Thesis for the Degree of Master of Engineering

Changes in Rupture Strength of Flying Fish Roe Analogs Prepared from the Calcium Alginate Gel with and without Hydrocolloids against Physicochemical Treatments

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친수성 콜로이드 첨가에 따른 인조 날치알의 이화학적 처리에 의한 파열 강도 변화

이승은

부경대학교 대학원 식품공학과

요 약

본 연구는 알긴산에 다양한 농도의 천연다당류를 첨가하여 제조된 인조 날치알을 이용하여 식염농도 및 가공조건에 따른 파열강도의 변화를 밝히는데 그 목적이 있다. 천연다당류의 혼합 후 식염내성 효과를 알아보기 위해 염화 나트륨 용액에 1시간 처리 후 파열강도를 측정하였으며, 물리적 처리로는 열탕, 동결-해동처리를 실시하였다. 천연다당류는 xanthan gum, glucomannan, agar, iota-carrageenan, kappa-carrageenan, gelatin, pullulan, β-cyclodextrin을 사용하였다. Xanthan gum, glucomannan, gelatin, iota-carrageenan, kappa-carrageenan, agar, pullulan 모두 sodium alginate와 혼합했을 때 파열강도가 상승하였으나 식염의 존재 하 에서는 파열강도가 급격히 감소하였다. 이에 반해, β-cyclodextrin을 혼합한 인조 날치알은 식염에 큰 영향을 받지 않아 식염내성이 가장 우수하였다. 식염의 내성을 갖는 β-cyclodextrin첨가 인조 날치알의 물리적 처리 효과를 알아보기 위해 95℃에서 20분 간격으로 80분간 열탕 처리를 하였고 -20℃이하로 5일간 동결 후 상온에서 해동하고 파열강도를 측정하였다. 그 결과, 95℃

열탕처리 이후 파열강도는 열탕 처리 20분까지는 증가하였으나, 그 이후에는 감소하는 것으로 나타났다. 또한 5일 간의 동결-해동 처리에 의하여 그 파열강도는 현저히 감소하였다.

Introduction

Encapsulation is a process where such active substances as flavors, drugs, enzymes, vitamins, essential oils and others are included in a matrix or wall system with the purpose to control their releases and to protect them from deteriorative processes like oxidation, evaporation and degradation (Deladino et al., 2008; Palzer., 2009). Among all these active materials, the most widely used for encapsulation in food applications are polysaccharides (Nedovid et al., 2011).

Alginic acid has been widely used as polymer materials for encapsulation, because it is nontoxic, biodegradable, and biocompatible (Gombotz et al., 1998). Alginic acid is a copolymer of two monomer units, 1,4-linked-*b*-D-mannuronic and *a*-L-guluronic acids containing carboxyl groups acting as an active site for the binding with metals (Soares et al., 2004). With these binding capacity of alginic acid, gel is formed by an ionic interaction between a multivalent cations and G residues from alginate chain and shape of 'egg-box' form cavities to accommodate divalent cations in a chelate type of binding, which is considered as the intermolecular junction having arrays of site-bound cations (Grant et al., 1973; Morris et al., 1990). The binding of

inorganic ions to the alginic acid makes it possible to show a number of properties and makes it a perfect choice for the use of various applications (Liu et al., 2002; Davis et al., 2003). In the food industry, alginate capsules and beads can be formed through the gelation reaction. Some disadvantages are often associated with this carrier, including high bio molecule leakage, low mechanical strength and large pore size (Elnashar et al., 2009). Howell et al. (1998) and Leo´n et al. (2000) reported available on interactions between hydrocolloids and alginic acid. In addition, it is known from rheological studies that mixtures of hydrocolloids in concentrated solution can interact synergistically (Shatwell et al., 1991). There is considerable interest in the use of mixed food grade hydrocolloids systems for use in functional foods and dietary or health products.

Sodium chloride influenced the sodium alginate gel strength (Yong et al., 2001). The physicochemical properties of flying fish roe analogs using alginate gel was also affected by sodium chloride treatments. This is caused by the liberation of calcium ion which came away from bounded G residues of calcium-alginate gel when performing sodium chloride treatment (Cho et al., 2015).

Generally, sodium chloride is used to improve the sensory properties of foods, by increasing saltiness, decreasing bitterness, and increasing sweetness and other congruent flavor effects (Keast et al., 2003). It is

inevitable to avoid adding salt to improve the taste and palatability of food. Therefore, it is necessary to develop sodium chloride resistance flying fish roe analog.

The present study aims to elucidate changes in rupture strength of flying fish roe analogs prepared from the calcium alginate with hydrocolloids against boiling and freeze-thaw processes.

Materials and Methods

1. Materials

1.1 Materials

Sodium alginate and calcium lactate were purchased from Junsei Chemical Corporation (Tokyo, Japan). Sodium chloride was purchased from Sigma Chemical Co. Iota-carrageenan, kappa-carrageenan, cyclodextrin, and glucomannan were purchased from MSC Co. Ltd., and agar was purchased from Junsei Chemical Corporation (Tokyo, Japan). Gelatin and xanthan gum were purchased from Sigma Chemical Co. and pullulan was purchased from Gogoong Co., Ltd. All reagents used in this study are of analytical grade.

2. Methods

2.1 Preparation of flying fish roe analogs

Flying fish roe analogs were prepared using sodium alginate concentration

of 1.66% and calcium lactate concentration of 1.86%, according to the optimum conditions. The flying fish roe ananlogs were prepared by using a double nozzle. The outer nozzle (1 mm in outer diameter × 3 cm in length) was fed with sodium alginate at a rate of 1.5 mL/s using a peristaltic pump (Micro Tube Pump MP-3N, Eyela, Tokyo, Japan), and the inner nozzle (0.28 mm in inner diameter × 4.4 cm in length) was fed with soybean oil at a rate of 0.58 mL/s using a second peristaltic pump (cassette tube pump SMP-23, Eyela, Tokyo, Japan). The calcium lactate solution as a stabilizing agent was stirred at 280 rpm with a magnetic stirrer and the drop distance from the nozzle to the surface of the stabilizing agent was fixed at 17 cm.

2.2 Preparation of flying fish roe analogs mixed with hydrocolloids

Flying fish roe analogs mixed with hydrocolloids were prepared by mixing 1.66% sodium alginate with hydrocolloids at concentrations of 0.01%, 0.1%, and 1.0%. The hydrocolloids used xanthangum, glucomannan, agar, pullulan, gelatin, carrageenan and β-cyclodextrin. The outer nozzle (1 mm in outer diameter × 3 cm in length) was fed with hydrocolloids mixed analogs at a rate of 1.5 mL/s using a peristaltic pump (Micro Tube Pump MP-3N, Eyela, Tokyo, Japan), and the inner nozzle (0.28 mm in inner diameter × 4.4 cm in length) was fed with soybean oil at a rate of 0.58 mL/s using a second

peristaltic pump (cassette tube pump SMP-23, Eyela, Tokyo, Japan). The calcium lactate solution as a stabilizing agent was stirred at 280 rpm with a magnetic stirrer and the drop distance from the nozzle to the surface of the stabilizing agent was fixed at 17 cm.

2.3 Sodium chloride treatment of flying fish roe analogs mixed with hydrocolloids

The sodium chloride treatment against the flying fish roe analogs were performed by storing the flying fish roe analogs prepared with and without hydrocolloids in sodium chloride solutions of various concentrations (0.2%, 0.4%, 0.6%, 0.8%, and 1.0%) at 20℃ for 1h. The hydrocolloids used were xanthangum, glucomannan, agar, pullulan, gelatin, carrageenan and β-cyclodextrin. Subsequently, the flying fish roe analogs were measured through the rupture strength test.

2.4 Boiling water treatment of flying fish roe analogs mixed with hydrocolloids

The flying fish roe analogs with and without hydrocolloids were immersed

in distilled water at 95 °C for different time intervals (20 min, 40 min, 60 min, and 80 min).

2.5 Freeze–thaw treatment of flying fish roe analogs mixed with hydrocolloids

The freeze–thaw treatment against flying fish roe analogs performed by storing the flying fish roe analogs with and without hydrocolloids at −20 °C for 5 days and then thawed the analogs to 20℃.

2.6 Measurement of rupture strength

Rupture strength was measured using five analogs prepared from different conditions by a rheometer (Model CR-100D, Sun Scientific Co., Ltd., Japan). The plunger used in this measurement was a circular disk with the diameter of 10 mm.

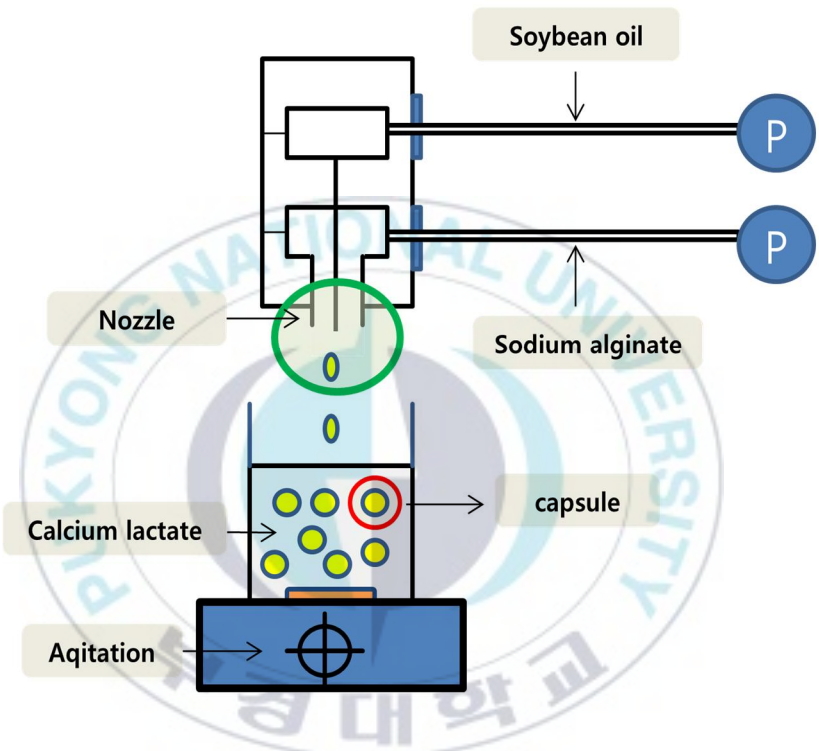

Fig. 1. Simple schematic diagram for preparing calcium alginate gel capsule with a double nozzle.

Results and Discussion

1. Changes in the rupture strength of flying fish roe analogs mixed with hydrocolloids against sodium chloride

1.1 Effect of xanthan gum

Xanthan gum (XG) is a naturally occurring white or yellowish white, free-flowing powder; soluble in both hot and cold water; practically insoluble in organic solvents (Rajesh., 2009). XG has been used in a wide variety of foods for a number of important reasons, including emulsion stabilization, temperature stability, compatibility with food ingredients (GarcõÂa-Ochoa et al., 2000). It is reported that the addition of natural gums such as XG can cause an increase in viscosity and elasticity (Wang et al., 2009).

Fig. 2 shows the rupture strength of the analogs mixed with XG (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs without XG was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,316.90±30.59 (kPa) for 0.01% XG, 1,176.90±52.36 (kPa) for 0.1% XG

and 602.41±45.21 (kPa) for 1.0% XG, respectively, in the absence of sodium chloride. The rupture strength decreased with the increment of XG amount under the conditions without sodium chloride amount. Generally, XG has unique rigid and influences gel strength. Their properties result from molecular interactions between XG and polysaccharides (Christianson et al., 1981). Nevertheless, the decrease in the rupture strength is caused by the decrease in calcium alginate concentrations of the analogs by the addition of XG. On the other hand, the rupture strength of analogs without XG decreased from 616.42±20.78 (kPa) to 350.24±56.92 (kPa), 266.18±98.51 (kPa), 182.12±80.63 (kPa), 126.09±28.02 (kPa) and 84.06±22.45 (kPa) by treatment of sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 0.01% XG decreased from 1,316.90±30.59 (kPa) to 770.52±24.26 (kPa), 630.43±54.52 (kPa), 434.29±47.69 (kPa), 364.25±53.96 (kPa) and 266.18±51.26 (kPa) by treating with sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Also, the rupture strength of analogs mixed with 0.1% XG decreased from 1,176.90±52.36 (kPa) to 980.67±15.23 (kPa), 784.53±25.63 (kPa), 728.49±74.21(kPa), 658.45±51.2 (kPa) and 378.26±59.95(kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. In case of the treatment with 1.0% XG, the rupture strength of the analogs sharply decreased from 602.41±45.21 (kPa) to 574.39±75.66

(kPa), 238.16±42.66 (kPa), 196.13±41.66 (kPa), 168.11±74.21 (kPa) and 140.10±12.51 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively.

The results show that the rupture strength decreased with the higher amount of XG and with higher concentration of sodium chloride. This indicates that sodium alginate and XG have a synergistic effect of gel strength, but the higher amount of XG results in the lower rupture strength due to the decrease in calcium alginate concentrations in the analogs. It is considered that the decreases in the rupture strength of the analogs in the presence of sodium chloride are caused by the self-association of gel structure of XG and liberation of calcium ions from calcium alginate gels (Pongjanyakul et al., 2007).

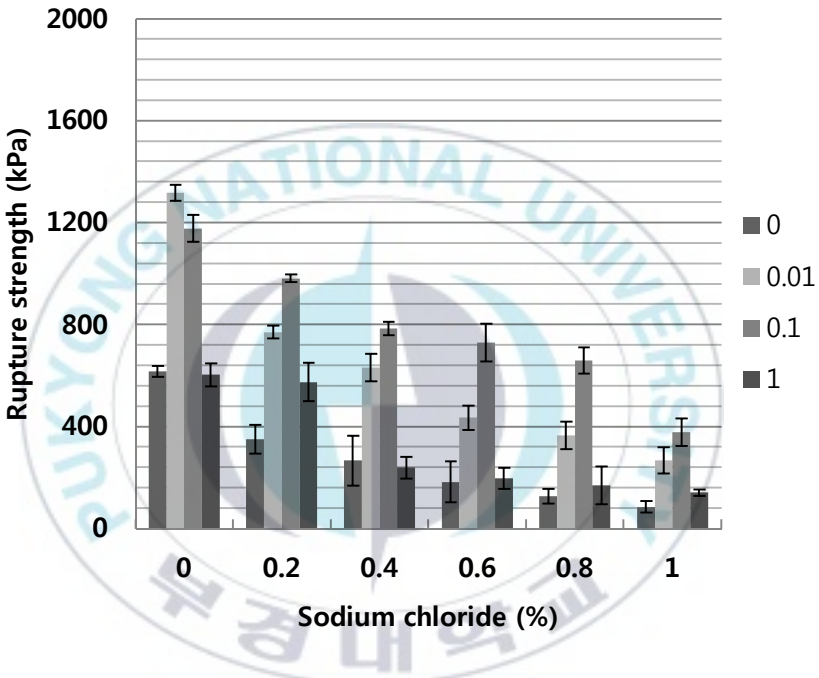

Fig. 2. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and xanthan gum (XG) by different sodium chloride concentrations.

1.2 Effect of glucomannan

Glucomannan (GM) is a food material having a very high gel-forming ability, thickening property, film forming ability, synergistic action with other gums and all kinds of fluids (Tye et al., 1991). Fig. 3 shows the rupture strength of the analogs mixed with GM (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h.

When no sodium chloride was present, the rupture strength of the analogs without GM was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,327.04±52.36 (kPa) for 0.01% GM, 1,471.00±41.53 (kPa) for 0.1% GM, 1,400.95±14.52 (kPa) for 1.0% GM, respectively. At three concentrations of GM, the rupture strength increased twice more than before the addition of GM. This may be caused by the stronger interactions between GM and sodium alginate. However, the decrease in the rupture strength is caused by the decrease in calcium alginate concentrations of the analogs by the addition of GM. The rupture strength of analogs mixed with 0.01% glucomannan concentration decreased from 1,327.04±52.36 (kPa) to 1,050.71±52.14 (kPa), 1,134.77±84.25 (kPa), 770.52±23.61 (kPa), 448.30±15.25 (kPa) and 238.15±85.21 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively.

In the same manner, the rupture strength of analogs mixed with 0.1% glucomannan concentration decreased from 1,471.00±41.53 (kPa) to 1,106.75±45.62 (kPa), 1,092.74±12.51 (kPa), 868.59±74.66 (kPa), 280.19±95.36 (kPa) and 56.04±45.23 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. In case of the treatment with 1.0% GM, the rupture strength of analogs decreased from 1,400.95±14.52 (kPa) to 1,064.72±46.25 (kPa), 854.58±85.62 (kPa), 966.66±24.62 (kPa), 462.31±47.31 (kPa) and 238.16±63.48 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Unlike the analogs mixed with XG, GM-mixed analogs showed higher rupture strength than that of XG in all sodium chloride solution. It indicates very strong interaction in dispersions between GM and sodium alginate, but the interaction is very sensitive to the ionic strength of the aqueous medium (Abdelhameed et al., 2010). GM has strong elasticity and thermal stability in the presence of calcium ions, but it loses these characteristics in the presence of chloride ions (P'erols et al., 1997). Thus, the structure of analogs mixed with GM was loosened, and calcium ion was released from the analogs and then the rupture strength was decreased.

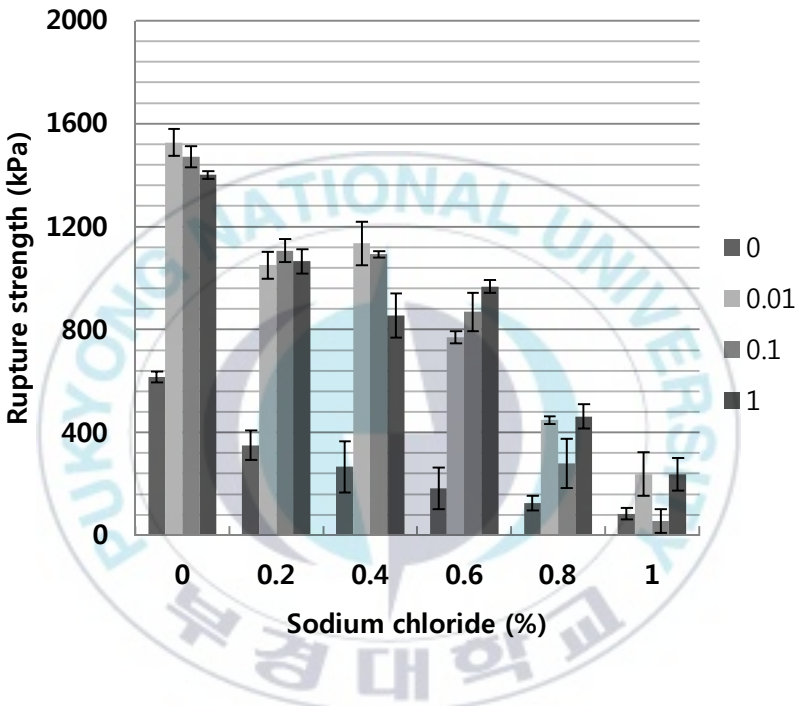

Fig. 3. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and glucomannan (GM) by different sodium chloride concentrations.

1.3 Effect of agar

Agar is known to melt on heating and set on cooling, and this cycle can be repeated for an indefinite number of times without compromising the mechanical properties of the gel. Such gel forming properties of agar make it a good candidate for blending with other biopolymers to enhance the mechanical properties (Rhim et al., 2013). In the food industry, agar is used mainly as a gelling agent and in a secondary way as a stabilizing agent and for controlling viscosity (Antonio et al., 2000). Fig. 4 shows the rupture strength of the analogs mixed with agar (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h.

The rupture strength of the analogs without agar was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,485.01±52.36 (kPa) for 0.01% agar, 1,569.06±45.63 (kPa) for 0.1% agar and 1,124.96±69.36 (kPa) for 1.0% agar, respectively, under conditions without sodium chloride. The rupture strength was the highest at 0.1% agar concentration. Generally, calcium lactate increases entanglement chain of agar and forms noncovalent bond between moderately orderly chains (Kwon et al., 1988).

The rupture strength of analogs mixed with 0.01% agar decreased from 1,485.01±52.36 (kPa) to 602.41±15.36 (kPa), 350.24±32.36(kPa), 280.19±45.52 (kPa), 266.18±74.52 (kPa) and 154.10±45.3 (kPa) by treating

sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. On the other hand, the rupture strength of analogs mixed with 0.1% agar decreased from 1,569.06±45.63 (kPa) to 1,302.88±42.0 (kPa), 994.67±78.52 (kPa), 672.46±86.54 (kPa), 322.22±87.62 (kPa) and 266.18±42.5 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 1.0% agar decreased from 1,124.96±69.36 (kPa) to 896.61±41.25 (kPa), 574.39±41.36 (kPa), 364.25±15.54 (kPa), 294.20±25.36 (kPa) and 168.11±75.15 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Among the tested hydrocolloids, agar-mixed analogs showed the fastest decrease in the rupture strength in 1.0% sodium chloride solution. When sodium chloride was added to agar-mixed analogs, agar increases electrostatic repulsion and then resulted in a more swollen structure (Nakamura et al., 1987). Therefore, the structure of agar-mixed analogs was loosened, and calcium ion was released from the analogs and then the rupture strength was decreased.

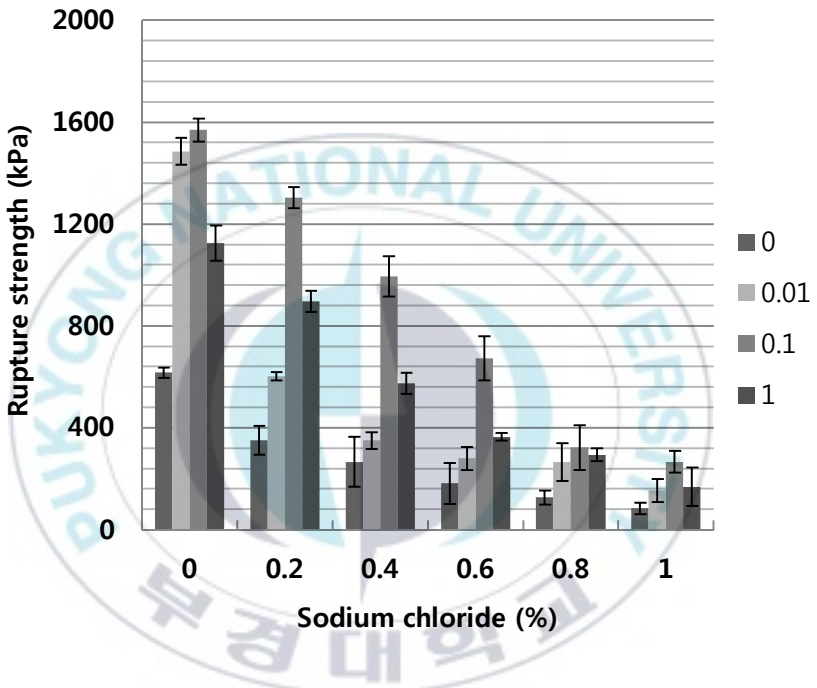

Fig. 4. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and agar by different sodium chloride concentrations.

1.4 Effect of carrageenan

Carrageenan is used as emulsion stabilization, for syneresis control and for bodying, binding and dispersion. They are mainly used in foods, particularly dairy applications (McHugh, 1987). Carrageenan gels are used to improve texture and flavor in reduced fat to simulate full-fat products by providing the necessary viscosity and stability (Izzo et al., 1995). Fig. 5 shows the rupture strength of the analogs mixed with carrageenan (0.01%, 0.1%, and 1.0%) measured after storing in sodium chloride solution at 20℃ for 1 h. The two types of carrageenan such as iota-carrageenan (ι-carrageenan) and kappa-carrageenan (κ-carrageenan) were used in this experiment. Fig 5-A shows the rupture strength of the analogs mixed with κ-carrageenan (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs without κ-carrageenan was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,549.45±35.41 (kPa) for 0.01% κ-carrageenan, 1,283.27±16.12 (kPa) for 0.1% κ-carrageenan and 1,070.33±24.69 (kPa) for 1.0% κ-carrageenan, respectively, in the absence of sodium chloride. The rupture strength of analogs mixed with 0.01% κ-carrageenan concentration decreased from 1,549.45±35.41 (kPa) to 1,445.78±35.21 (kPa), 1,389.74±13.24 (kPa), 972.26±75.32 (kPa), 882.40±35.21 (kPa), and

652.13±15.96 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 0.01% κ-carrageenan was maintained until the 0.4% sodium chloride solution but rapidly decreased over the 0.6% sodium chloride solution. The rupture strength of analogs mixed with 0.1% κ-carrageenan decreased from 1,283.27±16.12 (kPa) to 857.38±52.63 (kPa), 767.72±25.64 (kPa), 781.23±41.53 (kPa), 703.28±42.36 (kPa) and 599.61± 42.36 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Also, the rupture strength of analogs mixed with 1.0% κ-carrageenan decreased from 1,070.33±24.69 (kPa) to 735.50±12.36 (kPa), 844.02±35.24 (kPa), 667.79±21.23 (kPa), 691.14±48.52 (kPa) and 457.64±29.21 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Fig. 5-B shows the rupture strength of the analogs mixed with ι-carrageenan (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs showed 1,139.45±32.35 (kPa) for 0.01% ι-carrageenan, 1,033.27±25.36 (kPa) for 0.1% ι-carrageenan and 1,270.33±45.82 (kPa) for 1.0% ι-carrageenan, respectively, under conditions without sodium chloride. However, when the sodium chloride was present, the rupture strength of the analogs drastically decreased. The rupture strength of analogs mixed with 0.01% ι-carrageenan decreased from

1,139.45±32.35 (kPa) to 1,045.75±45.21 (kPa), 989.74±84.63 (kPa), 672.26±15.36 (kPa), 582.40±12.65 (kPa) and 452.13±85.62 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 0.1% ι-carrageenan decreased from 1,033.27±25.36 (kPa) and 957.38±12.25 (kPa), 767.72± 42.36 (kPa), 681.23±36.65 (kPa), 403.28±32.15 (kPa) and 399.61±14.6 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Also, the rupture strength of analogs mixed with 1% ι-carrageenan decreased from 1,270.33±45.82 (kPa) to 1,035.50±42.69 (kPa), 844.07±74.36 (kPa), 667.79±41.2 (kPa), 491.14±49.25 (kPa) and 457.64±77.25 (kPa) by treating with sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Comparing the κ-carrageenan and ι-carrageenan, the rupture strength of the analogs mixed with ι-carrageenan decreases slightly in the presence of sodium chloride. However, the rupture strengths of both types of carrageenan are sharply decreased in the presence of sodium chloride. This indicates that carrageenan loses gelling ability in a large amount of chloride and becomes soluble state regardless of the type of carrageenan (Maolin et al., 2000). Therefore, the rupture strength of carrageenan-mixed analogs decreased as affected by a loose binding force and release of calcium ion from the analogs.

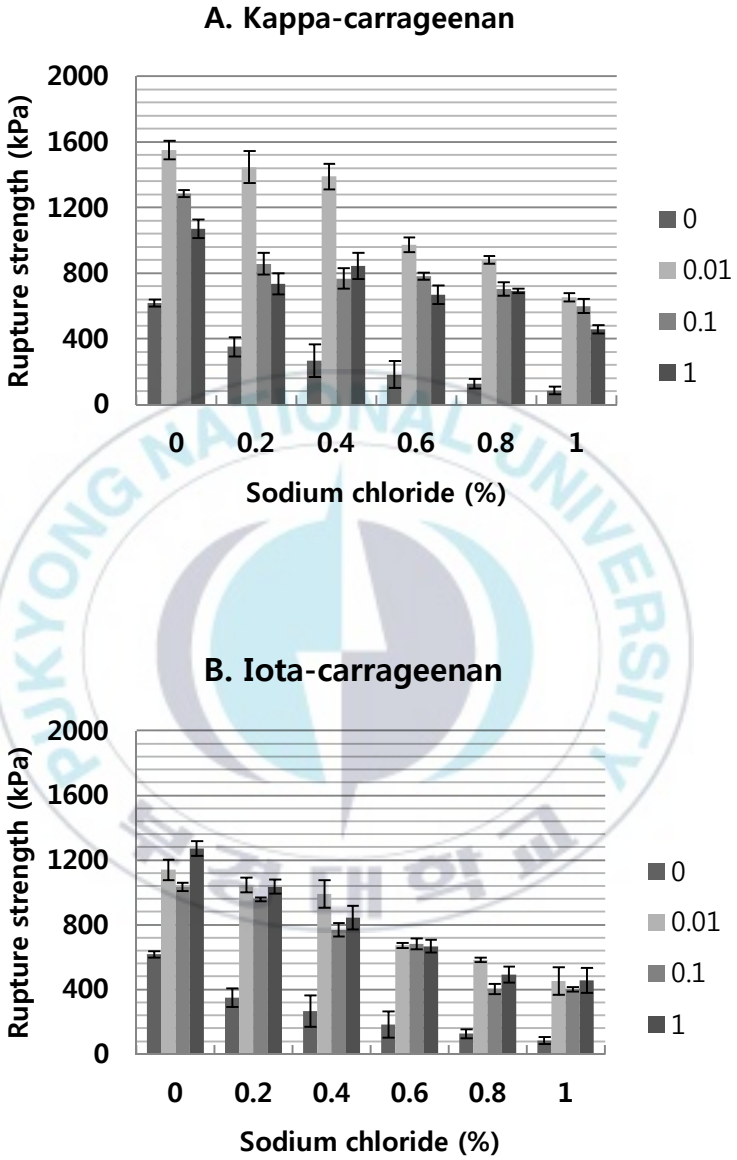

Fig.5. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and carrageenan by different sodium chloride concentrations.

1.5 Effect of gelatin

Gelatin is widely used in the pharmaceutical industry as well as in the biomedical field: hard and soft capsules, microspheres, wound dressing and adsorbent pad for surgical use are among its most frequent applications (Rose PJ et al,. 1987, Hastings et al,. 1984, Esposito et al,. 2009). An aqueous solution of gelatin sets to a transparent elastic gel on cooling below 35℃. On cooling, cross-linking occurs via a disorder to order transition, as the random coil gelatin molecules seek to return to the ordered triple helix conformation of collagen (Clark & Ross-Murphy 1987; Ledward, 1986). The gelatin gel is a reversibly crosslinked biopolymer network held together predominantly by hydrogen bonded junction zones. The gel strength is dependent on many factors such as the type and concentration of the gelatin and the time/temperature history of the sample. Fig. 6 shows the rupture strength of the analogs mixed with gelatin (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs without gelatin was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,625.10±21.26 (kPa) for 0.01% gelatin, 1,499.02±56.98 (kPa) for 0.1% gelatin and 1,442.98±45.30 (kPa) for 1.0% gelatin, respectively, in the absence of sodium chloride. Gelatin-mixed analogs showed the higher rupture strength without sodium

chloride solution. It is indicated that the distance between the gelatin molecules became close to each other and the crosslinking was facilitated (Hayashi et al., 1983). The rupture strength of analogs mixed with 0.01% gelatin decreased from 1,625.10±21.26 (kPa) to 1,527.04±65.12 (kPa), 1,260.86±63.85 (kPa), 812.56±21.63 (kPa), 574.39±42.36 (kPa) and 238.16±41.89 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 0.1% gelatin decreased from 1,499.02±56.98 (kPa) to 1,288.87±63.82 (kPa), 994.67±78.63 (kPa), 448.30±56.35 (kPa), 672.46±14.64 (kPa) and 56.04±25.36 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Also, the rupture strength of analogs mixed with 1% gelatin decreased from 1,442.98±45.30 (kPa) to 1,302.88±78.36 (kPa), 616.42±95.12 (kPa), 504.34±42.3 (kPa), 448.30±41.52 (kPa) and 238.16±26.35 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. It is because gelatin becomes low molecular weight in the presence of sodium chloride and the formation of cross-linking between molecules is inhibited. Most cases mixing two or more biopolymers result in a phase separation (Panouille & Larreta-Gacde., 2009). For this reason, calcium ion from the analogs is released and then the rupture strength decreases.

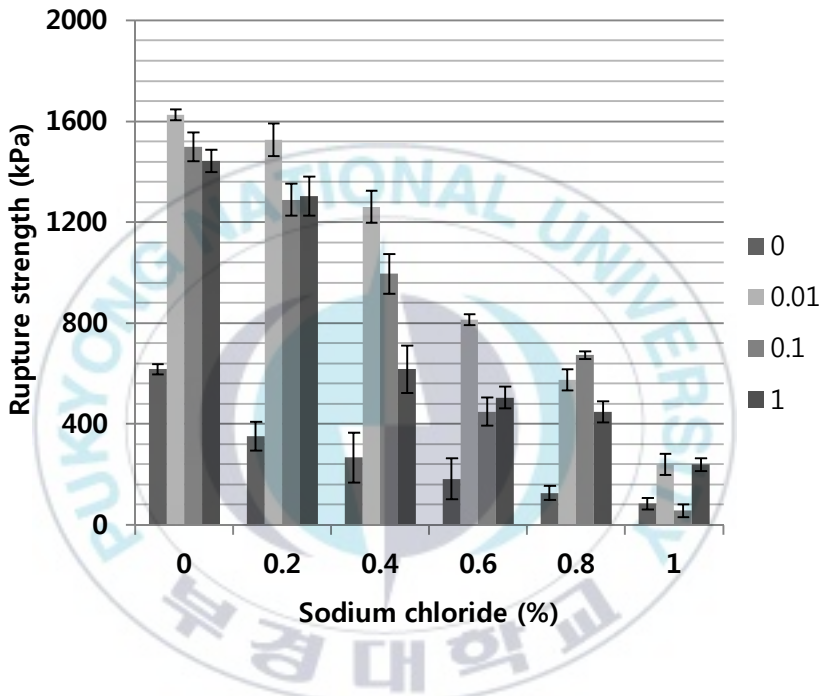

Fig. 6. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and gelatin by different sodium chloride concentrations.

1.6 Effect of pullulan

Pullulan is readily dissolved in water to form a stable and viscous solution that does not form a gel. It shows a relatively low viscosity as compared to other hydrocolloids (Singh et al., 2008). So, pullulan is an ideal material for coating and mixing food because it is colorless, tasteless, odorless, and transparent, as well as being low in thermal stability and permeability (Deshpande et al., 1992). Fig. 7 shows the rupture strength of the analogs mixed with pullulan (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs without pullulan was 616.42±20.78 (kPa). The rupture strength of the analogs showed 1,106.75±21.26 (kPa) for 0.01% pullulan, 1,485.01±56.98 (kPa) for 0.1% pullulan and 1,386.94±52.36 (kPa) for 1.0% pullulan, respectively, in the absence of sodium chloride. On the other hand, the rupture strength of the analogs mixed with 0.01% pullulan decreased from 1,106.75±21.26 (kPa) to 1,008.68±65.12 (kPa), 784.53±63.85 (kPa), 700.48±21.63 (kPa), 476.32±42.36 (kPa) and 196.13±41.86 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Also, the rupture strength of the analogs mixed with 0.1% pullulan decreased from 1,485.01±56.98 (kPa) to 1,456.99±63.82 (kPa), 1,190.81±78.63 (kPa), 980.67±56.35 (kPa), 532.36±14.64 (kPa) and 350.24±25.36 (kPa) by treating

sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of the analogs mixed with 1.0% pullulan decreased from 1,386.94±52.36 (kPa) to 1,204.81±78.36 (kPa), 812.55±95.21 (kPa), 294.20±56.52 (kPa), 266.18±14.64 (kPa) and 98.07±35.12 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. In particular, the rupture strength of the analogs mixed with 1.0% pullulan decreased sharply at 0.6% sodium chloride concentration. It is indicated that the analogs mixed with pullulan compete between pullulan and sodium alginate. Then, pullulan mixed analogs was phase separated in the presence of sodium chloride. For this reason, calcium ion from the analogs is released and then the rupture strength decreases.

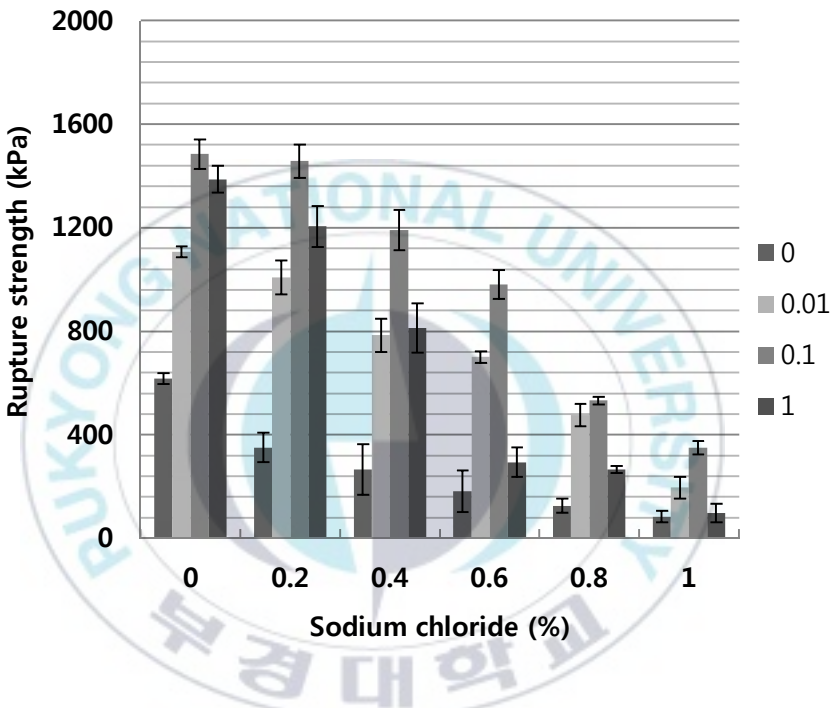

Fig.7. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and pullulan by different sodium chloride concentration.

1.7 Effect of β-cyclodextrin

β-Cyclodextrin (β-CD) is an oligosaccharide with unique structure, which the inner surface of the intracellular cavity is hydrophobic and the outer is hydrophilic. β-CD has the property of encapsulating various organic and inorganic compounds in its cavity (Chon et al., 1997). As well, β-CD is well known as a host molecule, which forms inclusion complexes with a variety of guests. It has been widely used as an excipient to improve the physicochemical properties (Uekama et al., 1998). Fig. 8 shows the rupture strength of the analogs mixed with β-CD (0.01%, 0.1%, and 1.0%) measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the analogs without β-CD was 616.42±20.78 (kPa). The rupture strength of the analogs showed 960.35 ± 59.63 (kPa) for 0.01% β-CD, 910.54 ±98.66 (kPa) for 0.1% β-CD and 820.78 ±52.36 (kPa) for 1.0% β-CD, respectively, in the absence of sodium chloride. The rupture strength didn't drastically increase compared to other hydrocolloids. The rupture strength of the analogs with 0.01% β-CD was 874.67±42.86 (kPa), 812.55±15.36 (kPa), 602.41±74.52 (kPa), 560.38±12.37 (kPa) and 532.36±26.35 (kPa) by treating sodium chloride (0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of the analogs with 0.1% β-CD was 810.62±87.86 (kPa), 560.38±48.52 (kPa), 448.30±63.1 (kPa),

364.25±89.52 (kPa) and 294.20± 15.39 (kPa) by treating sodium chloride (0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of the analogs with 1.0% β-CD was 616.42±56.98 (kPa), 588.40±74.2 (kPa), 506.27±125.39 (kPa), 448.30±53.69 (kPa) and 448.30± 85.36 (kPa) after treating sodium chloride (0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. Among hydrocolloids, β-CD played a major role in maintaining better rupture strength of the analogs against sodium chloride. When β-CD and sodium alginate are combined, β-CD mixed analogs formed novel asymmetric egg-box (Liu et al., 2016). β-CD and sodium alginate binds more tightly than other hydrocolloids by forming a hydrophobic bond (Uekama et al., 1998). Thus, β-CD mixed analogs form a more tightly bond to prevent the liberation of calcium ions from G residues of alginate gel.

2. Effect of sodium chloride against rupture strength of flying fish roe analogs mixed with β-CD by boiling and freeze-thaw

The analogs mixed with 0.008% showed the most similar rupture strength of natural flying fish roe. Fig.9. shows the rupture strength of the analogs mixed with 0.08% β-CD measured after storing in the different amount of sodium chloride at 20℃ for 1 h. The rupture strength of the natural flying

fish roe analogs was 803.68±21.48 (kPa). The rupture strength of the analogs with 0.008% β-CD showed 810.22±.82.68 (kPa), 784.85.55±84.49 (kPa), 789.98.±57.40 (kPa), 768.19±43.24 (kPa), 779.08 ±80.63 (kPa), and 773.63±61.88 (kPa) by treating sodium chloride (0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0%), respectively. The rupture strength of analogs mixed with 0.08% β-CD was not significantly affected in the presence of sodium chloride.

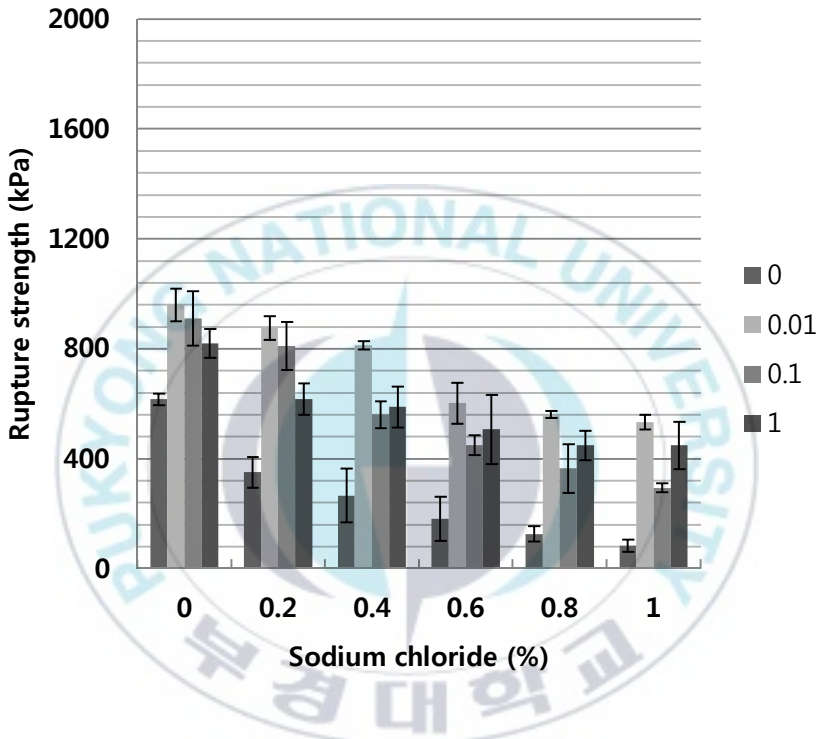

Fig. 8. Changes in the rupture strength of flying fish roe analogs prepared from the mixture of sodium alginate and β-cyclodextrin (β-CD) by different sodium chloride concentration.

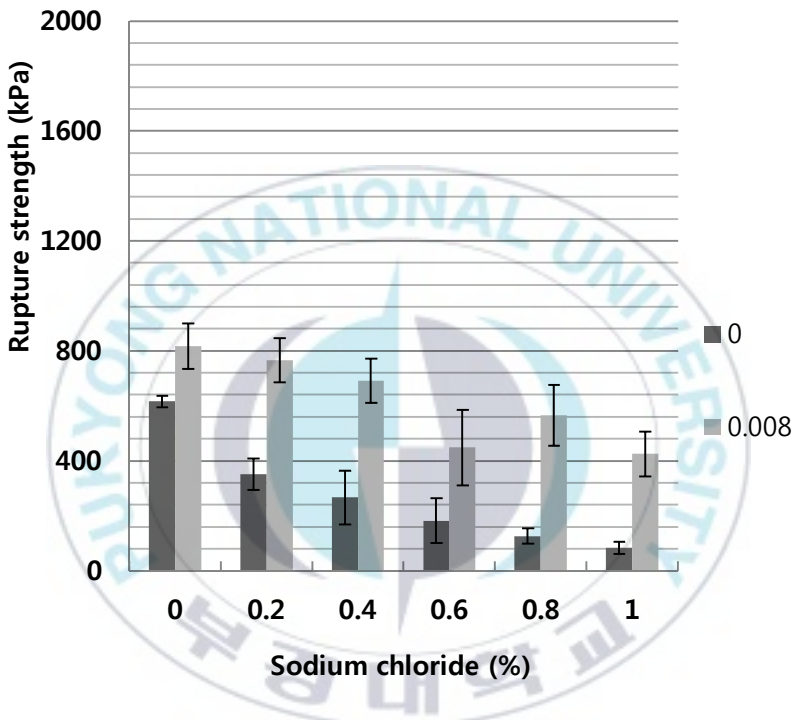

Fig.9. Effect of sodium chloride against the rupture strength of flying fish roe analogs mixed with β-CD by sodium chloride.

2.1 Effect of a boiling water

Generally, boiling treatment is used to enhance storage stability based on sterilization. Fig.10. shows the rupture strength of β-CD-mixed analogs by different boiling time at 95℃. The rupture strength of the analogs decreased from 817.22±83.24 (kPa) to 803.21±21.40 (kPa), 812.55±133.64 (kPa), 639.77±80.63 (kPa) and 490.33±28.02 (kPa) by treating with boiling (0, 20, 40, 60, 80 min), respectively. The rupture strength of the analogs was maintain until 40 min at 95℃ and then generally decreased by 80 min. β-CD starts to decompose at over 70℃ for 50 min (Martin Del Valle., 2004). Therefore, the β-CD-mixed analog is loosened due to the decomposition of β-CD and then the rupture strength generally decreased.

2.2 Effect of freeze-thaw process

The freeze-thaw process is essential for the frozen foods to keep up the qualities during a long-term. Fig.11 shows the rupture strength of β-CD-mixed analogs by freeze-thaw process as affected by storage time. The rupture strength of the analogs before freeze-thaw process was 817.22±83.24 (kPa). When the analogs were thawed after freezing for 5 days, the rupture

strength of the analogs decreased up to 428.69±99.39 (kPa). It suggests that the combinated β-CD networks or structures was easily disrupted by ice crystal formation and resulted from higher water separation on thawing (Yuan et al., 2010).

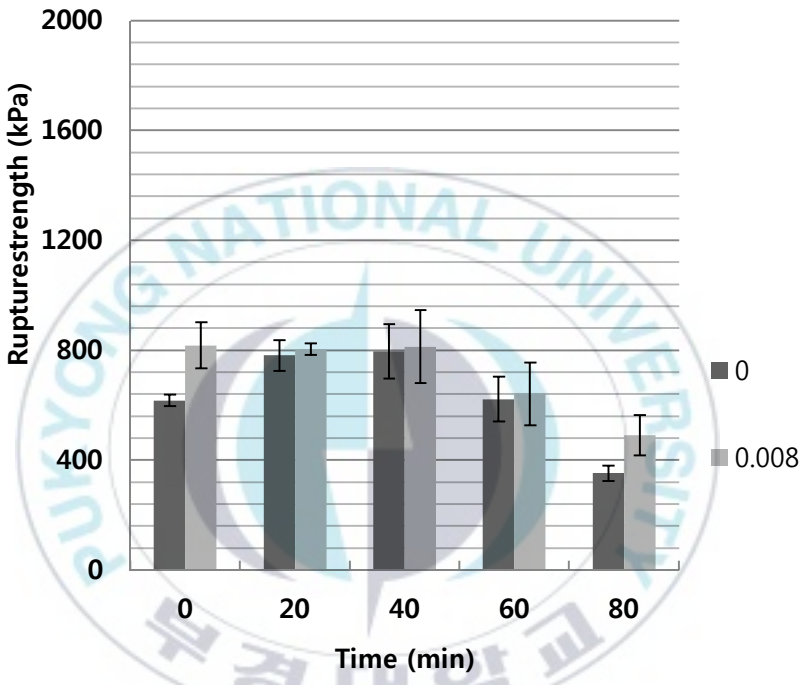

Fig.10. Effect of sodium chloride against the rupture strength of flying fish roe analogs mixed with β-CD by boiling water.

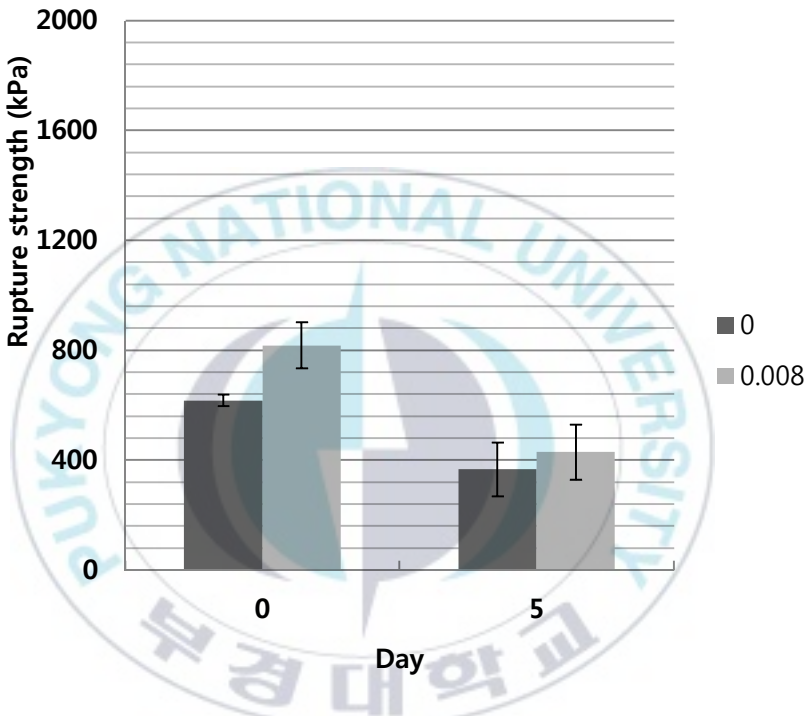

Fig.11. Effect of sodium chloride against the rupture strength of flying fish roe analogs mixed with β-CD by freeze-thaw process.

Conclusions

The present study conducted to find out changes in the rupture strength of the fish roe analog foods mixed with and without hydrocolloids as affected by treatments sodium chloride, boiling water and freeze-thaw process.

The rupture strength of the analogs mixed with xanthan gum, glucomannan, gelatin, pullulan, agar, iota carrageenan and kappa carrageenan decreased by treatment sodium chloride. Among hydrocolloids, β-cyclodextrin played a major role in maintaining better rupture strength against sodium chloride. The analogs mixed with 0.008% β-cyclodextrin showed the most similar rupture strength of natural flying fish roe. The rupture strength of the 0.008% β-cyclodextrin mixed analogs was maintained until 40 min at 95℃ and then generally decreased by 80 min. And, the rupture strength of the 0.008% β-cyclodextrin mixed analogs was decreased by treatment freeze-thaw process.

The results are considered for a potential application to substitutes of natural ones and development of other analog foods.

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