Carrageenan and Garlic Essensial Oil Edible Film as Protective Coating on Catfish Sausage

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ABSTRACT

The edible film based on carrageenan containing garlic essential oil (GEO) at different concentration (0%; 0.2%; 0.4%; and 0.6%) were added into carrageenan edible film (CEF) then applied on sausage, chilled storage for 10 days. The antioxidative allicin prevention on product determined its chemical characteristics such as TBA, TVBN, Aw, and pH. The addition of garlic essential oil on carrageenan based edible film was not significantly different on tensile strength. CEF with 0.6% of garlic essential oil produced the highest elongation value and the lowest Water Vapor Transmission Rate with the amount of 3.970% and 0.673%; respectively. The catfish sausage coated with 0.4% CEF produced TBA and TVBN value during chilled storage with the amount of 0.870 mg malonaldehyde/kg and 17,223 mgN/100g; respectively and not significantly different to CEF 0.6%. The result indicated that edible film containing garlic essential oil able to retard the oxidation process. Indicated from FTIR test, 0.2%; 0.4%; and 0.6% CEF containing garlic compound illustrated with S-S, N-H, C=O and C-H functional group with the wavelength of 408.91 cm⁻¹, 925.83 cm⁻¹, 1543.05 and 2931.8 cm⁻¹; respectively.

Keywords: Catfish Sausage, CEF, Chilled Storage, Garlic Essential Oil, Characteristic

ABSTRAK

Minyak atsiri bawang putih ditambahkan pada edible film berbasis karagenan bertujuan sebagai bahan pelindung terhadap kerusakan dari sosis ikan patin selama penyimpanan dingin. Minyak atsiri bawang putih dengan konsentrasi yang berbeda (0%; 0.2%; 0.4%; dan 0.6%) ditambahkan pada edible film karagenan dengan konsentrasi (1,8%). Edible film kemudian diaplikasikan sebagai pelapis pada suhu dingin (5⁰C) selama 10 hari. Sifat antioksidatif allicin yang terdapat pada minyak atsiri dan diaplikasikan pada produk sosis diuji aktivitasnya dengan mengukur TBA, TVBN, Aw, dan pH. Penambahan minyak atsiri bawang putih tidak memberikan hasil yang beda nyata pada kekuatan tarik (tensile strength) edible film. Misyak atsiri 0.6% menghasilkan nilai pemanjangan (elongation value) yang tertinggi dengan transmisi uap air (water vapor transmission rate) yang terendah yaitu 3,970% and 0.673%. Penambahan 0.4% minyak atsiri tidak berbeda nyata dengan penambahan pel顾客 0.870 mg malonaldehyde/kg dan 17,223 mgN/100g. Hasil penelitian menunjukkan penambahan minyak atsiri bawang putih dapat memperlambat terjadinya oksidasi lemak. Hasil ini ditunjukkan dengan adanya gugus fungsi minyak atsiri S-S, N-H, C=O dan C-H pada 408.91 cm⁻¹, 925.83 cm⁻¹, 1543.05 dan 2931.8 cm⁻¹ yang terkandung pada edible film pada semua konsentrasi minyak atsiri dengan konsentrasi yang berbeda.

Kata Kunci: Minyak atsiri bawang putih, edible film, karagenan, sosis ikan patin, mutu

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1. Introduction

Catfish (*Pangasius sp.*) is a freshwater fish which had a high nutritional content. Its fat content is high compared to other freshwater fish like snakehead fish (*Channa striatus*) and catfish (*Clarias macrocephalus*) (Muhammad and Muhammad, 2012). Its fat content consists of MUFA and PUFA (Zzaman et al., 2014). MUFA on catfish include of Omega-9 while PUFA consist of Omega-6 and Omega-3 (Muhammad and Muhammad, 2012). Instead of fat, catfish also contain protein (Dewita and Syahrul, 2015). Amino acid glutamate and lysine are known to be in catfish fillet in the high amount (Nurilmala et al., 2015). The high nutritional value on catfish is increasing the demand for catfish consumption, indicated by the amount of catfish production around 30,000-50,000 tons per year. Still, it cannot be sufficient the domestic needs (Meilisza, 2009). Catfish can be processed into several products, such as sausage.

Fish sausage is an emulsion containing a mixture of meat, starch, fat, water, and spices (Dincer and Cakli, 2015). Fish sausage using catfish as the main ingredients. According to its nutritional values, fish sausage easily damaged during storage. The fat content also easily oxidized due to the high of saturated fatty acids. Besides, endogenous protease enzyme also boosts the degradation of the protein. During storage, it is possible the growth of pathogens microorganism (Masniyom, 2011). Therefore, food additives are needed to protect the sausage during storage.

Garlic (*Allium sativum*) often used as spices. Garlic is known to have benefit for human’s health as contain polyphenol and flavonoid that works as the antioxidant (Angeles et al., 2016; Choi et al., 2014). The primary compounds on garlic called sulfur like diallyl disulfide, and diallyl trisulfide (El-Sayed et al., 2017). Still, the other sulfur compounds, allicin and polyphenol like chlorogenic acid, ferulic acid, and gallic acid (Fratianni et al., 2016).

Garlic essential oil potentially added to the edible film to produce biodegradable packaging for catfish sausage. The addition of essential oil in edible film able to affect the characteristic of the created edible film such as can form a matrix with the polymer used, enhance the ability as the water barrier, but its appearance is less transparent (Atareas and Chiralt, 2016). Based on the properties, an edible film containing garlic essential oil is allegedly able to protect catfish sausages during storage. This study aimed to determine the chemical characteristics of fish sausage coated with carrageenan based edible film containing garlic essential oil during storage.

2. Materials and Methods

2.1. Materials

Catfish, garlic, and sausage ingredients were obtained from a local market in Semarang, Central Java, Indonesia. Carrageenan was obtained from PT. Selalu Lancar Maju Karya, Jakarta, Indonesia. Sorbitol was purchased from PT. Multi Kimia Raya, Semarang, Central Java, Indonesia.

2.2. The making of garlic essential oil

Garlic essential oil was made based on Soltan et al., (2016) method. Pulled garlic was added to water at a ratio of 1:1 and chopped using the blender. The solution was distilled with distillation apparatus. The obtained essential oil then collected into Erlenmeyer coated with aluminum foil. Garlic essential oils added to the anhydrous Na₂SO₄ and stored in the refrigerator.

2.3. The making of carrageenan edible film (CEF)

Carrageenan edible film was made according to Abdou And Sorour (2014) method with some modification. 1.8% carrageenan was dispersed in 100 mL of distilled water (b/v) and heated to 60°C. Then glycerol 0.5% (v/v) was added. Next, the solution cooled down to 40°C and garlic essential oil was added in different concentration 0%; 0.2%; 0.4%; and 0.6%. The edible film solution then cast on the glass plate (dimension 20 cm x 30 cm) and dried using the oven at 50°C for 12 hours. All the films will be subjected to analyzes.

2.4. Preparation of catfish sausage

Catfish sausage was made according to Rauf et al., (2015) method with modification. Catfish meat was mashed using the grinder. Spices (salt, garlic, pepper, sugar, chili, and onion) were mashed using the blender. Meat and spices were mixed until homogeneous with ice added. The mixture then inserted into the sausage casing then steamed at 120°C for 20 min. The sausage was peeled off the casing and then coated with CEF which
containing different garlic essential oil concentration, such as 0%; 0.2%; 0.4%; and 0.6%. Each samples were packed into polyethylene bag. The samples were stored at 10°C for 10 days. The analysis was performed at days- 0, 2, 4, 6, 8, and 10.

2.5. The physical analysis of carrageenan based edible film

Tensile strength, elongation, and WVTR were analyzed based on Abdou and Sorour (2014). Tensile strength and elongation were measured using Texture Analyzer model TATX plus (LLOID, England), while WVTR using ASTM-E 96/1980 (38°C/90%) method.

2.6. Functional group analysis using Fourier Transform Infrared Spectroscopy (FTIR)

Carrageenan based edible film containing garlic essential oil analyzed its functional group at wavelength 400-4000 cm\(^{-1}\) using Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu, Japan) (Nagarajan and Kumar, 2017).

2.7. pH analysis

The pH of sausage measured using pH meter (pH meter TPX-90i Chemical Laboratories Co., Ltd.).

2.8. Aw analysis

The Aw of sausage measured using Aw meter (rotronic HYGROPALM).

2.9. Thiobarbituric Acid (TBA) analysis

TBA analysis was performed according to Zeb and Ullah (2016). One gram of sample was chopped then added 5 ml glacial acetic acid 100%. Shaked and filtered. 1 ml of sample extract was added with 1 ml of TBA reagent, then heated on the waterbath at 95°C for 1 hour. The sample was cooled and measured using spectrophotometer UV-Vis (Shimadzu, Japan) at wavelength 532 nm. TBA value expressed in mg malonaldehyde per kg lipid.

2.10. TVBN Analysis

TVBN analysis conducted following Idakwo et al., (2016). Sample (100 grams) mixed with 300 ml of 5% trichloroacetic acid and centrifuged for 60 minutes at 3000 rpm. Five ml of sample extract were added with 5 ml sodium hydroxide 2M. This solution next steam distilled until standard HCl 0.01 M containing 0.1 ml resolic indicator. The remaining acid on the sample after distillation then titrated with NaOH 0.01M until the solution become pink. The blank solution prepared without the sample. The TVBN value measured in mgN/100 g sample using this following formula:

\[
\text{TVBN (mg N/100 g sample)} = (\text{M} \times (\text{Vb} - \text{Vs}) \times 14 \times (300 + W)) / 5
\]

M = Molarity of NaOH, Vb = ml NaOH used for blank titration, Vs = ml NaOH used for sample titration, W = Moisture of sample

2.11. Statistical analysis

This study using Factorial Completely Randomized Design. The data obtained then analyzed using software SPSS 23. Tukey method was performed as the post-hoc test.

3. Results and Discussion

3.1. The characteristics of the edible film

The edible film containing garlic essential oil was tested its tensile strength, elongation, and WVTR. The result showed in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
<th>WVTR (g/m²/hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CEF 0%</td>
<td>31.15 ± 4.97(^{a})</td>
<td>2.09 ± 0.33(^{a})</td>
<td>0.82 ± 0.03(^{b})</td>
</tr>
<tr>
<td>2</td>
<td>CEF 0.2%</td>
<td>30.14 ± 5.13(^{ab})</td>
<td>2.51 ± 0.24(^{ab})</td>
<td>0.79 ± 0.01(^{b})</td>
</tr>
<tr>
<td>3</td>
<td>CEF 0.4%</td>
<td>26.98 ± 1.75(^{ab})</td>
<td>3.00 ± 0.21(^{b})</td>
<td>0.75 ± 0.01(^{ab})</td>
</tr>
<tr>
<td>4</td>
<td>CEF 0.6%</td>
<td>21.15 ± 1.06(^{b})</td>
<td>3.97 ± 0.33(^{c})</td>
<td>0.67 ± 0.07(^{a})</td>
</tr>
</tbody>
</table>

Note: Data ± Deviation Standard
Data is the result of triplication
Different superscript on the same column are significantly different (P<0.05).
3.2. Tensile Strength

According to Table 1, the tensile strength of carrageenan based edible film containing garlic essential oil decreased along with the increasing of garlic oil concentration. Supardan et al., which adding lemongrass essential oil into cassava flour based edible film. The similar study conducted by Suput et al., (2016) and Teixeira et al., (2014) that tensile strength decreased along with the addition of essential oil. The maximum pressure applied to the film before broken or torn called tensile strength. This related to the matrix of film produced. The addition of lipid into film cause the discontinuity of tissue and decrease the tensile strength of the polysaccharides-based film. The result of this study showed the tensile strength of CEF 0.6% was 21.150 MPa. This not significantly different to CEF 0.2% and CEF 0.4% but significantly different to 0%. The result showed by Nisar et al., (2018), the tensile strength increases along with the increasing concentration of clove essential oil, while 1.5% addition producing 33.78 MPa of tensile strength.

3.3. Elongation (%)

Elongation or percent elongation is the edible film properties that relate to its ability to resist the load before broken (Nisar et al., 2018). The elongation value associated with tensile strength. The increasing of essential oil to the film can reduce the tensile strength while the elongation increase. This related to the film plasticity properties due to the addition of essential oil (Suput et al., 2016). In this study, the results showed that the elongation value increase along with the increasing of garlic essential oil. CEF 0.6% had the highest elongation value of 3,970% and significantly different with the others. These results similar to Suput et al., (2016) stating that the elongation values increase along with the increasing of black cumin or oregano oil addition with the highest elongation values found on 2% black cumin or oregano oil.

3.4. Water Vapor Transmission Rate

WVTR is the most important properties of the edible film. These properties related to the ability to resist water into the product and prevents water loss (Sung et al., 2014). WVTR related to the film's ability to be penetrated by vapor. The low WVTR value indicated the low of film ability to be penetrated by vapor. The water vapor transmission occurred on the hydrophilic part of the film (Indrarti and Indriyati, 2016; Suput et al., 2016). WVTR edible film decrease along with the increasing of garlic essential oil concentration. The addition of essential oil into edible film filling the hydrophobic phase and increasing the ability of edible film as the water barrier. 0.6% CEF produced the lowest WVTR of 0.673 g/m²/hour. This not significantly different to CEF 0.4% but significantly different to CEF 0% and CEF 0.2%. Nisar et al., (2018), stated that WVTR value decrease along with the increasing of clove essential oil concentration, while the 1.5% addition produced WVTR 6.52 x 1011gm⁻²s⁻¹Pa⁻¹. The different result showed by Sung et al., (2014) while LDPE film with 6% garlic essential oil produced WVTR value of 1,34 g/m²/days.

3.5. Fourier Transform Infrared Spectroscopy

The edible film containing garlic essential oil tested its functional group using FTIR. The result showed in Figure 1. The results show that there are several garlic function groups not present in the 0% CEF. CEF 0.2%; 0.4% and 0.6% contain sulfur, carbonyl-carboxyl, and aromatic components of garlic, there were S-S, N-H, C=O, and C-H at the wavelength of 408.91 cm⁻¹, 925.83 cm⁻¹, 1543.05 and 2931.8 cm⁻¹, respectively. Nagarajan and Kumar (2017) stated that garlic contains the functional groups of S-S, N-H, C=O, and C-H at wavelengths 463.31 cm⁻¹, 923.78 cm⁻¹, 1571.26 and 2937.40 cm⁻¹, respectively. Different results are shown by Divya et.al., (2017) that garlic contains a functional group C=O at a wavelength of 1619 cm⁻¹ and a C-H group at a wavelength of 2916 cm⁻¹. Garlic also contain organosulfur (S-O) at the wavelength of 1036 cm⁻¹. The sulfur components and polyphenol are the main components of garlic that act as antioxidants (Fratianni et al., 2016).
3.6. Application of edible film on catfish sausage

Carrageenan based edible film applied on catfish sausage then chilled storage for 10 days, after that the chemical characteristic was conducted such as TBA, pH, Aw, and TVBN every two days.

3.7. Thiobarbituric Acid (TBA)

TBA value used to measure the malonaldehyde content on the sample. The presence of malonaldehyde on sample indicated the lipid oxidation process during storage (Reitznerová et al., 2017). Fat on catfish containing polyunsaturated fatty acid (Kakroodi et al., 2014) which are prone to oxidation. Catfish sausage coated with CEF 0%, CEF 0,2%, CEF 0,4%, and CEF 0,6% had increased its TBA value during 10 days of storage. Sausage coated with CEF 0,6% on days-10 had the lowest TBA value of 0,857 mg malonaldehyde/kg. This not significantly different to CEF 0,4% with TBA value 0,870 mg malonaldehyde/kg, but significantly different to the others. This related to the garlic essential oil in the edible film which contains antioxidant compounds and able to inhibit oxidation (Naheed et al., 2017). This result was higher compared to Kaleem et al., (2018) which coating sausage with the edible film containing Terminalia arjuna, where 1% concentration produced TBA value of 0,62 mg. malonaldehyde/kg during 21 days of storage.

![Figure 1. FTIR edible film (A) CEF 0%; (B) CEF 0,2%; (C) CEF 0,4%; (D) CEF 0,6%](image)

![Figure 2. TBA of catfish sausage during storage](image)
3.8. Aw and pH

Activity water (Aw) used to determine the activity of microorganism (Kumar et al., 2013). The activity water of sausage during storage ranged between 0.898-0.924. Bacteria can grow in that range. Aw related to the rise of pH. The pH of sausage increased during storage around 6.2-6.6 and not significantly different. Noor et al., (2018), stating that pH of chevon sausages coated with calcium alginate based edible film increased during 21 days of storage. The similar result showed by Kaleem et al., (2018) that pH of sausage increased during storage. This increasing of pH value indicated the presence of microbial activity that produced different alkaline compounds (Soto-Valdez et al., 2015).

![Figure 3. Aw of catfish sausage during storage](image)

![Figure 4. pH of catfish sausage during storage](image)

3.9. TVBN

TVBN Value showed the presence of bacterial activity which produced dimethylamine, trimethylamine, ammonia and volatile base nitrogen compounds (Asik and Candogan, 2014). TVBN value related to the Aw and pH which increases during storage. The TVBN value on sausage increasing during storage. The catfish fish sausage coated CEF 0.6% on days-10 had TVBN value of 16.79 mgN/100 g and not significantly different to sausage coated CEF 0.4% with TVBN value 17.223 mgN/100 g. Until days-10 of storage, the TVBN value of all samples was still under the maximum limit 35 mgN/100 g (Kumar et al., 2013). These results were lower than Asik and Candogan (2014) study, which coating shrimp using edible chitosan coating containing 1.5% onion oil, on days-10 of storage TVBN value produced around 120 mg/100 g. The low level of TVBN on this study related to allicin contained in garlic essential oil, known as antibacterial (Horita et al., 2016; Petropoulos et al., 2018) which able to damage cell membranes and causing death to microbial (Chen et al., 2018).
4. Conclusion

CEF 0.4% produced the best characteristics indicated by the high tensile strength value and low WVTR and not significantly different to CEF 0.6%. Also, the CEF 0.4% able to inhibit the damage of sausage, indicated by TBA and TVBN value which below the maximum limit for 10 days of chilled storage.

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