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Antibacterial and amine scavenging properties of silver–silica composite for post-harvest storage of fresh fish

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ABSTRACT

Polypropylene (PP) films containing silver–silica ($AgSiO_2$) were prepared using hot pressing. Incorporating $AgSiO_2$ into PP films enhanced the antimicrobial properties, and tensile and compressive strengths of the composite by 5.85 MPa, 4.08 MPa respectively. The pH of the fresh chub mackerel with PP + $AgSiO_2$ composite increased from 6.17 to 6.76 during storage at 2 ± 0.5 °C for seven days, whereas the pH of the control sample initially increased from 6.17 to 6.55, and then decreased to 6.48. The control-sample thiobarbituric acid (TBA) value increased during storage, but remained low in the PP + $AgSiO_2$ composite. Total psychrophilic counts for fish stored in the composite containing 5.0% and 10.0% $AgSiO_2$, were 3.06 and 3.11 log CFU/g, respectively, whereas the count reached 4.81 log CFU/g in the control sample. Trimethylaimne values of the control sample increased from 1.6 to 2.5 mg TMA/100 g; however, there was no change in the composite sample. The hue angle increased from red to yellow for the control sample, while remaining between the red and yellow zones for composite samples, indicating that the quality of the treated fish was retained.

1. Introduction

Fish and fish products have high nutritional value and contain beneficial amounts of protein, lipids, essential minerals, and vitamins. However, fish are often considered to be difficult culinary objects because they are prone to spoilage and oxidation, and develop off-flavors from improper handling or incorrect storage. The shelf life of chilled fish is generally limited by the growth of Gram-negative microorganisms such as *Pseudomonas*, *Shewanella putrefaciens*, and *Aeromonas*, under aerobic conditions (Ravi Sankar et al., 2008). Chub mackerel starts spoiling rapidly after 3 days, and will be putrid after 5–6 days. Fish with a higher fat content spoil even faster.

Preservation of the high nutritional quality of fish is significantly influenced by several parameters, such as the diet of the fish, and fish handling and storage. Estimating freshness is a key aspect because it is closely linked to the overall quality of the fish. Consumers are increasingly concerned about the quality of what they eat, with specific attention to price and freshness (Brunsø, 2003; Oehlenschläger and Sörensen, 1997; Ahn et al., 2016; Choi et al., 2016; Singh et al., 2017).

Antimicrobial active packaging is a promising technology for improving safety, and delaying spoilage during processing and handling of fish (Gaikwad and Lee, 2016; Matsumura et al., 2003). Applying antibacterial substances directly onto the fish surface has limited benefits, because they are neutralized on contact, or diffuse rapidly into the fish. However, incorporating antimicrobial agents into fish formulations could result in partial inactivation of the active substances by product constituents, and is therefore expected to have only limited effects on surface microflora.

Application of inorganic antimicrobial agents is a wide area of research for seafood packaging. Antimicrobial polymers containing silver ions (Ag^+) are preferred for their wide spectrum of antimicrobial activity, safety, and heat stability. Some researchers have reported that Ag particles have an aggregation problem, which decreases their antimicrobial activity. Ag combined with SiO_2 to provide improved antimicrobial activity and less aggregation (Kim et al., 2007). Forming Ag on supporting materials delays its release, and such materials have greater potential for antibacterial applications (Shi et al., 2004). Ag-containing SiO_2 materials, such as SiO_2 glass and thin films, are

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expected to be good candidates for antibacterial materials, owing to their chemical durability and high antibacterial activity (Kawashita et al., 2000; Blaker et al., 2004; Hadad et al., 2007). Ag nanoparticles adsorbed on the surface of a SiO_2 particle offer more opportunities for bacterial contact. The antibacterial mechanism of Ag can also be partially explained by the fact that Ag particles formed on the SiO_2 surface carry opposite charge as the Gram-negative bacteria *Pseudomonas aeruginosa*, thereby killing them more easily than Gram-positive bacteria owing to electrostatic attraction (Patra et al., 1999; Pol et al., 2002). Jeon et al. (2003) used a sol gel method to develop Ag-doped SiO_2 films, which showed excellent antibacterial performance against *Escherichia coli* and *Staphylococcus aureus*. The combination of SiO_2-doped Ag for synthesis of particles has also been studied, showing that they have excellent antibacterial effects (Yong et al., 2013; Singh et al., 2016a,b).

Some researchers have demonstrated the antimicrobial activity of inorganic substances incorporated into packaging (Kazemi and Rezaei, 2015) against pathogenic microorganisms, resulting in extended seafood shelf-life. Chub mackerel (*Scomber japonicus*) is a common fish in the Mediterranean Sea, and is usually sold as a raw product. Application of antimicrobial packaging for shelf-life extension is of interest, given that chub mackerel is a fatty fish that generally spoils easily.

Incorporation of $AgSiO_2$, which has both antimicrobial and amine-absorbing properties, holds promise for active packaging applications (Gaikwad et al., 2016, 2017; Benhacine et al., 2016, 2015). In preliminary research (Singh et al., 2018), antimicrobial films containing $AgSiO_2$ were successfully developed for packaging applications. However, to the best of our knowledge, there have been no previous studies on the use of PP films containing $AgSiO_2$ (PP + $AgSiO_2$) for shelf-life extension of fish. Therefore, the objective of this investigation was to study the effects of PP + $AgSiO_2$ composites on the shelf-life extension of chub mackerel stored at $2 \pm 0.5\,^{\circ}C$.

2. Materials and methods

2.1. Materials

PP (Lotte Chemical Limited, Seoul, South Korea) in pellet form, with a density of $895\,kg/m^3$, was used as the matrix material. $AgSiO_2$ (Sigma-Aldrich, South Korea) was used as the antimicrobial material in the film.

2.2. Preparation of antimicrobial composite

Prior to blending, the $AgSiO_2$ and PP were dried for 12 h in a hot air oven at $40\,^{\circ}C$ to remove moisture. PP + $AgSiO_2$ (5.0 and 10.0%) was compounded using a laboratory twin-screw extruder (L40/D19, Bautek Co., Gyeonggi, South Korea) equipped with a flow convergence system (feed-block), and a hollow die with one void (200 mm × 50 mm × 200 mm). The extruder barrel had 7 temperature zones, which were set at 160, 160, 210, 210, 220, 200, and $200\,^{\circ}C$, and a 200 rpm screw speed was used. The master batch obtained from the extruder was dried for 12 h in a hot air oven at $40\,^{\circ}C$ to remove moisture. The composite (200 mm × 200 mm × 1.07 mm) was prepared in a pneumatic heat transfer press (In Ye Machinery Co. Ltd., Taichung Hsien, Taiwan), with a upper plate temperature of $200\,^{\circ}C$, a lower plate (feed zone) temperature of $198\,^{\circ}C$, and a pressure of $150\,kg/m^2$. The overall process took 14 min; 6 min for machine preheating, 5 min for pressing, followed by 3 min for water cooling under compression.

2.3. Characterization

2.3.1. Scanning electron microscopy (SEM)

Composite sheet samples were prepared by cutting with a sharp scalpel, mounted on aluminum stubs, and sputtered with gold to make them conductive. Sample surface morphologies were examined (SEM; LEICA S 360, Leica Cambridge Ltd., USA) at an acceleration voltage ranging from 10 to 15 kV.

2.3.2. Compression tests

Compression testing was performed (Series IX Automated Materials Testing System, Instron, USA) according to ASTM D695-02a, at a crosshead speed of 10 mm/min, and using a load cell of $500\,kg_f$ maximum capacity. The sample dimensions were 7.85 mm × 2.50 mm × 1.07 mm. The average compressive strength and elongation at yield were calculated using the five highest measurements (±standard deviation).

2.3.3. Melt flow index (MFI) measurement

The fluidity of the composite formulation was determined at different temperatures in the range of 190–210 °C, using a load of $2.16\,kg_f$. A valuation procedure according to ISO 1133 was used to study the melt flow quick index of the material. Each experiment was carried out in triplicate to obtain an average MFI.

2.4. Collection and preparation of fish samples

Fresh chub mackerel, a Mediterranean Sea pelagic species, were purchased from H-mart (Wonju, Gangwon-do Province, South Korea). Fish were kept in ice ($0\,^{\circ}C$) with a fish/ice ratio of 1:2 (w/w), and transported to the Department of Packaging, Yonsei University, within 30 min. The weight and length of the fish studied were 150 ± 27.6 g and 23.4 ± 4.37 cm, respectively. Fish were prepared in a room with an ambient temperature of $10\,^{\circ}C$; each fish was cut with the skin still attached, beheaded, gutted manually and washed. Individual pieces weighted (50.7 ± 18.2 g) were placed in an 11 × 11 cm expanded polystyrene tray, as shown in Fig. 1, with a 1.07 mm thick PP + $AgSiO_2$ sheet (8 × 8 cm). Stretch wrap cling film (Stretch-Tite, Massachusetts, USA) with a thickness of 10 μm, OTR-2.19 cm^3 ml/100 in^2 day atm, and WVTR-1.8 (g/100 in^2/24 h) was used to wrap the trays, which were then placed in a cold room at $2 \pm 0.5\,^{\circ}C$. The fish-preparation day (first day of analysis) was considered as day A01 of the study (Cardenas Bonilla et al., 2007). On days 0, 3, 5, and 7, a single box was withdrawn, and the fish sample was analyzed. Each fish sample was processed in the same way, as described below.

2.5. Quality analysis

2.5.1. TMA (GC analysis)

As a first step in method optimization, the effects of NaCl concentration and solution pH were evaluated. For this, 50 g of fish was blended with 100 ml of 30.0% (w/w) NaCl solution, and the pH was adjusted to >13 using NaOH. On each day, the filtrate was analyzed in triplicate as follows: 11 ml of diluted filtrate was poured into SPME vials, and 4.4 μl of 1, 2-dimethylpropylamine standard solution was added with one potassium hydroxide pellet. The vials were then hermetically sealed.

Next, hermetically sealed vial sample was transferred to the extraction chamber, heated, and shaken at 500 rpm