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Biodegradable Halochromic Optical Nose for Monitoring Spoilage of Seafood

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Abstract

Development of halochromic thin film sensor for measuring the degree of spoilage of packed seer fish is described in the present study. A halochromic sensor is prepared from polyvinyl alcohol in combination of mixed indicator dyes. The thin film is characterized by Fourier-transform infrared spectroscopy and thermogravimetric analysis. The halochromic sensor is used to track the deterioration of packed seer fish at room temperature, 4ºC and -2ºC. The color changes are visibly distinguishable and in line with the spoilage of the packed seer fish. Image processing by means of colour measurements such as CIE Lab and RGB values were determined from the halochromic response of the sensor. The color changing patterns of the sensor were at part with the results of estimation of volatile amine, microbial counts, and sensory evaluation. The developed halochromic thin film sensor could be a potential material to detect the deterioration of packaged seafood in real time.

Keywords: Optical nose, halochromic sensor, fish spoilage, real-time monitoring

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Introduction

Fish is a perishable commodity and important protein food. Today's working population lacks the time to purchase, clean, and prepare fish-related items. Fish that is packaged and ready to cook might be one way to increase per capita fish intake. Additionally, it might be difficult to determine the extent of seafood deterioration without opening the package. Consumers could benefit from a sensor that detects seafood deterioration after it has been packaged.

Numerous studies [1-7] have shown the effectiveness of both invasive and non-invasive methods for detecting seafood spoilage in packaging. Most of these investigations used pricey parts and procedures as well as unsustainable techniques. Authors have investigated various halochromic thin film sensors as suitable candidates for surveillance of packed fish spoilage [8-13]. The key in the development of on-package sensors is that it should be economical, ecofriendly, non-toxic to the product as well as efficient. Its noted from the previous researches that visibility of the color changes, interference of the moisture within the pack, and color change pattern are key issues to be addressed. In this view point, in the present study a new combination of mixed-indicators is combined with a known biocompatible polymer, polyvinyl alcohol to fabricate halochromic sensor. The results are presented in the following sections.

Materials

Bromothymol blue (BTB), polyvinyl alcohol (PVA), chlorophenol red (CPR), dimethyl formamide, and bromocresol purple (BCP) among other chemicals and reagents, were bought from HIMEDIA in Mumbai. Methyl violet, bromocresol green (BCG) and thymolphthalein were procured from NICE Chemicals (P) LTD in Cochin, Kerala.

Mixed indicator solution

BTB, BCP, MV, BCG, CPR, CRP, and thymolphthalein were each dissolved in ethanol at a concentration of 50 ppm. After that, 1 mL of each dye solution was mixed together. 2.0Wt. percent citric acid was added to the above, and the mixer was then made up to 10 mL. The mixed indicator (MI) solution was kept at 4°C until further use.

MI/PVA thin film preparation

2 g of polyvinyl alcohol was weighed and taken in a beaker. Then 25 mL of cold water was added. Then the solution was stirred using magnetic stirrer for 12 h. This solution became little sticky. 5 mL of universal indicator solution was added to that PVA solution. This solution was mixed evenly. Then the solution was poured and spread in an aluminium sheet. Then the film was allowed to dry for 48 h at ambient temperature. The dried thin film was separated from the aluminium sheet. The film was dried and stored under vacuo.

Characterization of thin films

Ultraviolet (UV)-vis spectroscopy (Perkin Elmer, LAMDA 35) and Fourier transform-infrared spectroscopy (FT-IR) (Perkin Elmer, Spectrum TWO) were used to examine the MI/PVA thin film.

Measurement of color

The CIELAB values were determined using digital images taken with a 13 MP camera to compare the colour patterns in MI/PDA/S thin film. ADOBE PHOTOSHOP 7.0 was used to measure the Lab and RGB values.

Halochromic behavior of the sensor

The fresh seer fish (*Scomberomorus guttatus*), which was cleaned and rinsed carefully was used in this study. The cleaned fish was sliced into 50-gram fillets and put in a clear PP plastic container. The thin film sensor, measuring about 1 cm x 1 cm, were cut and adhered to the inside of the container's lid. The containers were then sealed and maintained at room temperature (4°C and -2°C) for observation. The trials were carried out three times.

Microbial analysis

The total plate count and the total psychrophile count were determined in accordance with the standard protocol (APHA, 2001).

Estimation of Total Volatile Base Nitrogen

For the packed seer fish samples that were incubated at room temperature, Total Volatile Base Nitrogen (TVBN) was determined using the distillation method. 5 g of fish total were homogenised in 20 mL of a 6% solution of perchloric acid. The mixture was filtered with Whatmann filter paper. The filtrate was then treated with 10 mL of 40% sodium hydroxide, and the distillate was extracted with 50 mL of 0.1 N boric acid. Utilising back titration with 0.1 N hydrochloric acid, the concentration of TVBN was determined.

Sensory Evaluation

A ten-person trained and untrained panel group evaluated the packed fishes during the course of storage using a 9-point hedonic scale. The fish's appearance, odour, texture and general acceptability were evaluated.

Biodegradability

100g of fertile soil was put in a 250 mL beaker. The soil was then thoroughly wetted and churned until it was saturated. Before each biosensor film was placed separately in the beaker, it was cut into 2 x 2 cm^2, weighed, and noted. After two weeks, the buried films were unearthed, and each one was weighed and recorded. The discrepancies between these two weights were used to determine the biodegradability percentage.

Results and Discussion

The MI/PVA was prepared successfully and incorporation of indicators was verified using UV-visible and FT-IR spectroscopic data. The band observed at 610 nm in UV-visible spectrum for MI/PVA (**Figure 1**) indicates successful incorporation of mixed indicator in thin films.

The stretching vibrations of –OH at 3450 cm^{-1}, -NH at 2930 cm^{-1}, -C=O at 1630 cm^{-1} and -C-H at 1387 cm^{-1} confirms successful preparation of MI/PVA thin films (**Figure 2**).

The halochromic behavior of the sensor was tested using ammonia solution and the thin film sensor found to change its color from blue to grey (**Figure 3**).

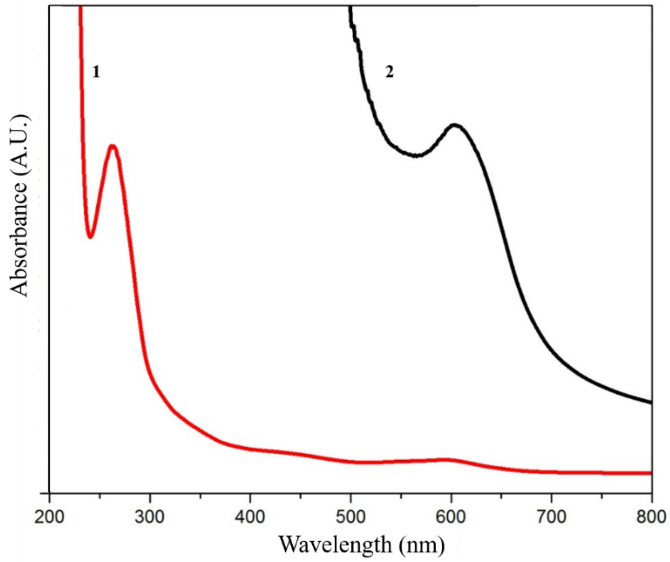


Figure 1 UV-visible spectrum of PVA (1) and MI/PVA (2)

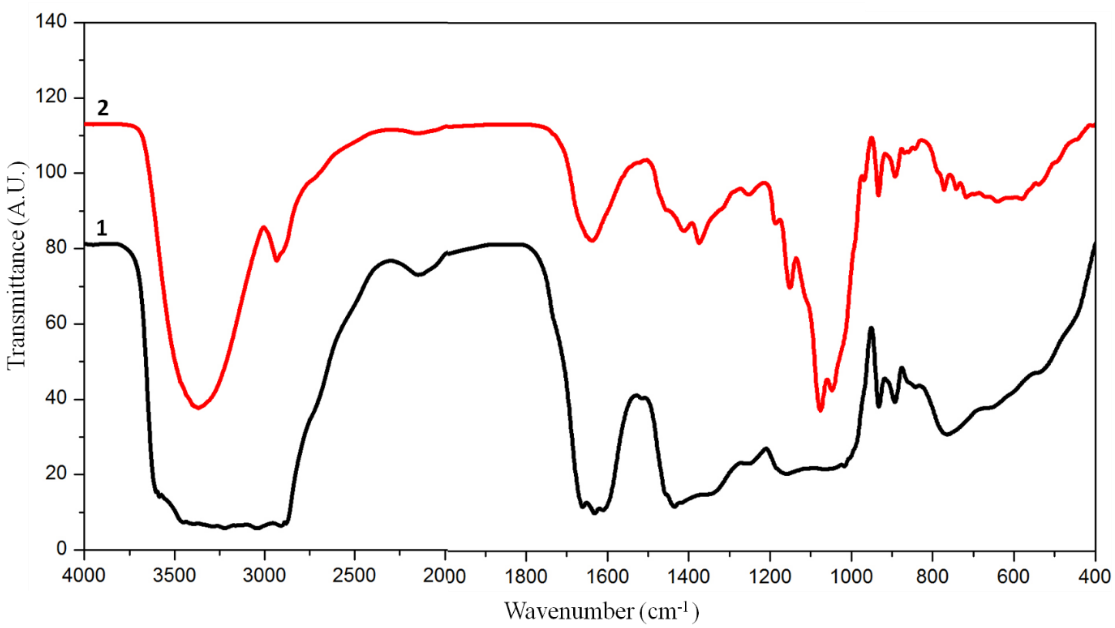
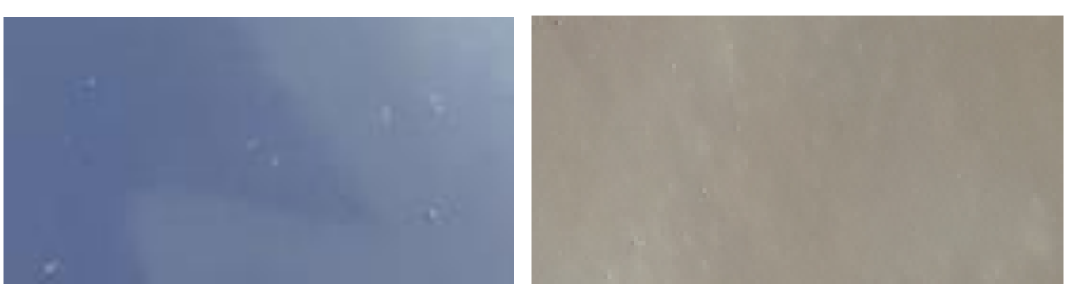


Figure 2 FT-IR spectrum of PVA (1) and MI/PVA (2) thin film



(a) (b)

Figure 3 Optical image of MI/PVA (a) and halochromic behavior of MI/PVA in response to ammonia (b).

Thermogravimetric analysis (TGA) is a powerful analytical technique used to investigate the thermal stability and decomposition behavior of materials by measuring changes in mass as a function of temperature.

Upon subjecting the MI/PVA composite to TGA, distinct stages of thermal decomposition were observed, each shedding light on the underlying molecular transformations within the material. The initial stage of the thermograms exhibited a characteristic weight loss, typically occurring around 100 °C. This phenomenon is attributed to the dehydration process, a well-known property of Polyvinyl Alcohol (PVA). PVA has a propensity to absorb moisture from the environment, and the release of this moisture manifests as a weight loss during the initial heating phase. This dehydration stage serves as a crucial precursor to subsequent thermal events and is indicative of the material's sensitivity to moisture content.

Following the dehydration stage, a second decomposition step was observed within the temperature range of 150 °C to 280 °C. This decomposition event is specifically attributed to the degradation of dyes present within the MI/PVA composite. The dyes, being organic compounds, undergo thermal degradation upon heating, leading to the release of volatile decomposition products and subsequent weight loss. The distinct temperature range associated with this decomposition step provides valuable insight into the thermal stability and behavior of the dyes incorporated into the MI/PVA matrix.

Thus, the thermogravimetric analysis of the MI/PVA composite unveiled critical information regarding its thermal properties and decomposition behavior. The correlation between the observed thermal events and the known characteristics of PVA moisture absorption, coupled with the identification of dye decomposition, offers valuable insights into the structural integrity and thermal stability of the composite material. Such knowledge is essential for optimizing processing conditions and predicting the performance of MI/PVA composites in various applications, ranging from packaging materials to biomedical devices.

Monitoring the deterioration of packed seer fish in real-time

At the beginning (0 h), the sensor exhibited a visible light blue color. The sample and the sensor monitored continuously. The halochromic sensor exhibited light grey color at 24 h. The color change is in line with the spoilage of the packed fish. It should be noted that at 48 h, most of the MI/PVA were dissolved due to the presence of high moisture content evolved within the pack. Similar results were observed for storage at refrigerated condition and frozen temperature (**Figure 4-6**).

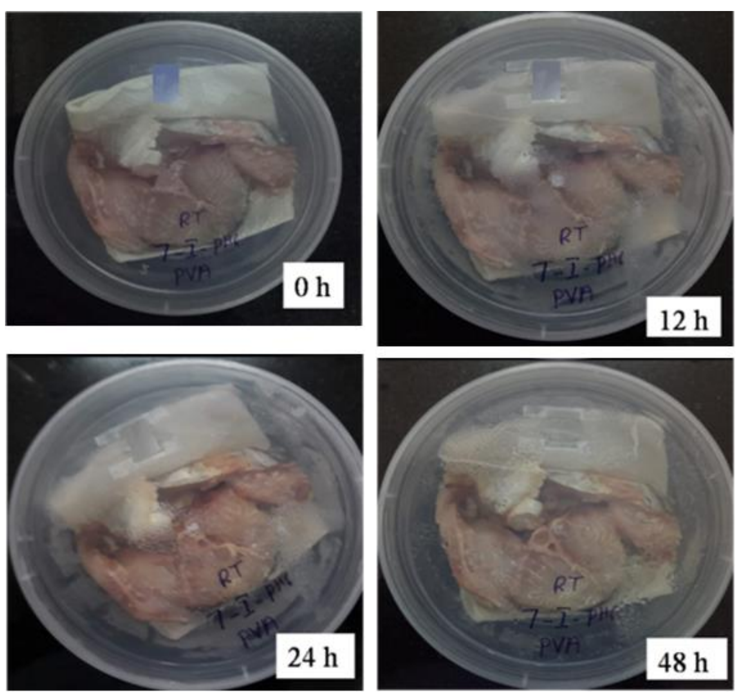


Figure 4 Halochromic response of MI/PVA at room temperature during monitoring of spoilage of seer fish.

On time scale, all the three colors decreased at first and then increased in a pattern. After 24 h decrease in the color was attributed to the partial dissolution of the thin film sensor in the package (**Figure 7**).

The MI/PVA was subjected to soil test to assess its biodegradability. After 14 days of incubation in fertile soil, no fragments of MI/PVA were found. Thus, the result indicate that developed MI/PVA thin film sensor is highly biodegradable.

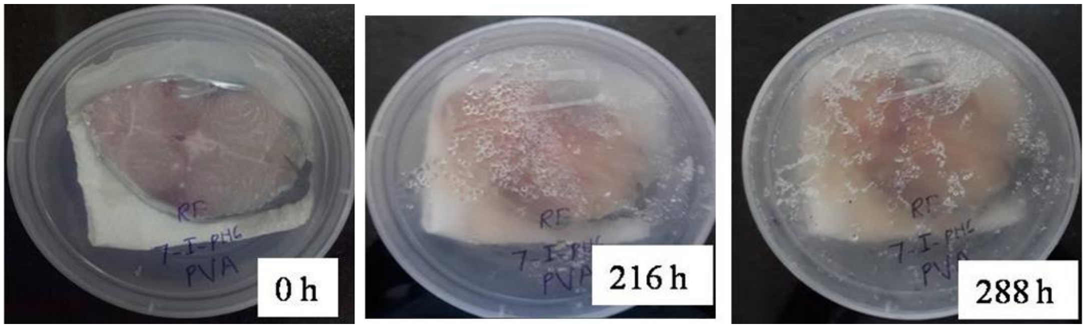


Figure 5 Halochromic response of MI/PVA at refrigerated condition during monitoring of spoilage of seer fish.

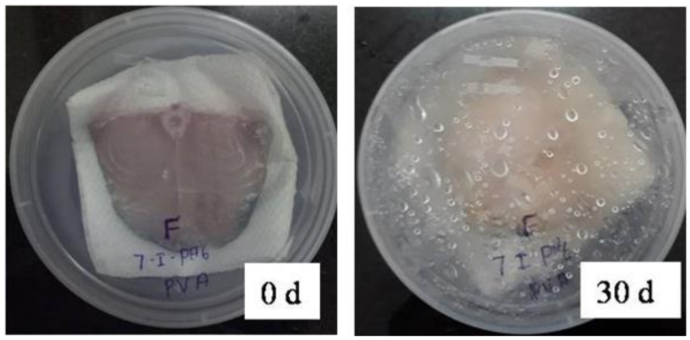


Figure 6 Halochromic response of MI/PVA at frozen condition during monitoring of spoilage of seer fish

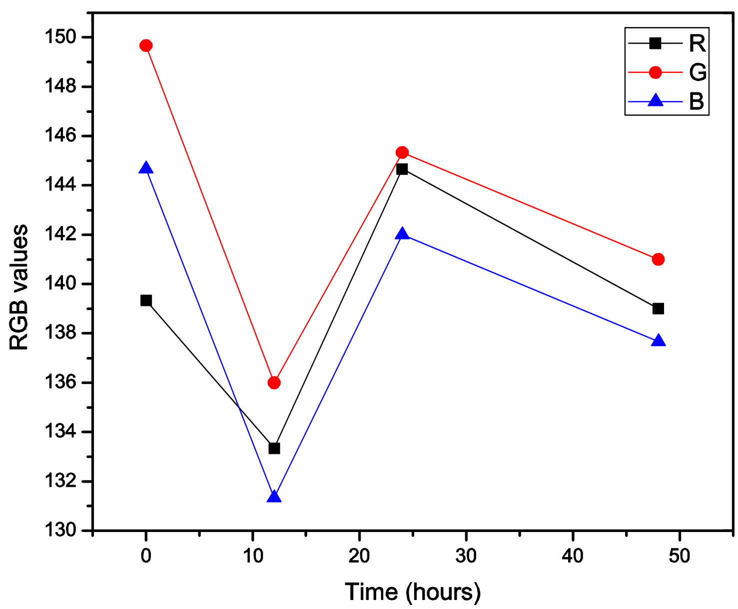


Figure 7 The RGB values exhibited by MI/PVA for monitoring spoilage of seer fish at room temperature

After 24 hours of storage at room temperature, the seer fish's initial bacterial count of 7.7×10^6 cfu/g had decreased to 2.8×10^9 cfu/g. The fish held up well after 12 hours of room temperature storage. Up to 24 hours into the storage period, there were no psychrophiles at all. The initial TVBN concentration in packed seer fish was 5.8 mg/100 g at 0 hours. After 24 and 48 hours of incubation at room temperature, the concentration of TVBN rose to 19.6 mg/100 g and 25.8 mg/100 g, respectively. The packed fishes were subjected to sensory evaluation for sensory properties such as appearance, texture, smell, and general acceptance. For freshly packed fishes at 0 h the fish was rated between 8 and 9 for all the properties with overall acceptability score of 9. However, the packed fish stored for 24 hours was scored between 1 to 3 for all the properties with value 1 for overall acceptability, which indicated that the fish was completely spoiled

Hence, the color-changing pattern of the halochromic sensor formulated in this research is consistent with sensory assessment as well as spoiling markers like TVBN and microbiological count.

Conclusion

An halochromic sensor from PVA and mixed indicator dyes is prepared in this study. The UV and FT-IR spectral results indicated successful incorporation of the indicator dyes into the thin film. The thin film sensor was cut into small pieces and stuck with the packs of fishes. The sensor exhibited visible and distinguishable color change from blue to grey at all the three tested storage conditions. The soil test revealed that the halochromic sensor developed in this study is fully biodegradable at ordinary conditions. The color changing patterns of the sensor were at par with the spoilage indicators such as amount of TVBN, microbial count, and also sensory evaluation. Thus, the MI/PVA is an eco-friendly sensor that has potential for monitoring spoilage of packed seer fish.

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