Chemical Science Review and Letters ISSN 2278-6783

www.chesci.com Research Article

Halochromic Cellulose Acetate-Based Composite Film for Real-Time Monitoring of Packed Seer Fish Spoilage

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Abstract

Real-time, non-invasive assessment of spoilage in packaged seafood remains a challenge for both retailers and consumers. This study describes the fabrication of a mixed-indicator/cellulose acetate/potato dextrose agar/starch (MI/CA/PDA/S) composite film, prepared in a single casting step, for halochromic monitoring of packed seer fish (*Scomberomorus guttatus*) spoilage. FT-IR spectroscopy confirmed strong intermolecular hydrogen bonding between CA and PDA, supporting homogeneous immobilization of MI within the composite matrix. The film exhibited a rapid, visually distinct colour change on exposure to ammonia vapour, with colorimetric analysis (ΔE) showing values of 50.48 and 80.89 at 24 and 48 h during room-temperature storage, and 34.29 and 67.65 at 6 and 10 days under refrigeration, exceeding the sensitivity previously reported for a membrane-protected MI/PVA sensor. RGB analysis further supported smartphone-compatible digital monitoring. The film showed a swelling index of 42.62%, indicating restricted water uptake, and 41.46% biodegradability, intermediate between pure CA- and agar/starch-based films. These results demonstrate that the MI/CA/PDA/S film is a low-cost, sensitive and biodegradable sensor suitable for real-time spoilage monitoring of packed seafood.

Keywords: Halochromic sensor, fish spoilage, packed fish, cellulose acetate, polysaccharides.

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Introduction

Fish and other seafood are valuable sources of complete protein and are widely recommended as part of a balanced diet, apart from their contribution to livelihood and export earnings in many coastal economies (Birch et al., 2018; Khalili Tilami and Sampels, 2018). Seer fish, in particular, holds considerable commercial importance owing to its taste, nutritional value and year-round demand. However, seafood is highly perishable, and preparing it remains inconvenient for working consumers because of the time required for cleaning and the strong odour associated with raw fish (Hicks, 2016). This has encouraged a shift towards hygienically packaged, ready-to-cook seafood. In such packages, the conventional sensory evaluation of gills, eyes and texture cannot be performed without opening the pack, which makes real-time, non-invasive assessment of spoilage essential for both retailers and consumers.

Spoilage of fish is accompanied by microbial and enzymatic breakdown of proteins and amino acids, releasing total volatile base nitrogen (TVBN) compounds such as ammonia, dimethylamine and trimethylamine. As TVBN accumulates within a sealed package, it raises the local pH of the headspace, and this pH shift can be exploited as a proxy for the degree of spoilage (Kuswandi et al., 2012). Halochromic dyes, which undergo a visible and reversible colour change with pH, are therefore well suited as simple, on-package indicators that allow spoilage to be read at a glance without instrumentation (Devarayan, 2018). For such indicators to be practically useful, the host matrix must retain the dye without leaching, remain biocompatible and inexpensive, and be biodegradable so that it does not add to packaging waste.

The authors have previously developed a series of halochromic sensor films for monitoring seafood spoilage. A mixed-indicator system incorporated into potato dextrose agar (PDA) produced a distinct colour transition on exposure to ammonia and was effective for monitoring packed seer fish (Devarayan et al., 2020), and related biodegradable, silver-nanoparticle- and natural-dye-based sensors extended this approach to sardine and

other packaged fish (Devarayan et al., 2021; Devarayan et al., 2022b). However, condensation and moisture accumulated within refrigerated packs was found to leach the chromic material from these agar- and starch-based matrices, reducing sensitivity during prolonged cold storage. To improve leaching resistance, cellulose acetate (CA) was subsequently introduced as a host polymer (Devarayan et al., 2022a), and a cellulose-based composite film was further correlated with TVBN, pH and microbial load for packed seer fish (Devarayan et al., 2024). Recently, a porous cellulose acetate membrane was used to physically shield a polyvinyl alcohol-based indicator film, which improved chromatic sensitivity (ΔE up to 48.4) but required the sensor and the protective membrane to be fabricated as two separate layers (Devarayan et al., 2026).

These studies indicate that cellulose acetate imparts leaching resistance and mechanical stability, whereas potato dextrose agar and starch provide a compatible, biodegradable gel-forming environment for the mixed indicator, but no single-step film reported so far has combined all three attributes within one matrix. In this view, the present study was formulated with the following strategies: (i) fabrication of a mixed-indicator (MI) film in a single casting step by combining cellulose acetate (CA), potato dextrose agar (PDA) and starch (S) as the composite matrix and characterization; (ii) evaluation of the halochromic response and ammonia sensitivity of the MI/CA/PDA/S film; (iii) real-time monitoring of the spoilage of packed seer fish at room temperature and under refrigerated condition using colorimetric (ΔL, Δa, Δb, ΔE) and RGB measurements; and (iv) assessment of the swelling behaviour, moisture stability and biodegradability of the developed film.

Materials and Methods

Materials

Cellulose acetate (CA), potato dextrose agar (PDA) and starch (S) were purchased from Sigma-Aldrich and HIMEDIA, Mumbai. Bromothymol blue (BTB), bromocresol purple (BCP), phenolphthalein and Congo red powder (CRP) were purchased from HIMEDIA, Mumbai, and were used as the components of the mixed indicator (MI). *N,N*-dimethylformamide (DMF) and ethanol used as solvents were of analytical grade. Fresh seer fish (Scomberomorus guttatus) was procured from the Nagapattinam fish landing centre, India, and was cleaned thoroughly before use.

Formulation of the mixed indicator (MI) solution

A 10 ppm solution each of BTB, BCP, phenolphthalein and CRP was prepared separately in ethanol. Aliquots of 0.1 mL of each of the four dye solutions were combined and made up to 2 mL with distilled water. This combined solution, denoted as MI, was used as the halochromic component in film fabrication.

Fabrication of MI/CA/PDA/S composite film

CA (1.5 g) was dissolved in 10 mL of DMF under continuous stirring for 2 h at room temperature to obtain a clear, viscous solution. Separately, 1.0 g of PDA and 0.5 g of S were dissolved in 20 mL of distilled water and heated at 60–70°C with continuous stirring until a homogeneous solution was obtained. The PDA/S solution was then added dropwise to the CA solution under vigorous stirring, and stirring was continued for a further 30 min to obtain a homogeneous casting solution, denoted CA/PDA/S. Subsequently, 1 mL of the MI solution was added and stirred for 15 min to ensure uniform dispersion of the dyes. The resulting solution was cast onto a levelled glass plate and allowed to dry at ambient temperature for 24 h, followed by drying under vacuum to obtain the MI/CA/PDA/S composite film. A film of PDA and S alone (PDA/S), without CA or MI, was similarly prepared and used as a reference in the biodegradability study.

Characterization

Fourier transform-infrared (FT-IR) spectra of pure CA, PDA and S, and of the CA/PDA/S and MI/CA/PDA/S composites, were recorded using a Perkin Elmer Spectrum Two FT-IR spectrophotometer over the range of 4000–400 cm^{-1}, to identify the functional groups involved and to confirm intermolecular interaction between the components of the composite matrix.

Evaluation of halochromic response and ammonia sensitivity

The halochromic response of the MI/CA/PDA/S film was evaluated using an ammonia vapour exposure test to simulate the alkaline environment generated during fish spoilage. A 1 mL aliquot of 10 ppm ammonia solution was placed in a 300 mL polypropylene (PP) container, and a 1 × 1 cm piece of the MI/CA/PDA/S film, affixed to the inner side of the container lid, was used to seal the container. The colour change of the film was recorded photographically at fixed intervals, and the stability of the colour change was subsequently monitored by colorimetric measurement, as described below.

Colour measurement

The CIELab colour space was used to quantify the colour changes exhibited by the films, where L denotes lightness, a denotes the position between red and green, and b denotes the position between yellow and blue. Digital images of the films were captured under uniform lighting conditions with a 13-megapixel camera and were analysed for L, a, b and RGB (red, green, blue) values using Adobe Photoshop 7.0. The total colour difference (ΔE) between the initial and spoiled states of the film was calculated using the following equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

where ΔL, Δa and Δb represent the differences in lightness, redness and yellowness, respectively, between the reference and test readings.

Real-time monitoring of spoilage of packed fish

Cleaned seer fish fillets (40–50 g) were placed in transparent PP containers. The MI/CA/PDA/S film was cut into 1 × 1 cm pieces and affixed to the inner side of the container lid, after which the container was sealed. For monitoring at room temperature (27–30°C), the packed samples were observed at 0, 24 and 48 h. For monitoring under refrigerated condition (4°C), separate packed samples were observed at 0, 6 and 10 days. All experiments were performed in triplicate, and colour changes of the film were recorded at each time point and analysed for L, a, b, RGB and ΔE values as described above.

Swelling index

The swelling index of the MI/CA/PDA/S film was determined gravimetrically. A film piece of 2 × 2 cm was weighed to obtain the initial weight (W_1) and immersed in distilled water in a Petri dish, followed by shaking at 60 rpm for 5 min in an orbital shaker. The film was then removed, allowed to air-dry for 10 min to remove surface water, and reweighed to obtain the final weight (W_2).

The swelling index (%) was calculated as $[(W_2 - W_1)/W_1] \times 100$.

Biodegradability test

The biodegradability of the MI/CA/PDA/S and PDA/S films was evaluated by soil burial, as described elsewhere (Devarayan et al., 2020; Goswami and Maiti, 1998). Briefly, 100 g of fertile soil was moistened with 20 mL of distilled water, and a 2 × 2 cm piece of each film, of known initial weight (W1), was buried in the moistened soil and left undisturbed for 14 days. The films were then carefully recovered, cleaned and reweighed (W2), and the percentage biodegradability was calculated from the difference between the initial and final weights.

Result and Discussion

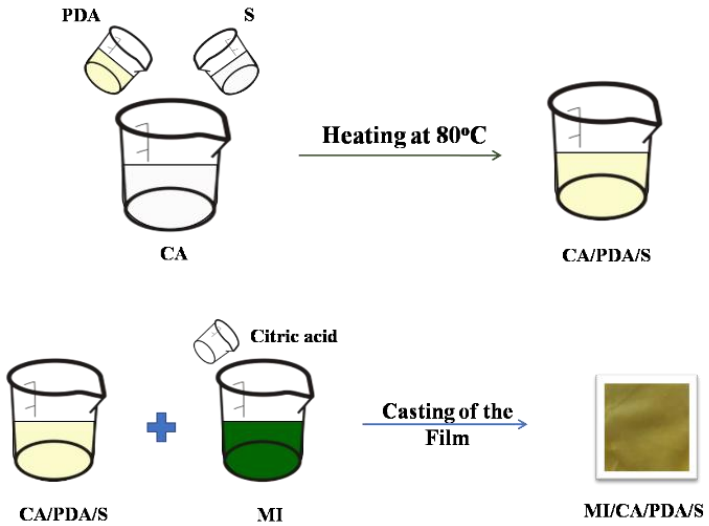

Figure 1. Preparation of MI/CA/PDA/S film.

The MI and PDA were homogeneously incorporated into the CA/S matrix, giving rise to a uniform film in which no phase separation was observed (Figure 1). Formation of strong intermolecular interactions within the composite was confirmed by FT-IR analysis of pure CA, PDA and S, as well as of the CA/PDA/S and MI/CA/PDA/S composites. Broadening and shifting of the carbonyl absorption, together with a corresponding shift in the O–H stretching region, indicated enhanced hydrogen bonding between CA and PDA, while the characteristic absorption bands of MI were retained in the composite spectrum, confirming successful incorporation of the dye system within the matrix. These

intermolecular associations are expected to confer good dye retention, colour stability and mechanical integrity during application. The adhesive character of PDA further promoted homogeneous distribution of MI within the polymer blend and improved its compatibility with CA, consistent with the leaching-resistant role previously attributed to cellulose acetate in the author's earlier sensor films (Devarayan et al., 2022a).

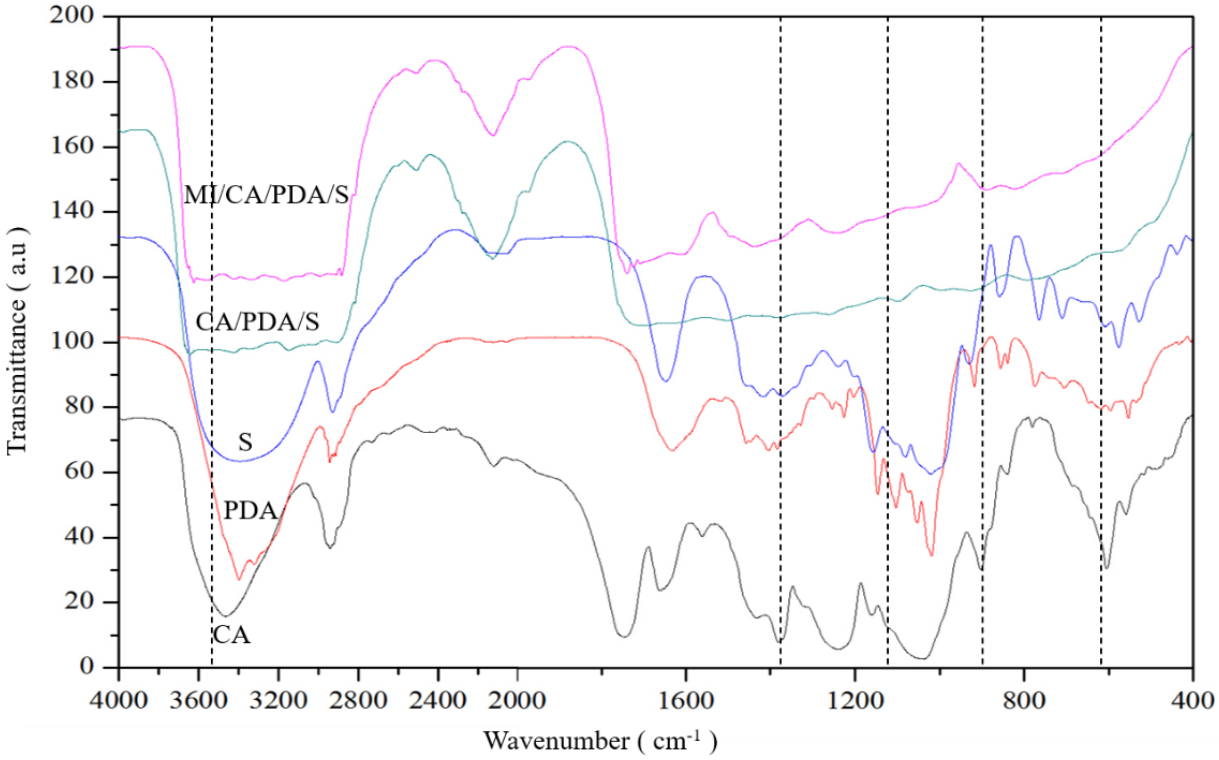

Figure 2. FT-IR spectra of CA, PDA, S, CA/PDA/S, and MI/CA/PDA/S.

The ammonia vapour exposure test, used to simulate the alkaline environment generated during fish spoilage, was performed to evaluate the halochromic response of the developed film (Figure 3). The original colour of the MI/CA/PDA/S film changed markedly within a short exposure period, indicating that the MI immobilized within the composite matrix underwent efficient protonation/deprotonation in response to the ammonia vapour. The enhanced colour response relative to CA or CA/S alone is attributed to the role of PDA in stabilizing MI within the matrix and limiting dye diffusion, consistent with the FT-IR evidence for hydrogen bonding between CA and PDA.

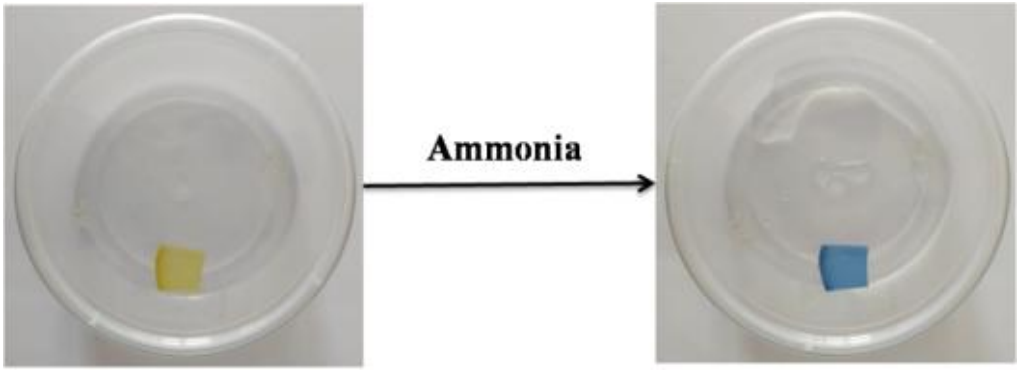

Figure 3. Ammonia test for MI/CA/PDA/S. Halochromic response of MI/CA/PDA/S film color changing pattern of the film against ammonia

The halochromic response is attributed to the reversible interaction between volatile basic nitrogen compounds, principally ammonia, and the active sites of MI. During spoilage, the rise in local pH deprotonates the MI molecules, generating a conjugated chromophore system with a narrower energy band gap and a correspondingly visible colour shift. The strong interaction of PDA with MI, together with the electrostatic stabilization provided by CA, is considered to keep the dye system immobilized within the matrix while preserving its responsiveness to pH change.

The practical performance of the sensor film was assessed by monitoring real-time spoilage of packed seer fish stored at room temperature (Figure 4). Colour changes were quantified using ΔL, Δa, Δb and ΔE. At 0 h, the negligible ΔE value confirmed that the film remained stable in the absence of spoilage. This was followed by

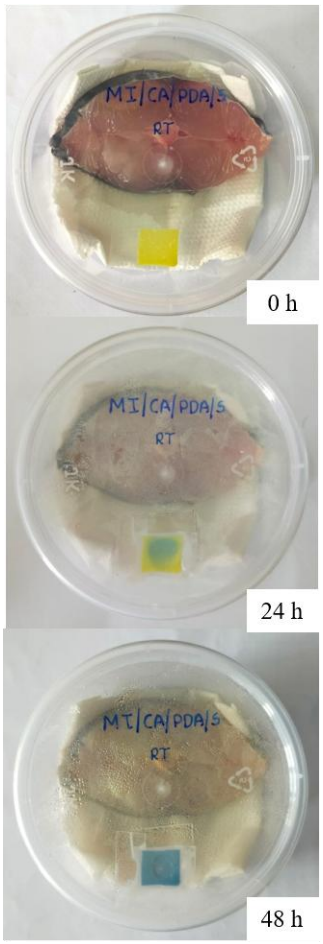

Figure 4. Real-time monitoring of spoilage of packed fish using MI/CA/PDA/S sensor film at room temperature

pronounced shifts in the individual colour coordinates with the progression of spoilage. A progressive decrease in ΔL, indicating darkening of the film surface. A shift in Δa from negative to positive values, reflecting a transition towards a redder tone; and a marked increase in Δb, indicating increasing yellowness.

Collectively, these coordinate shifts produced a pronounced overall colour change, with ΔE increasing from 50.48 at 24 h to 80.89 at 48 h. This trend is consistent with the rapid accumulation of TVBN compounds expected at ambient storage temperature (Kuswandi et al., 2012). The colour transition was distinguishable by the naked eye, without recourse to instrumentation, supporting the suitability of the film for direct visual assessment by consumers.

Fish samples stored under refrigerated condition (4°C) were monitored to evaluate sensor performance during cold storage (Figure 5). Spoilage progressed more slowly than at room temperature, but the MI/CA/PDA/S film retained its sensitivity, with ΔE increasing from 34.29 at 6 days to 67.65 at 10 days relative to the fresh sample, and by a further 33.37 between day 6 and day 10, reflecting continued accumulation of spoilage metabolites during cold storage. This response is comparable to, and in magnitude exceeds, that reported for a cellulose-acetate-porous-membrane-protected MI/PVA sensor under equivalent refrigerated storage (ΔE = 32.7 at day 6 and 48.4 at day 10; Devarayan et al., 2026), despite the present film requiring no separate protective membrane layer. The corresponding shifts in ΔL, Δa and Δb indicated the following: a continued decrease in ΔL, indicating progressive darkening, an initial negative shift in Δa followed by a gradual increase; and a further increase in Δb as spoilage progressed.

The film did not exhibit a false-positive response during the early stages of refrigerated storage and remained sensitive to the low ammonia concentrations characteristic of early spoilage, despite exposure to condensation within the pack. In comparison with conventional chemical-based spoilage assays, this optical method offers a low-cost and instantaneous means of assessment that is applicable under both ambient and chilled supply-chain conditions. The RGB profile of the film provides a basis for quantitative, smartphone-based sensing of the colour changes described above (Figure 6). At room temperature, the red channel intensity increased sharply and the blue channel intensity declined as spoilage progressed, consistent with rapid deterioration, whereas under

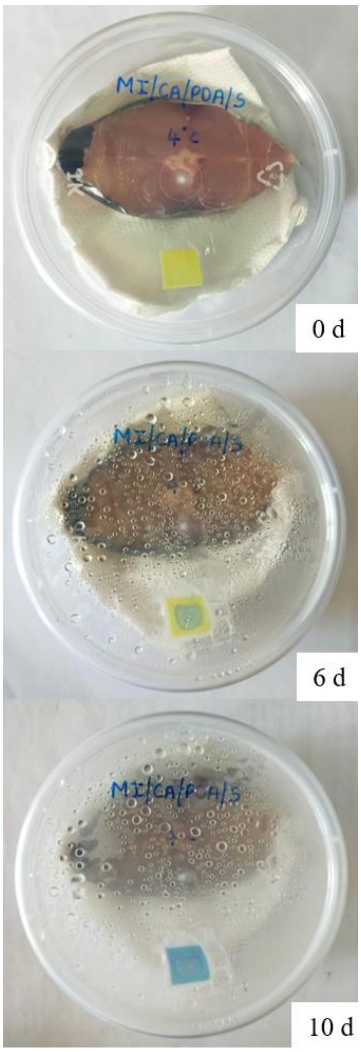

Figure 5. Real-time monitoring of spoilage of packed fish using MI/CA/PDA/S sensor film at refrigerated temperature.

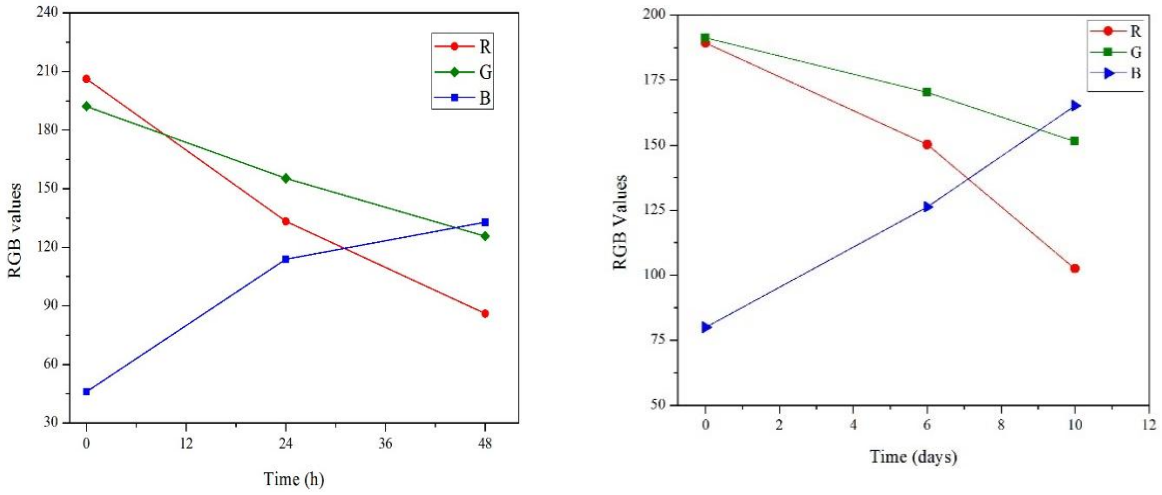

Figure 6. RGB values exhibited by MI/CA/PDA/S for monitoring spoilage of seer fish at room temperature (a) and refrigerated condition (b).

refrigeration the corresponding changes in the red and blue channels were more gradual. The proportionality of these changes indicates consistent, predictable chromatic behaviour of the composite film.

The RGB values complement the ΔE measurements: whereas ΔE reflects perceptual colour difference, RGB values are directly compatible with digital image-processing pipelines used in mobile vision systems, supporting the extension of this sensor film from passive visual indication to smartphone-based digital monitoring of spoilage.

Moisture stability is an important requirement for food-packaging sensors. The MI/CA/PDA/S film exhibited a swelling index of 42.62%, markedly lower than that previously reported for cellulose-acetate-based (70%) and agar/starch-based (85%) halochromic films (Devarayan et al., 2022a), indicating more restricted and controlled water uptake within the present composite. This is attributed to the crosslinking and hydrogen bonding between CA and PDA identified by FT-IR, which is expected to limit excessive swelling, structural disruption and consequent leaching of the dye system, while still permitting sufficient water ingress for the film to respond to moisture-borne volatile amines.

Biodegradability is a relevant consideration for the environmental impact of packaging sensors. The MI/CA/PDA/S composite exhibited 41.46% biodegradability over the 14-day soil-burial period, compared with 100% for the PDA/S reference film prepared without CA. This intermediate value is consistent with previous observations that cellulose acetate imparts hydrophobicity and correspondingly limits the biodegradability of composite films, with a CA-based halochromic film previously reported to degrade by only 12% under comparable conditions (Devarayan et al., 2022a), while agar/starch-based films without CA exhibited substantially higher biodegradability of 61.87–68.50% (Devarayan et al., 2022b). The biodegradability of the MI/CA/PDA/S film therefore reflects a compromise between the mechanical and moisture stability conferred by CA and the biodegradability conferred by PDA and S, and remains considerably higher than that of conventional petroleum-based packaging materials.

Conclusion

The present study demonstrates the fabrication of a mixed-indicator/cellulose acetate/potato dextrose agar/starch (MI/CA/PDA/S) composite film for real-time monitoring of packed seer fish spoilage. FT-IR analysis confirmed that hydrogen bonding between CA and PDA immobilizes MI within the composite matrix, conferring the film with a stable sensing matrix with restricted dye leaching, evidenced by a swelling index of 42.62%, along with a rapid and pronounced halochromic response to ammonia vapour that exceeded that of CA or CA/S alone. The film also enabled effective real-time spoilage detection of packed seer fish at both room temperature (ΔE up to 80.89 at 48 h) and refrigerated condition (ΔE up to 67.65 at 10 days), with colour changes discernible by the naked eye and quantifiable via RGB values, supporting smartphone-based digital monitoring. In addition, the film exhibited moderate biodegradability (41.46%), consistent with the intermediate hydrophobicity of the CA/PDA/S matrix.

Relative to the authors' earlier halochromic sensors, the MI/CA/PDA/S film combines the leaching resistance associated with cellulose acetate and the biodegradable, dye-compatible character of potato dextrose agar and starch within a single casting step, without requiring the separate protective membrane layer used in a previous design (Devarayan et al., 2026). This represents a simplification of fabrication relative to earlier two-layer sensor designs, while achieving comparable or greater colorimetric sensitivity.

Thus, the MI/CA/PDA/S film constitutes a low-cost, visually interpretable and moderately biodegradable sensor suitable for real-time monitoring of seafood spoilage under both ambient and refrigerated storage conditions. Its compatibility with RGB-based digital image analysis further supports its potential integration into smartphone-based food-safety monitoring, offering a practical addition to intelligent packaging for the seafood supply chain.

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Publication History
Received 03.08.2026
Revised 19.08.2026
Accepted 20.08.2026
Online 20.08.2026