased starting at 65°C (2.20 mm). The difference in knot conditions of meshes from various heat-treatment temperatures were observed through an optical microscope with images shown in Figure 6. The knot of the mesh heat-treated at 55°C was not completely bonded and its bar had undergone severe bending. As the heat treatment temperature increased, the bars of the mesh were straightened, and the knots were completely bonded. For nets heat-treated at 55°C and 60°C, slip phenomenon occurred upon tension, rendering them unsuitable for netting.

Discussion

Most of nets for fishing use synthetic fibers based on petroleum compounds. These synthetic fibers remain in the sea without degradation when discarded or lost. They continue to function as a fishing gear (Anonymous, 1990; Wright & Doulman, 1991; Richards, 1994), causing ghost fishing, resulting in trapping and death of fish. The accumulation of dead organisms in a marine ecosystem leads to several marine environmental problems such as the destruction of habitats and spawning grounds (Matsuoka, Nakashima, & Nagasawa, 2005).

To solve this problem, a biodegradable net was developed capable of being completely degraded in sea water and carbon dioxide by microorganisms and bacteria (Tokiwa, Calabia, Ugwu, & Aiba, 2009). These were designed considering the impact of lost or discarded gill nets and fish pots. Since gill nets occupy a significant amount of space in a limited fishing boat, they should be as compact as possible. Hence, heat-

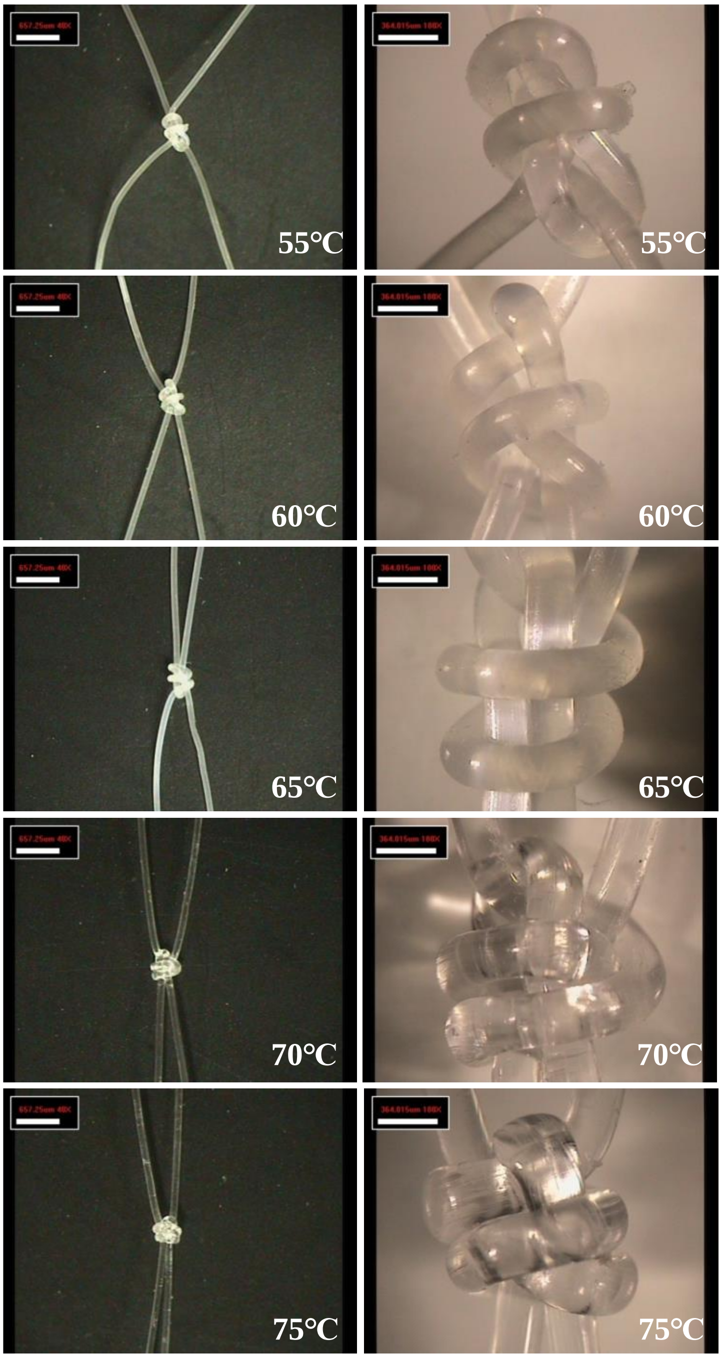

Figure 6. Heat treated condition and mesh shape of biodegradable net according to heat treatment temperature

Table 5. Distance between the bars of the mesh in the biodegradable net according to the heat treatment temperature

Item	Heat-treatment temperature (°C)					
	0	55	60	65	70	75
Distance(mm)[1)]	9.47±0.73[2)]	3.85±0.61	3.34±0.21	2.2±0.20	1.99±0.09	1.91±0.16

1) Distance between mesh bars
2) Average and standard deviation

treatment after mesh weaving was performed at controlled conditions. Heat-treatment is crucial in determining the performance of the net. Steam heat treatment with too high temperature or too long processing time weakens the net or melts a part of the netting twine. In contrast, if the heat-treatment temperature is too low, the knot of the net will not completely bond, leading to curl formation and net inflation. When the knot of the net is tightened, slip occurs in the netting twine, thereby twisting the net or loosening the knot. Therefore, heat treatment temperature and time must be well regulated to stabilize net performance and produce straight nets. If the net is not straightened and a curl is formed, it will easily be blown by weak winds, presenting higher probability of catching the feet of the worker or wrapping around the net hauler or fishing equipment, which reduces the work efficiency (Park, Kim, Lim, & Choi, 2015).

The heat-treatment equipment used by manufactural manufacturers has not been standardized for net-making yet. The method used by each manufacturer is similar and only vary in scale, heat treatment facilities, and process. Consequently, there is also a difference in the performance of the nets produced. In addition, since the heat treatment process uses steam, temperature variation in the actual chamber is large, and temperature control is difficult, thereby causing significant variance in the physical properties of the net. Therefore, the performance of nets from different heat treatment temperatures and period must be investigated. To solve this problem and induce uniform heat transfer, a submerged immersion heat treatment method has been developed, where the net is immersed in a water tank containing hot water (Park *et al.*, 2015). However, despite the uniformity of heat transfer and standardization of the process, it requires a significant amount capital and uses plenty of water, which makes it commercially impractical.

In this study, the physical properties of biodegradable nets from five heat treatment temperatures were evaluated. At temperatures below 65 °C, the bars of the net did not straighten, and the binding force of the knots was weak. Uniform shape was obtained at 65 °C or higher, and the knots became firmer as temperature increased. However, the breaking strength and elongation slightly decreased, similar to the observations by Park *et al.* (2015) in their submerged heat treatment. The biodegradable net based on PBS resin has been reported to have a softening point of 95 °C (Cao, Okamura, Nakayama, Inoue, & Masuda, 2002). Furthermore, its strength reportedly sharply decreases and changes in its physical properties intensify towards the softening point. Therefore, optimum heat treatment temperature and time should be determined in consideration of the shape of the net, the quantitative property evaluation, and the marine performance test.

Conclusions

This study investigated the physical properties, knot condition, and marine catching performance of biodegradable net from the resin blend of PBS and PBAT with different heat treatment temperatures. The heat treatment for 20 min was varied between 55 and 75 °C at 5 °C intervals. The breaking strength of the net heat-treated at 55 °C was 25,754 $N{\cdot}cm^{-2}$ in dry condition and 23,099 $N{\cdot}cm^{-2}$ in wet condition. It was 21,854 $N{\cdot}cm^{-2}$ in dry condition and 21,736 $N{\cdot}cm^{-2}$ in wet condition for the net heat-treated at 70 °C. Thus, the effect of dry and wet conditions on breaking strength was not significant from 55 to 70 °C. However, a significant difference was observed for the sample under the heat-treatment at 75 °C with 20,002 $N{\cdot}cm^{-2}$ in dry condition and 20,511 $N{\cdot}cm^{-2}$ in wet condition. The elongation exhibited stronger dependence on temperature in dry condition but was not evident in wet condition from 65 °C or higher. The distance between the bars of the mesh was decreased with increasing heat-treatment temperature. For 55 °C heat-treatment, the bars of the mesh were 3.85 mm apart, 2.02 times greater than that in the heat-treated mesh at 75 °C. As the heat-treatment temperature increased, the pores inside the knot decreased, thereby increasing the binding strength.

Moreover, the shape of the net became more uniform as the heat-treatment temperature increased. Finally, the performance of the biodegradable net was highest when it was heat-treated for 20 min at 75 °C in terms of shape, physical properties, and fishing performance.

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