International Journal of Food Science +Technology

Institute of Food Science +Technology ifst

Review

Recent developments in the application of natural pigments as pH-sensitive food freshness indicators in biopolymer-based smart packaging: challenges and opportunities

Bongekile K. Ndwandwe,[1] Soraya P. Malinga,[2] Eugenie Kayitesi[3] & Bhekisisa C. Dlamini[1]*

1 Department of Biotechnology and Food Technology, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Doornfontein, Johannesburg 2028, South Africa

2 Department of Chemical Sciences, University of Johannesburg, P.O Box 17011, Doornfontein, Johannesburg 2028, South Africa

3 Department of Consumer and Food Sciences, University of Pretoria, Private Bag X20, Hatfield 0028, South Africa

(Received 21 November 2023; Accepted in revised form 4 February 2024)

Summary Recently, the assimilation of pH-sensitive natural pigments into biopolymers has shown promising prospects for pH-reactive based smart packaging material. Unlike synthetic pigments, which have potential safety problems due to migration, natural pigments have negligible toxicity levels both to humans and the environment and some even possess nutritional and pharmacological properties. To complement the advantages of natural pigments, natural biopolymers have proven to be ideal candidates for the development of smart packaging because of their biocompatibility, availability, biodegradability, stability, minimum toxicity and good film-forming capability. Smart packaging gives consumers real-time signals on the quality of packaged food via food deterioration indicators like pH alteration. This review will consider the recent progress in the development of pH-responsive smart packaging based on natural pH-sensitive pigments and natural biopolymers from 2013 to the present. It will further discuss the challenges and opportunities of colorimetric smart packaging.

Keywords Biopolymers, food freshness indicator, natural pigments, pH-sensitive, smart packaging.

Introduction

Packaged food undergoes numerous variations during storage resulting in alterations in the composition of the micro-environment of the packaged food (Amin *et al.*, 2022). The variation includes changes in key food quality parameters such as pH, gaseous composition, and emission of chemicals such as ammonia, amines and hydrogen sulphide (Naghdi *et al.*, 2021; Amin *et al.*, 2022; Liu *et al.*, 2022a). Detection and identification of these parameters are critical for the determination of the quality degradation status of the packaged food. Recently, smart packaging with the ability to provide real-time evidence of food freshness during storage has been developed (Bhargava *et al.*, 2020; Wang *et al.*, 2022). Smart packaging displays and communicates the changes in the quality or condition of the packaged food product to consumers without opening the packaging (Bhargava *et al.*, 2020; Naghdi *et al.*, 2021; Zhao *et al.*, 2022; Cheng *et al.*, 2022a). In smart packaging, **indicators** that detect changes in a specific compound or a class of compounds are **incorporated** into a solid matrix, mainly biopolymers, during the manufacturing of the packaging material (Bumbudsanpharoke & Ko, 2019; Amin *et al.*, 2022; Azman *et al.*, 2022; Poudel *et al.*, 2023). The **incorporated** indicators range from nanomaterials, synthetic pigments, and natural pigments which exhibit obvious colour changes depending upon the variation in stimuli of the packaged food (Poudel *et al.*, 2023). In respect of smart packaging material, some work has been carried out on indicators such as time–temperature, food freshness, humidity and gas to monitor food quality (Soltani *et al.*, 2021; Liu *et al.*, 2022b; Oun *et al.*, 2023). However, except for freshness indicators, the other stated indicators are indirect indicators of food quality, i.e., they provide data about an extrinsic factor in food alterations rather than the actual variations (Azeredo & Correa, 2021). This review's objective is to reflect on recent advances, challenges and opportunities in the application of plant-based natural pH-sensitive pigments and natural biopolymers in the development of smart packaging material for food freshness monitoring.

---

*Correspondent: E-mail: bcdlamini@uj.ac.za

doi:10.1111/ijfs.16990

Food freshness indicators

The application of freshness indicators enables visual observation of the quality of packaged food by detecting alterations that occur due to microbial proliferation and presence of their metabolites within the package in real-time (Ghaani *et al.*, 2016; Schumann & Schmid, 2018; Hwa *et al.*, 2023). The accumulation of microbial metabolites in food is usually accompanied by variation in the pH of the food and its micro-environment (Bhargava *et al.*, 2020; Azman *et al.*, 2022). The variation in pH can be monitored by a costly pH-detector that is based on an electrochemical potentiometer with pH-detecting electrodes attached to it (Sobhan *et al.*, 2021; Xu *et al.*, 2022; Choi *et al.*, 2023). Recently, pH-responsive pigments have emerged as a simple tracking technique for pH change in food. They rely on colour variation that occurs on the indicator as the pH of packaged food is altered during the degradation process (Becerril *et al.*, 2021; Szadkowski *et al.*, 2022; Oun *et al.*, 2023). During degradation, the chemical structure of the packaged food deteriorates due to enzymatic and microbial reactions (Shao *et al.*, 2021; Xu *et al.*, 2022; Zhao *et al.*, 2022). Subsequently, numerous acidic and basic gases like carbon dioxide (CO_2), dimethylamine (DMA), ammonia (NH3), trimethylamine (TMA), hydrogen sulfide (H_2S) are produced and released into the confined micro-environment (Bumbudsanpharoke & Ko, 2019; Becerril *et al.*, 2021; Shao *et al.*, 2021; Almasi *et al.*, 2022). The compounds become concentrated in the package headspace and gradually interact with the natural pH-sensitive−biopolymer complex. This interaction alters the structure of the pH-sensitive pigment resulting in visual colour changes as illustrated in Fig. 1 (Becerril *et al.*, 2021; Zhang *et al.*, 2021; Szadkowski *et al.*, 2022; Liu *et al.*, 2022a).

pH-sensitive freshness indicators that are based on artificial pigments have been widely used (Bhargava *et al.*, 2020) due to their colour stability, inexpensiveness and simplicity (Wu *et al.*, 2022). These include bromocresol green, cresol red, bromocresol purple, methyl red, chlorophenol, xylenol and bromine thymol blue (Bhargava *et al.*, 2020; Ezati & Rhim, 2020a; Ran *et al.*, 2021). However, artificial pigments have numerous disadvantages including increased toxicity potential to both humans and the environment due to their possible migration into the packaged food and environment (Charoensit *et al.*, 2021; Cheng *et al.*, 2022b; Liu *et al.*, 2022b; Shen *et al.*, 2023). Consequently, researchers have been investigating the potential of natural pH-sensitive pigments as alternatives to synthetic dyes (Becerril *et al.*, 2021). The relatively low toxicity and eco-friendly nature of natural pigments have made them be increasingly favoured over synthetic dyes (Naghdi *et al.*, 2021; Hamidin *et al.*, 2022; Kim *et al.*, 2022; Cheng *et al.*, 2022a). Natural pigments have been used in different fields such as textile, toxicology, and pharmacology as well as in the fish and dairy industry (Di Salvo *et al.*, 2023).

Sources of natural pigments

Natural pigments can be obtained from microorganisms, animals and plants (Lian *et al.*, 2019; dos Santos & Bicas, 2021; Li *et al.*, 2021; Martins *et al.*, 2022; Lan *et al.*, 2023; Singh *et al.*, 2023). Microbial sources of natural pigments may include bacteria such as *Escherichia coli*, *Dietzia natronolimnaea*, fungi like *Blakeslea trispora*; and yeasts such as *Xanthophyllic dendrorhous*, *Yarrowia lipolytica*, *Saccharomyces cerevisiae* (Ye *et al.*, 2019; Singh *et al.*, 2023). Microbial pigments have proven to be non-toxic and eco-friendly; however, microorganisms require special growth conditions and time-consuming culturing, isolation and purification steps (Di Salvo *et al.*, 2023). Recently, novel classes of natural pigments from marine animals with potential economic significance have been recorded (Ye *et al.*, 2019). Edible pigments that have been extracted from mammals (livestock) are bilirubin and heme. Despite this, there is limited research and development in animal pigments (Lan *et al.*, 2023; Shen *et al.*, 2023). Insects such as ladybugs and cochineal bugs are also a source of edible pigments like carminic acid (Renita *et al.*, 2023; Shen *et al.*, 2023; Singh *et al.*, 2023). Amongst the sources of natural pigments, pigments of plant origin are mostly preferred because of their abundance, easy-accessibility, non-toxicity, safety, and good pH-responsivity (Aguirre-Joya *et al.*, 2020; Zheng *et al.*, 2022; Nabi *et al.*, 2023). They can be stored in the plant roots, leaves, stems, fruits and flowers (dos Santos & Bicas, 2021; Li *et al.*, 2021; Shao *et al.*, 2021; Ghosh *et al.*, 2022; Hamidin *et al.*, 2022; Nabi *et al.*, 2023). Plant pigments are broadly categorised based on their chemical structure as shown in Table 1.

Classification of pigments from plants

Pyrrole derivatives: Chlorophyll

Chlorophyll is the green pigment that is well known for the photosynthesis process in green plants, alga and cyanobacteria. It is distributed largely in the plant kingdom including green fruits and vegetables (Zielinski *et al.*, 2021). Chlorophyll is hydrophobic and it possesses antioxidant, anti-inflammatory and anti-mutagenic properties (Zheng *et al.*, 2022). The chlorophyll pigments belongs to the major class of tetrapyrroles and it consists of a divalent magnesium ion attached to its centre (Ghosh *et al.*, 2022; Zheng *et al.*, 2022). Chlorophyll can be further categorised into five major classes which are a, b, c, d, e and f (Ghosh *et al.*, 2022). However, two classes of

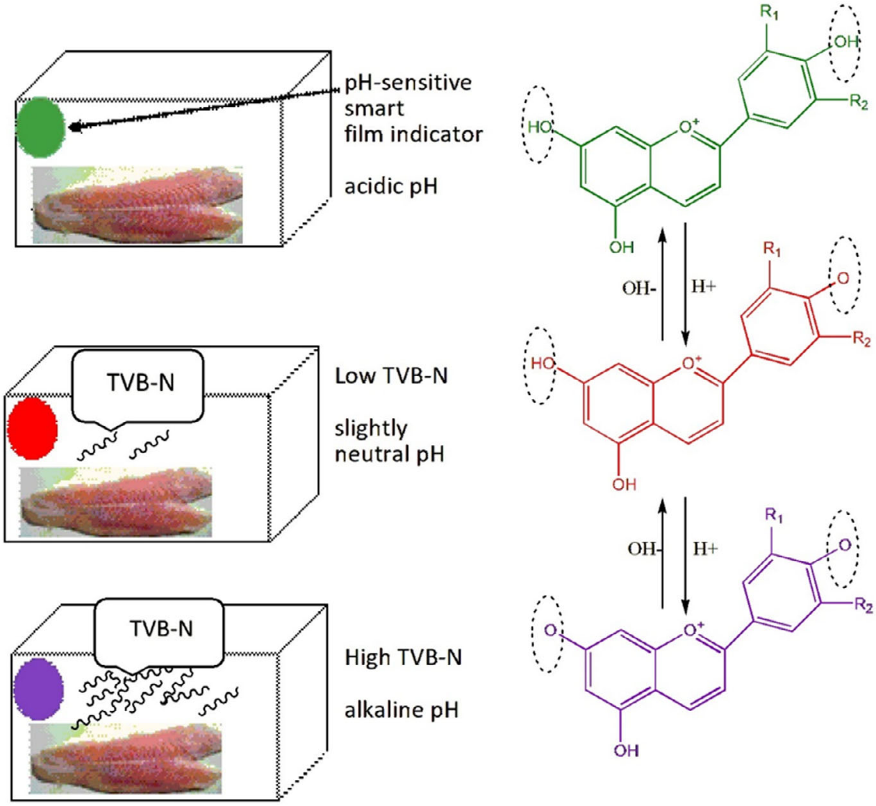


Figure 1 An illustration of pH-sensitive indicator mechanism (Becerril *et al.*, 2021).

chlorophyll; chlorophyll a and chlorophyll b are present in higher plants, while chlorophyll c, d and e are found in cyanobacteria and algae (Nabi *et al.*, 2023; Singh *et al.*, 2023). Chlorophyll can change colour easily due to the variation of external factors such as temperature and pH. At high temperature and under acidic environment, chlorophyll changes from bright green to olive green because of the displacement of the central magnesium ion by hygrogen ions (Zheng *et al.*, 2022; Parlak *et al.*, 2024). Currenty, chlorophyl pigment is utilised in various industries ranging from cosmetic, pharmaceuticals and food industry (Nabi *et al.*, 2023). In the food industry, chlorophylls (E-40) are mostly used as a natural food colourant and their aplication can be extended to act as natural pH-responsive food freshness indicator.

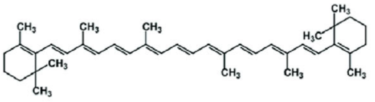
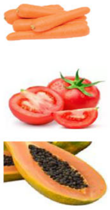
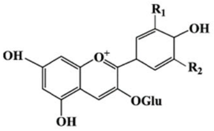
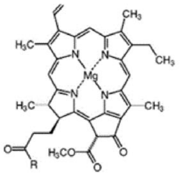
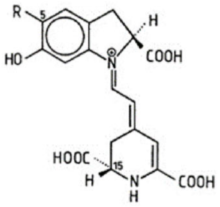
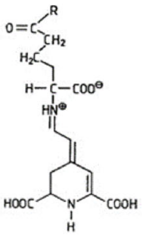
Isoprenoid derivatives: Carotenoids

Carotenoids are fat-soluble isoprenoid natural pigments that are widely distributed in nature (Zheng *et al.*, 2022; Lan *et al.*, 2023). They are found mostly in fruits and vegetables exhibiting the yellow, orange and red colours due to their conjugated double bond chromophores (Ghosh *et al.*, 2022; Rodríguez-Mena *et al.*, 2023). These pigments are categorised into two main classes: carotenes and xanthophylls. Their categorization is based on the variation of the atoms forming their molecular structure. Carotenes consist of only carbon and hydrogen in their structure, whereas xanthophylls consist of oxygen in addition to the carbon, and hydrogen atoms (Bocker & Silva, 2022). Carotenoids are further classified into primary and secondary carotenoids according to their functionality. The primary carotenoids are β-carotene, lutein, and zeaxanthin and the secondary carotenoids consists of α-carotene, lycopene, and astaxanthin (Bocker & Silva, 2022; Singh *et al.*, 2023). Even though the two classes of carotenoids vary in molecular structure and biological properties, their colourful compound disintegrates under alkaline conditions rendering them suitable for incorporation as natural indicators for monitoring food freshness (Huang *et al.*, 2022).

Flavonoid derivatives: Anthocyanin

Anthocyanins belong to the class of polyphenol-based flavonoids consisting of glycosylated poly-hydroxy and

Table 1 Broad classification of pigments of plant origin

Group	colour spectrum	chemical structure	sources	Reference
Triterpenoid pigments (Carotenoids)	**yellow, orange and red**	 **β- carotene**		**(Ghosh, Sarkar and Chakraborty, 2023)**
Poly-phenolic compounds	**red-blue and violet**	 **anthocyanins**		**(Pandiselvam *et al.*, 2023)**
Pyrrole derivatives	**green**	 **chlorophyll**		**(Zielinski *et al.*, 2021)**
Nitrogenated compounds	**red-violet**	  **betacyanin** **betaxanthin**		**(Nabi *et al.*, 2023)**

polymethoxy structures with two aromatic rings that are linked by a linear three-carbon chain (Priyadarshi *et al*., 2021). They are hydrophilic pigments found in a variety of flowers, fruits and vegetables. Anthocyanins are identified by their vibrant purple, red and blue shades (Ghosh *et al*., 2022; Parlak *et al*., 2024). The most used anthocyanins in food include petunidin, pelargonidin, peonidin, cyanidin, delphinidin and malvidin (Roy & Rhim, 2021; Parlak *et al*., 2024). Anthocyanins exhibit a unique structure and chemistry, which renders them highly sensitive to variation in environmental factors such as temperature, light and pH (Priyadarshi *et al.*, 2021). Their sensitivity affects their stability and colour. Anthocyanins are more stable in acidic pH (1–3) where they exist as flavylium cations exhibiting a red or orange colour (Zheng *et al.*, 2022). Increasing the pH results in the generation of colourless species of carbinol pseudobase and chalone, which slowly turns into a purple colour at a pH 7 (neutral pH) followed by a deep blue colour under alkaline conditions (pH 8–10). With a further increase in pH, the colour changes to light yellow chalcone (Priyadarshi *et al.*, 2021; Liu *et al.*, 2022a). Amongst the natural pH-sensitive pigments, anthocyanins are the most researched pigments due to their excellent colour variation and commercial accessibility (Ghorbani *et al.*, 2021).

Nitrogen-heterocyclic derivatives: Betalains

Betalains are water-soluble nitrogenous plant pigments that are derived from betalamic acid [4-(2-oxoethylidene)-1,2,3,4- tetrahydropyridine-2,6-dicarboxylic acid] (Zielinski *et al.*, 2021; Ghosh *et al.*, 2022; Martins *et al.*, 2022). They belong to two major classes, which are the yellow-orange betaxanthin and the red-violet betacyanin (Di Salvo *et al.*, 2023; Rodríguez-Mena *et al.*, 2023). Betalains are more dominant in the edible parts of plants such as leaves, flowers and stems (Ghosh *et al.*, 2022). In the UV region, betaxanthin and betacyanin exhibit a characteristic absorbance at the maximum absorption wavelengths of 480 and 540 nm, respectively (Di Salvo *et al.*, 2023). Betalains have been used as natural food colourant and in drink formulations and functional foods (Nabi *et al.*, 2023). This may be due to that their colour is stable over a wide pH range (3–7). However, betalains rapidly disintegrates in alkaline conditions (Echegaray *et al.*, 2023). This pH-related colour variation is a desirable property for potential application in pH-sensitive smart packaging.

Polymer support

Smart packaging material is mostly composed of a solid polymeric base matrix and the natural pH-responsive pigment which responds to the by-products of food spoilage process (Almasi *et al.*, 2022; Zheng *et al.*, 2022). The polymer's core function is to confine the natural pH-reactive pigment in the food packaging material (Zheng *et al.*, 2022). The polymer-natural pigment complex may be achieved either via hydrogen bonding, ionic bonding, covalent bonding and/or adsorption of pigment to a polymer support (Zeng *et al.*, 2019; Liu *et al.*, 2022b). Synthetic polymers and biopolymers are the most used solid supports in smart packaging. Synthetic polymers which are mostly petroleum derivatives have the advantages of being thermal stable, low production costs, have durable mechanical and barrier properties (Priyadarshi *et al.*, 2021; Gürler *et al.*, 2023). However, they are a serious threat to the environment as they are non-biodegradable, non-recyclable and may be lethal to some form of life in the ecosystem (Gürler, 2023; Parlak *et al.*, 2024). Due to these undesirable qualities of petroleum-based polymers, recently scientists are focusing on the use of natural biopolymers as an alternative to synthetic polymers.

Natural biopolymers

Biopolymers are natural polymers sourced from different living organisms such as animals, plants, bacteria and algae (Alizadeh-Sani *et al.*, 2020; Li *et al.*, 2022a, 2022b). Numerous types of biopolymers, such as lipids, carbohydrates and proteins, have been employed to resolve ecological problems due to non-degradable plastic packaging waste and to fabricate high-value functional packaging materials (Latos-Brozio & Masek, 2020; Sharifi & Pirsa, 2021; Ran *et al.*, 2022). The most researched biopolymeric base for pH-sensitive pigments include carbohydrate-based biopolymers such as starch, agar, carrageenan, chitosan, cellulose derivatives, and proteins like zein and gelatin (Priyadarshi *et al.*, 2021). These biopolymers possess desired properties envisaged in smart food packaging material such eco-friendliness, biodegradability, biocompatibility, non-toxic nature and good film forming ability (Shao *et al.*, 2021; Liu *et al.*, 2022a; Hwa *et al.*, 2023; Yu *et al.*, 2023). Furthermore, these biopolymers are easily accessible and cost-effective due to the fact that they can be sourced from agricultural waste products and abundant algal seaweed (Priyadarshi *et al.*, 2021; Liu *et al.*, 2022b). Hence, biopolymers are a viable alternative for the construction of natural pH-sensitive based smart packaging.

However, the usage of a single biopolymer matrix base carries some inherent limitations like poor mechanical properties and hydrophilic nature of some of the biopolymers (Liu *et al.*, 2017; Jayakumar *et al.*, 2019; Kanatt, 2020; Tanwar *et al.*, 2021). The use of blended polymers is one method that has been employed to alleviate some of the limitations of individual biopolymers. For example, some scientists have proportionately incorporated biocompatible synthetic polymers such as polyvinyl alcohol (PVA) into natural biopolymers (Zeng *et al.*, 2019; Chen *et al.*, 2020; Yao *et al.*, 2022; Liu *et al.*, 2022a; Akhila *et al.*, 2023). The resultant blended films exhibited the desired attributes such improved physical and mechanical structure. Another method of improving the physico-chemical properties of biopolymer is the incorporation of nano-sized reinforcements such as nano cellulose, nanometals and nano-clay (Yu *et al.*, 2021). The incorporation of nanoparticles into biopolymers does not only improve the biopolymer's structure but also enhances its biological properties such as antibacterial and antioxidant activities (Alizadeh-sani *et al.*, 2021; Ndwandwe *et al.*, 2022; Ran *et al.*, 2022; Zheng *et al.*, 2023a).

Application of natural plant-based pH-responsive pigment and biopolymers for smart packaging

The desirable and favourable inherent properties for both natural pigments and natural biopolymers such as abundance in nature, easy preparation, non-toxicity, biodegradability and environmental friendliness have increased the appetite for their application in the food industry. Lately, researchers have focused in developing smart packaging material based on natural pH-sensitive pigments immobilised in biopolymers for food freshness monitoring in real time (Ezati & Rhim, 2020b; Ran *et al.*, 2022; Zhang *et al.*, 2023). This innovation does not only communicate the packaged food's quality status but it also has the potential to reduce food waste and food poisoning incidences. In pH-sensitive smart packaging, food freshness is determined visually through observation of packaging colour change. This eliminates the use of invasive, expensive, complex equipment, laborious and time-consuming procedures such as sensory evaluation and microbiological analysis (Ding *et al.*, 2020; Priyadarshi *et al.*, 2021; Liu *et al.*, 2022b). The recent development of visual pH-indicator smart packaging technology has enabled monitoring of food quality from production to the consumer. Table 2 highlights recent advances in the application of natural plant-based pH-responsive pigments and natural biopolymers for smart packaging technology.

Various polysaccharides and proteins have been widely used as a polymer base for the immobilisation of the pH-sensitive-pigments. Amongst the natural pigments, anthocyanins are mostly investigated as pH-sensitive indicator because of their wide colour variation in different pH environments (Echegaray *et al.*, 2023; Shi *et al.*, 2023). Anthocyanins at different concentrations (0, 10, 15, and 20 wt% based on chitosan weight) were immobilised in chitosan by Yan *et al.* (2021). The developed chitosan-anthocyanins polymer composite was used to monitor fish freshness. It was observed that the pH varied as the fish freshness deteriorated. The pH variation corresponded with colour change of the chitosan-anthocyanin composite from purple/blue to dark green when the fish was completely decayed. Other researchers incorporated anthocyanins in carboxymethyl cellulose (Sani *et al.*, 2021), locust bean gum (Fathi *et al.*, 2022b), gelatin (Mousazadeh *et al.*, 2021), and soy protein isolate (Ran *et al.*, 2022). These fabricated smart packaging materials were used to monitor real food samples and a visible colour variation was observed as the packaged food deteriorated. Betalains, another group of plant-based pH-sensitive pigments, have also been studied for their potential application as pH-responsive pigments in smart packaging for food freshness monitoring. In a study by Naghdi *et al.* (2021), *Bougainvillea glabra* was used as a source of betalains. The betalains were incorporated into potato starch to fabricate a pH indicator film for real-time monitoring of fish freshness. The film changed colour from pink to yellow, indicating the quality degradation of the monitored fish. Curcumin is another emerging natural pigment with potential application in smart packaging. Curcumin consists of pH-responsive enols and ketones with colour variation ranging from yellow in acidic pH to red with increase in pH (up to 8), while in more basic pH, its colour changes to brown (Echegaray *et al.*, 2023; Liu *et al.*, 2023). Fathi *et al.* (2022a) blended pectin and polyvinyl alcohol and then added curcumin for fish spoilage monitoring. The resultant packaging did not only exhibit improved physico-chemical properties but it also indicated the packaged fish quality. The initial colour of the film was yellow for fresh fish which changed to red for deteriorated fish quality. Alizarin presents a red colour at natural pH and at acidic pH, the red colour changes to yellow due to oxygen anions generation in its structure. An increase in pH results in creation of intramolecular hydrogen bonds between carbonyl oxygen atoms and hydroxyl groups of alizarin leading to a purple colour (Echegaray *et al.*, 2023). An alizarin-based smart film was developed by Ezati *et al.* (2019b) and it was used to indicate minced beef freshness status. As the storage time of the packaged minced beef increased the colour of the film changed from brown to purple indicating changes in the quality status of the minced beef. Shikonin, a naphthoquinone pigment is another pH-responsive natural pigment that have also been studied for potential use in smart packaging development. Ezati *et al.* (2021a, 2021b) incorporated shikonin into cellulose biopolymer at 0.1% w/v and used the developed smart film for fish and pork quality monitoring. The colour of the packaging was initially light brown, which changed to purple as the food products quality deteriorated.

Additionally, plant-based pH-sensitive pigments smart packaging with improved functionality has been achieved by incorporating antimicrobials and/or antioxidants into the biopolymer thus extending the shelf-life of the packaged food (Sani *et al.*, 2021; Abedi-Firoozjah *et al.*, 2023). These additives may include nanoparticles from inorganic and organic sources. For example, Mousazadeh *et al.* (2021) enhanced the antioxidant property of a gelatin-anthocyanins based smart packaging material by integrating zinc oxide nanoparticles. The latter nanoparticles were incorporated into soy protein-anthocyanins based packaging material resulting in an smart film with antioxidant and antimicrobial activities (Ran *et al.*, 2022). In another study, titanium dioxide nanoparticles

Table 2 Recent application of natural pH-sensitive pigment based smart packaging material

Natural pigment category	Polymer source	Pigment source	Pigment concentration	Additives	Real food application	Colour change	References
Anthocyanins	Chitosan	Butterfly pudding extract	0, 10, 15, and 20 wt% based on chitosan weight	None	Monitoring fish freshness	Purple/blue – blue – grey – blue/grey – dark green	Yan *et al.* (2021)
	Cornstarch/ polyvinyl alcohol (PVA)	Blueberry	0.3 mg/mL anthocyanins	Ovalbumin-carboxymethyl cellulose nanocomplexes	Mushroom freshness	Purple – reddish/ brown – pink	Liu *et al.* (2022a, 2022b)
	Carboxymethyl cellulose (CMC)	Red barberry	3% w/v red barberry anthocyanins	Chitin nanofiber	Fish freshness monitoring	Reddish – pale pink	Alizadeh-sani *et al.* (2021)
	Locust bean gum	*Viola odorata*	5 wt %	Graphene oxide	Monitor freshness of lamb meat	Beige – light indigo	Fathi *et al.* (2022b)
	Gelatin	Red cabbage	1:1 to gelatin	Zinc oxide nanoparticles (ZnONPs)	Not stated	Not stated	Mousazadeh *et al.* (2021)
	Sodium alginate/ chitosan	Blueberry	Not stated	Titanium oxide (TiO_2)	Pork freshness indicator	Red – blue	Cao *et al.* (2023)
	Soy protein isolate	Red grape skin	0, 2, 4, 6, and 8 wt% of soy protein isolate powder	ZnONPs	Pork freshness indicator	Green – light green – yellow – green – brown – yellow brown	Ran *et al.* (2022)
	Agar/sodium alginate	Purple sweet potato	1.5 wt% anthocyanin extract	Quercetin-loaded chitosan nanoparticles	Shrimp freshness indicator and preservation	Not stated	Dong *et al.* (2023)
	Corn starch/ chitosan	Rose	40, 60, 80 and 100 mg / 100 mL solution	Amylopectin nanoparticles	Shrimp freshness indicator	Grey – orange	Zheng *et al.* (2023a)
	Collagen/chitosan	Mulberry extract	0.5, 1.0, and 2.0% wt based on the dry weight of total polymer	ZnONPs	Pork freshness monitoring	Deep purple – lilac – blue – pale blue	Zheng *et al.* (2023b)
	Gelatin/agar	*Clitoria tematea* flower (butterfly pea)	10 wt% based on polymer	ZnONPs	Monitoring shrimp freshness	Bright pink – purple – green	Kim *et al.* (2022)
	Chitosan/gelatin	Black peanut seed coat	0, 30, 60, 90 mg/g based on the amounts of polymers	ZnONPs	Shrimp freshness indicator	Dull red – light red – light green	Lu *et al.* (2022)
	κ-carrageenan	Butterfly bean flower	20 mg/100 mL polymer solution	TiO_2NPs	Monitoring *Penaeus chinensis* freshness	Sky blue – light yellowish green	Zhang *et al.* (2023)
	Gelatin	Blueberry	1, 2, 3, 4, and 5 mg/mL	Chitosan nanoparticles	Milk freshness indicator	Red – light blue	Ma *et al.* (2020)
	Gelatin/κ-carrageenan	Saffron	3% v/v	TiO_2NPs	Monitoring fish spoilage	Violet/bluish – green	Alizadeh Sani *et al.* (2022)
	Sodium alginate/ pectin	Red cabbage	50.74 mg/100 g	Cellulose nanocrystals	Shrimp freshness monitoring	Lilac – dark green – greenish yellow	Lei *et al.* (2023)

Table 2 (*Continued*)

Natural pigment category	Polymer source	Pigment source	Pigment concentration	Additives	Real food application	Colour change	References
Betalains	Locust bean gum/PVA/agar	Red pitaya	48 mg/240 mL biopolymer solution	TiO_2NPs	Shrimp freshness indicator	Red violet – dark red – brown	Yao *et al.* (2022)
	Potato starch	Paper flower (*Bougainvillea glabra*)	5, 10, and 15 mg/g (w/w polymer powder)	None	Fish freshness monitoring	Pink – yellow	Naghdi *et al.* (2021)
Curcuminoids	Pectin	Not stated	1 wt% based on pectin	Sulphur nanoparticles (SNPs)	Shrimp packaging	Yellow – orange	Ezati & Rhim (2020b)
	Pistachio green hull pectin/poly vinyl alcohol (PVA)	Not stated	10, 30 and 50 (mg g^{-1})	None	Fish spoilage indicator	Yellow – red	Fathi *et al.* (2022a)
Shikonin	Cellulose	*Lithospermum erythrorhizon*	0.1% w/v	None	Fish and pork quality	Light brown – purple	Ezati *et al.* (2021a)
	Cellulose	*Arnebia euchroma*	Not stated	None	Monitoring freshness of shrimp and pork	Red/rose – purple – bluish violet	Dong *et al.* (2020)
	Starch/agar	*Lithospermum erythrorhizon*	Not stated	None	Shrimp freshness monitoring	Pink – pale blue	Ezati & Rhim (2021)
	CMC/cellulose nanofibers	*Lithospermum erythrorhizon* roots	1 wt% of polymer	None	Monitor fish freshness	Reddish pink – blue purple	Ezati *et al.* (2021b)
Alizarins	Starch/cellulose	Madder root	1% w/v	None	Monitor fish spoilage	Orange – bright brown – reddish brown	Ezati *et al.* (2019a)
	Cellulose/chitin	Madder root	1% w/v	None	Minced beef freshness indicator	Brown – purple	Ezati *et al.* (2019b)

were added into betalains/locust bean gum/PVA/agar hybrid film to improve its antimicrobial and antioxidant capabilities (Yao *et al*., 2022). There are various other nanoparticles that have been added into polymer and plant-based pH-sensitive composites including mesoporous silica nanoparticles (Kong *et al*., 2023), ovalbumin-carboxymethyl cellulose nanocomplexes (Liu *et al*., 2022a), Quercetin-loaded chitosan nanoparticles (Dong *et al*., 2023), Curcumin/zein/epigallocatechin gallate/carrageenan nanoparticles (Han *et al*., 2023), and amylopectin nanoparticles (Zheng *et al*., 2023b).

Effectiveness of plant-based pH-sensitive smart packaging

To further establish the effectiveness of natural pH-responsive-based smart packaging as food freshness indicators, its application potential has been verified on different real food samples. Ezati *et al*. (2019a) developed an alizarin-based starch/cellulose (ASC) film, which was further used to monitor fish freshness. The initial pH value of fish samples was recorded as 6.24 and it progressively increased with storage time up to 7 in day eight. Also, the total volatile basic nitrogen (TVB-N) was also monitored and it was recorded as 13.53 mg/100 g (fresh fish), which was below 25 mg/100 g (spoiled fish). The TVB-N value of the fish increased up to 27.26 mg/100 g on day 8 which was an indication of fish decay. During the storage period, ASC indicator exhibited an orange colour at fresh stage of fish and it was bright brown in colour at the best eat stage. Finally, the ASC indicator exhibited a reddish-brown colour confirming fish quality deterioration. In another study, anthocyanins in in three different concentrations were immobilised in a starch polymer. The fabricated anthocyanins/starch films were used to monitor pork freshness status for 48 h. The initial TVB-N of fresh pork was recorded and it was 6.56 mg/100 g which gradually increased to 41.19 mg/100 in 48 h. The increase in TVB-N corresponded to an increase in pH value from 5.96 to 7.45 after 48 h. It was observed that as the TVB-N and pH values of the pork varied, also, the colour of the starch-anthocyanins films varied from pink/red/purple to green/yellow after 48 h. It was further noted that the film without anthocyanins presented no obvious colour change while the films with anthocyanins, their colour intensity improved with increase in anthocyanins concentration incorporated, suggesting that anthocyanins-starch composite films can be used for meat freshness monitoring (Qin *et al*., 2019). Other similar studies whereby the efficiency of pH-responsive smart films was evaluated in real-food applications such as fish (Sani *et al*., 2021; Yan *et al*., 2021; Bao *et al*., 2022; Dong *et al*., 2023), pork (Cao *et al*., 2023), chicken (Ebrahimi *et al*., 2022; Wang *et al*., 2023), mushrooms (Liu *et al*., 2022b), Lamb meat (Alizadeh-sani *et al*., 2021; Fathi *et al*., 2022a) were conducted by various researchers.

Challenges and opportunities of pH-sensitive pigments

The usage of natural pH-sensitive pigments and natural biopolymers has become a promising alternative to synthetic pigments and polymers due to their eco-friendliness, less toxicity, and abundant resources. pH-sensitive pigments-based food packaging have the potential to improve safety and quality of packaged foods by communicating real-time freshness status and extending shelf-life of packaged foods. Natural pigments are appreciated and accepted by both the food industry and consumers due their properties such as increased water solubility, pH sensitivity and other numerous health-related bioactivities. However, their commercialization is still distant due to various reasons. The capacity of food freshness indicators to reliably provide accurate food freshness status is dependent on the adaptability of the polymer matrix, type of indicator pigment and preparation technique. Natural pigments interact with biopolymers differently according to the charge nature of the natural pigment and biopolymer. The molecular interactions do not only affect the physico-chemical properties of the packaging material but also the pH-sensitivity of the material fabricated. Therefore, compatibility and suitability of biopolymer matrix and the natural pigment may present challenges such as stability of pigment during use. Another downside of food packaging based on natural pigment and biopolymer freshness indicator may include the migration of packaging materials components from the packaging material into the food. Leaching of packaging components into food may result in variation of the organoleptic properties of the food and food safety and quality issues may arise and that may limit the commercial application of natural pigments as food freshness indicators. Practical strategies that can be used to improve stability of natural piments is the adoption of hydrophobic biopolymer matrices and/or construction of a double layer or blended film.

The depletion of natural supply of raw material due to increasing market demand may be another challenge that may be encountered with the use of natural pigments and natural biopolymers. Furthermore, plant pigments are dependent on weather conditions, they are available in low concentrations and their separation and purification techniques may be costly for commercial purposes. To alleviate these challenges the plant tissue culture technique can be employed. This technique shortens the plant growth cycle under controlled environmental conditions, thus increasing production and availability of raw material without compromising the natural source. More research focusing on efficient extraction and purification techniques associated to the physico-chemical properties of natural pigments is still necessary. The use of colour is subject to approval by regulatory bodies such as the Food and Drug Administration (FDA), and must be applied only in agreement with permitted applications, conditions, and restrictions. Presently, only betalains are an FDA-approved natural pigment for application in food (Nirmal *et al.*, 2021; Martins *et al.*, 2022) and the absence of approval for a wider range of natural pigments limits their application. Laws and regulations governing the use and safety standards of smart materials, and specialised technology required for development of smart packaging material, may escalate the cost of smart packaging, hence limiting their use. The stability of natural pigment is one important factor in the development of food freshness indicator packaging. Natural pigments are inherently sensitive to environmental factors such as light, oxygen, pH and temperature. Although stabilisation technologies such as encapsulation, co-pigmentation, and surface modification on biopolymer exist, they increase the cost of natural pigment production. These costs are factored in the product price which then become less competitive in the market.

Nevertheless, there is potential for the application natural pH-sensitive pigments as food freshness indicators. There is still an opportunity to investigate underutilised natural resource to extract pigments with improved stability or research cost-effective solutions that will improve their stability. There are also prospects of identifying and/or modifying natural pigment carrier biopolymers to improve their compatibility and suitability with natural pigments. Natural pigments may have antimicrobial and antioxidant attributes, however, other additives such nanomaterials may be explored to reinforce the multi-functional property of smart packaging materials. These additives may also improve performance and structural integrity of the polymeric material. Some of the natural pigments exhibits health promoting properties, advocating for their approval by regulatory bodies may enhance health benefits of the packaged food.

Conclusion

The application of natural pH-sensitive pigments in smart food packaging as food freshness indicators is an innovative technology, to deliver valuable information, which could extend shelf-life and help consumers judge the quality of packaged food by visible colour variation during storage. Natural pigments can track pH alterations associated with food deterioration by colour change which can be visually detected by consumers. Biopolymers such as starch, chitosan and cellulose have exhibited good compatibility with natural pH-sensitive pigments hence they have been used to immobile the natural pigments. Smart packaging based on natural pH-responsive pigments have demonstrated a huge potential for monitoring freshness of a variety consumed fresh food such as seafood, meat and fruits. However, there are still challenges that should be overcome for a successful adoption of natural pH-responsive pigments in smart packaging. For an example, the stability of natural pigments-based food freshness indicators should be achieved during storage and distribution. Pigments losses due to migration should be minimised and the hydrophobic nature of pigments should be enhanced. The future of smart packaging is based on biopolymers and natural pigments. There are still under researched plant pigment resource that may have improved stability and hydrophobic in nature. Other technologies such as nanotechnology can be employed to reinforce the immobility of pigments into biopolymers and simultaneously improving multifunctionality of the smart packaging material. To scale-up smart packaging technology based on natural pigments, more investigations are still required as well as development of cost-effective and technical feasible techniques.

Acknowledgments

The authors would like to acknowledge the University Research committee, University of Johannesburg, for funding this research.

Author contributions

Bongekile K. Ndwandwe: Conceptualization; writing – original draft; methodology; investigation. **Soraya P. Malinga:** Supervision; writing – review and editing. **Eugenie Kayitesi:** Writing – review and editing; supervision. **Bhekisisa C. Dlamini:** Supervision; methodology; writing – review and editing; conceptualization; funding acquisition.

Conflict of interest

The authors declare they have no conflict of interest.

Ethical approval

Ethics approval was not required for this research.

Peer review

The peer review history for this article is available at https://www.webofscience.com/api/gateway/wos/peer-review/10.1111/ijfs.16990.

Data availability statement

Data sharing is not applicable to this article as no new data were generated or analysed during this study.

References

Abedi-Firoozjah, R., Chabook, N., Rostami, O. *et al.* (2023). PVA/starch films: an updated review of their preparation, characterization, and diverse applications in the food industry. *Polymer Testing*, **118**, 107903.

Aguirre-Joya, J.A., Chacon-Garza, L.E., Valdivia-Najar, G. *et al.* (2020). Nanosystems of plant-based pigments and its relationship with oxidative stress. *Food and Chemical Toxicology*, **143**, 111433.

Akhila, K., Sultana, A., Ramakanth, D. & Gaikwad, K.K. (2023). Monitoring freshness of chicken using intelligent pH indicator packaging film composed of polyvinyl alcohol/guar gum integrated with Ipomoea coccinea extract. *Food Bioscience*, **52**, 102397.

Alizadeh Sani, M., Tavassoli, M., Salim, S.A., Azizi-lalabadi, M. & McClements, D.J. (2022). Development of green halochromic smart and active packaging materials: TiO_2 nanoparticle-and anthocyanin-loaded gelatin/κ-carrageenan films. *Food Hydrocolloids*, **124**, 107324.

Alizadeh-Sani, M., Mohammadian, E., Rhim, J. & Jafari, S.M. (2020). pH-sensitive (halochromic) smart packaging films based on natural food colorants for the monitoring of food quality and safety. *Trends in Food Science and Technology*, **105**, 93.

Alizadeh-sani, M., Tavassoli, M., Mohammadian, E. *et al.* (2021). pH-responsive color indicator fi lms based on methylcellulose/chitosan nano fiber and barberry anthocyanins for real-time monitoring of meat freshness. *International Journal of Biological Macromolecules*, **166**, 741.

Almasi, H., Forghani, S. & Moradi, M. (2022). Recent advances on intelligent food freshness indicators; an update on natural colorants and methods of preparation. *Food Packaging and Shelf Life*, **32**, 100839.

Amin, U., Khan, M.K.I., Maan, A.A. *et al.* (2022). Biodegradable active, intelligent, and smart packaging materials for food applications. *Food Packaging and Shelf Life*, **33**, 100903.

Azeredo, H.M.C. & Correa, D.S. (2021). Smart choices: mechanisms of intelligent food packaging. *Current Research in Food Science*, **4**, 932.

Azman, N.H., Khairul, W.M. & Sarbon, N.M. (2022). A comprehensive review on biocompatible film sensor containing natural extract: active/intelligent food packaging. *Food Control*, **141**, 109189.

Bao, Y., Cui, H., Tian, J. *et al.* (2022). Novel pH sensitivity and colorimetry-enhanced anthocyanin indicator films by chondroitin sulfate co-pigmentation for shrimp freshness monitoring. *Food Control*, **131**, 108441.

Becerril, R., Nerín, C. & Silva, F. (2021). Bring some colour to your package: freshness indicators based on anthocyanin extracts. *Trends in Food Science and Technology*, **111**, 495–505.

In this article freshness indicators based on anthocyanin extracts which is a natural pH-sensitive pigment was discussed. The article further elaborated on anthocyanin-based sensor packaging materials developed for smart packaging applications, highlighting the key factors that may affect the applicability of the developed smart packaging material. This article further discussed the potential application of anthocyanins-based packaging on real food. This article is relevant to this article as it demonstrates the potential of natural pH-sensitive pigments based smart packaging.

Bhargava, N., Sharanagat, V.S., Mor, R.S. & Kumar, K. (2020). Active and intelligent biodegradable packaging films using food and food waste-derived bioactive compounds: a review. *Trends in Food Science and Technology*, **105**, 385.

Bocker, R. & Silva, E.K. (2022). Pulsed electric field assisted extraction of natural food pigments and colorings from plant matrices. *Food Chemistry: X*, **15**, 100398.

Bumbudsanpharoke, N. & Ko, S. (2019). Nanomaterial-based optical indicators: promise, opportunities, and challenges in the development of colorimetric systems for intelligent packaging. *Nano Research*, **12**, 489.

Cao, S., Wang, S., Wang, Q. *et al.* (2023). Sodium alginate/chitosan-based intelligent bilayer film with antimicrobial activity for pork preservation and freshness monitoring. *Food Control*, **148**, 109615.

Charoensit, P., Sawasdipol, F., Tibkawin, N., Suphrom, N. & Khorana, N. (2021). Development of natural pigments from Tectona grandis (teak) leaves: agricultural waste material from teak plantations. *Sustainable Chemistry and Pharmacy*, **19**, 100365.

Chen, H., Zhang, M., Bhandari, B. & Yang, C. (2020). Novel pH-sensitive films containing curcumin and anthocyanins to monitor fish freshness. *Food Hydrocolloids*, **100**, 105438.

Cheng, H., Xu, H., McClements, D.J. *et al.* (2022a). Recent advances in intelligent food packaging materials: principles, preparation and applications. *Food Chemistry*, **375**, 131738.

Cheng, M., Yan, X., Cui, Y. *et al.* (2022b). An eco-friendly film of pH-responsive indicators for smart packaging. *Journal of Food Engineering*, **321**, 110943.

Choi, I., Choi, H., Lee, J. & Han, J. (2023). Novel color stability and colorimetry-enhanced intelligent CO_2 indicators by metal complexation of anthocyanins for monitoring chicken freshness. *Food Chemistry*, **404**, 134534.

Di Salvo, E., Lo Vecchio, G., De Pasquale, R. *et al.* (2023). Natural pigments production and their application in food, health and other industries. *Nutrients*, **15**, 1923.

Ding, L., Li, X., Hu, L. *et al.* (2020). A naked-eye detection polyvinyl alcohol/cellulose-based pH sensor for intelligent packaging. *Carbohydrate Polymers*, **233**, 115859.

Dong, H., Long, Z., Zhang, X., Zhang, X., Ramaswamy, S. & Xu, F. (2020). Smart colorimetric sensing films with high mechanical strength and hydrophobic properties for visual monitoring of shrimp and pork freshness. *Sensors and Actuators, B: Chemical*, **309**, 127752.

In this study, biodegradable cellulose and naphthoquinone dyes from *Arnebia euchroma* were used to develop calorimetric sensing film with high tensile strength of 227 MPa and hydrophobic properties. The fabricated film was used for real-time monitoring of the freshness of shrimp and pork by measuring the TVB-N and total viable count (TVC). On visual inspection, the film proved to be sensitive by changing colour in correlation with the variations of the monitored food spoilage parameters *viz* TVB-N and TVC. This study is relevant to this article as it demonstrated the potential of plant based pH-responsive pigments applicability as food freshness indicators.

Dong, S., Zhang, Y., Lu, D., Gao, W., Zhao, Q. & Shi, X. (2023). Multifunctional intelligent film integrated with purple sweet potato anthocyanin and quercetin-loaded chitosan nanoparticles for monitoring and maintaining freshness of shrimp. *Food Packaging and Shelf Life*, **35**, 101022.

dos Santos, M.C. & Bicas, J.L. (2021). Natural blue pigments and bikaverin. *Microbiological Research*, **244**, 126653.

Ebrahimi, V., Nafchi, A.M., Bolandi, M. & Baghaei, H. (2022). Fabrication and characterization of a pH-sensitive indicator film by purple basil leaves extract to monitor the freshness of chicken fillets. *Food Packaging and Shelf Life*, **34**, 100946.

Echegaray, N., Guzel, N., Kumar, M., Guzel, M., Hassoun, A. & Lorenzo, J.M. (2023). Recent advancements in natural colorants and their application as coloring in food and in intelligent food packaging. *Food Chemistry*, **404**, 134453.

Ezati, P., Bang, Y.J. & Rhim, J.W. (2021b). Preparation of a shikonin-based pH-sensitive color indicator for monitoring the freshness of fish and pork. *Food Chemistry*, **337**, 127995.

Ezati, P., Priyadarshi, R., Bang, Y. & Rhim, J.W. (2021a). CMC and CNF-based intelligent pH-responsive color indicator films integrated with shikonin to monitor fish freshness. *Food Control*, **126**, 108046.

Ezati, P. & Rhim, J.W. (2020a). pH-responsive chitosan-based film incorporated with alizarin for intelligent packaging applications. *Food Hydrocolloids*, **102**, 105629.

Ezati, P. & Rhim, J.W. (2020b). pH-responsive pectin-based multifunctional films incorporated with curcumin and sulfur nanoparticles. *Carbohydrate Polymers*, **230**, 115638.

Ezati, P. & Rhim, J.-W. (2021). Starch and agar-based color-indicator films integrated with Shikonin for smart packaging application of shrimp. *ACS Food Science & Technology*, **1**, 1963.

Ezati, P., Tajik, H. & Moradi, M. (2019b). Chemical fabrication and characterization of alizarin colorimetric indicator based on cellulose-chitosan to monitor the freshness of minced beef. *Sensors and Actuators B: Chemical*, **285**, 519–528.

Ezati, P., Tajik, H., Moradi, M. & Molaei, R. (2019a). Intelligent pH-sensitive indicator based on starch-cellulose and alizarin dye to track freshness of rainbow trout fillet. *International Journal of Biological Macromolecules*, **132**, 157–165.

Fathi, M., Babaei, A. & Rostami, H. (2022b). Development and characterization of locust bean gum-Viola anthocyanin-graphene oxide ternary nanocomposite as an efficient pH indicator for food packaging application. *Food Packaging and Shelf Life*, **34**, 100934.

Fathi, M., Rostami, H., Miri, N.Y., Samadi, M. & Delkhosh, M. (2022a). Development of an intelligent packaging by incorporating curcumin into pistachio green hull pectin/poly vinyl alcohol (PVA) film. *Journal of Food Measurement and Characterization*, **16**, 2468–2477.

Ghaani, M., Cozzolino, C.A., Castelli, G. & Farris, S. (2016). An overview of the intelligent packaging technologies in the food sector. *Trends in Food Science and Technology*, **51**, 1–11.

Ghorbani, M., Divsalar, E., Molaei, R. *et al.* (2021). A halochromic indicator based on polylactic acid and anthocyanins for visual freshness monitoring of minced meat, chicken fillet, shrimp, and fish roe. *Innovative Food Science and Emerging Technologies*, **74**, 102864.

Ghosh, S., Sarkar, S., Das, A. & Chakraborty, R. (2022). Natural colorants from plant pigments and their encapsulation: an emerging window for the food industry. *LWT – Food Science and Technology*, **153**, 112527.

Ghosh, S., Sarkar, T. & Chakraborty, R. (2023). Underutilized plant sources: a hidden treasure of natural colors. *Food Bioscience*, **52**, 102361.

Gürler, N. (2023). Development of chitosan/gelatin/starch composite edible films incorporated with pineapple peel extract and aloe vera gel: mechanical, physical, antibacterial, antioxidant, and sensorial analysis. *Polymer Engineering and Science*, **63**, 426.

Gürler, N., Pasa, S., Erdogan, O. & Cevik, O. (2023). Physicochemical properties for food packaging and toxicity behaviors against healthy cells of environmentally friendly biocompatible starch/citric acid/polyvinyl alcohol biocomposite films. *Starch/Staerke*, **75**, 1.

Hamidin, N.A.S., Abdullah, S., Nor, F.H.M. & Hadibarata, T. (2022). Isolation and identification of natural green and yellow pigments from pineapple pulp and peel. *Materials Today Proceedings*, **63**, S406.

In this work, green and yellow pigments were isolated from pineapple pulp and peels. The isolated pigments were evaluated for phytochemicals and antimicrobial activity and it was found to contain phytochemicals which may act as antimicrobial agents. This work is relevant to this article as demonstrated that natural pigments cannot only act as food freshness indicators but can also act as antimicrobial agents which may play a role in the shelf-life extension of the packaged food.

Han, Y., Zhou, M., McClements, D.J. *et al.* (2023). Investigation of a novel smart and active packaging materials: nanoparticle-filled carrageenan-based composite films. *Carbohydrate Polymers*, **301**, 120331.

Huang, J., Hu, Z., Li, G., Hu, L., Chen, J. & Hu, Y. (2022). Make your packaging colorful and multifunctional: the molecular interaction and properties characterization of natural colorant-based films and their applications in food industry. *Trends in Food Science & Technology*, **124**, 259.

Hwa, J., Kang, H.J., Adedeji, O.E. *et al.* (2023). Development of a pH indicator for monitoring the freshness of minced pork using a cellulose nanofiber. *Food Chemistry*, **403**, 134366.

Jayakumar, A., Hera, K.V., Sumi, T.S. *et al.* (2019). Starch-PVA composite films with zinc-oxide nanoparticles and phytochemicals as intelligent pH sensing wraps for food packaging application. *International Journal of Biological Macromolecules*, **136**, 395.

Kanatt, S.R. (2020). Development of active/intelligent food packaging fi lm containing Amaranthus leaf extract for shelf life extension of chicken/fish during chilled storage. *Food Packaging and Shelf Life*, **24**, 100506.

Kim, H.J., Roy, S. & Rhim, J.-W. (2022). Gelatin/agar-based color-indicator film integrated with Clitoria ternatea flower anthocyanin and zinc oxide nanoparticles for monitoring freshness of shrimp. *Food Hydrocolloids*, **124**, 107294.

Kong, J., Ge, X., Sun, Y. *et al.* (2023). Multi-functional pH-sensitive active and intelligent packaging based on highly cross-linked zein for the monitoring of pork freshness. *Food Chemistry*, **404**, 134754.

Lan, T., Qian, S., Song, T., Zhang, H. & Liu, J. (2023). The chromogenic mechanism of natural pigments and the methods and techniques to improve their stability: a systematic review. *Food Chemistry*, **407**, 134875.

Latos-Brozio, M. & Masek, A. (2020). The application of natural food colorants as indicator substances in intelligent biodegradable packaging materials. *Food and Chemical Toxicology*, **135**, 110975.

Lei, Y., Yao, Q., Jin, Z. & Wang, Y.C. (2023). Intelligent films based on pectin, sodium alginate cellulose nanocrystals, and anthocyanins for monitoring food freshness. *Food Chemistry*, **404**, 134528.

Li, N., Zhou, S., Yang, X. & Lin, D. (2022a). Applications of natural polysaccharide-based pH-sensitive films in food packaging: current research and future trends. *Innovative Food Science and Emerging Technologies*, **82**, 103200.

Li, S., Mu, B., Wang, X. & Wang, A. (2021). Recent researches on natural pigments stabilized by clay minerals: a review. *Dyes and Pigments*, **190**, 109322.

Li, Y., Tang, X. & Zhu, L. (2022b). Bilayer pH-sensitive colorimetric indicator films based on zein/gellan gum containing black rice (*Oryza sativa L.*) extracts for monitoring of largemouth bass (*Micropterus salmoides*) fillets freshness. *International Journal of Biological Macromolecules*, **223**, 1268.

Lian, W., Fan, M., Li, T. *et al.* (2019). A novel green synthesis approach for natural bluish-violet pigments derived from water extracts of *Vaccinium bracteatum Thunb*. leaves. *Industrial Crops and Products*, **142**, 111862.

Liu, B., Xu, H., Zhao, H., Liu, W., Zhao, L. & Li, Y. (2017). Preparation and characterization of intelligent starch/PVA films for simultaneous colorimetric indication and antimicrobial activity for food packaging applications. *Carbohydrate Polymers*, **157**, 842.

Liu, D., Zhang, C., Pu, Y. *et al.* (2022a). Recent advances in pH-responsive freshness indicators using natural food colorants to monitor food freshness. *Foods*, **11**, 1884.

Liu, L., Wu, W., Zheng, L., Yu, J., Sun, P. & Shao, P. (2022b). Intelligent packaging films incorporated with anthocyanins-loaded ovalbumin-carboxymethyl cellulose nanocomplexes for food freshness monitoring. *Food Chemistry*, **387**, 132908.

Liu, Y., Ma, M. & Yuan, Y. (2023). The potential of curcumin-based co-delivery systems for applications in the food industry: food preservation, freshness monitoring, and functional food. *Food Research International*, **171**, 113070.

Lu, M., Zhou, Q., Yu, H., Chen, X. & Yuan, G. (2022). Colorimetric indicator based on chitosan/gelatin with nano-ZnO and black peanut seed coat anthocyanins for application in intelligent packaging. *Food Research International*, **160**, 111664.

Ma, Y., Li, S., Ji, T. *et al.* (2020). Development and optimization of dynamic gelatin/chitosan nanoparticles incorporated with blueberry anthocyanins for milk freshness monitoring. *Carbohydrate Polymers*, **247**, 116738.

Martins, V.G., Santos, L.G., Romani, V.P. *et al.* (2022). Bio-based sensing: role of natural dyes in food freshness indicators. In: *Bio- and Nano-sensing Technologies for Food Processing and Packaging* (edited by A.K. Shuklar). Pp. 37. London: The Royal Society of Chemistry.

Mousazadeh, S., Ehsani, A., Kia, E.M. & Ghasempour, Z. (2021). Zinc oxide nanoparticles and periodate oxidation in developing pH-sensitive packaging film based on modified gelatin. *Food Packaging and Shelf Life*, **28**, 100654.

Nabi, B.G., Mukhtar, K., Ahmed, W. *et al.* (2023). Natural pigments: anthocyanins, carotenoids, chlorophylls, and betalains as colorants in food products. *Food Bioscience*, **52**, 102403.

Naghdi, S., Rezaei, M. & Abdollahi, M. (2021). A starch-based pH-sensing and ammonia detector film containing betacyanin of paper-flower for application in intelligent packaging of fish. *International Journal of Biological Macromolecules*, **191**, 161.

Ndwandwe, B.K., Malinga, S.P., Kayitesi, E. & Dlamini, B.C. (2022). Selenium nanoparticles – enhanced potato starch film for active food packaging application. *International Journal of Food Science and Technology*, **57**, 6512–6521.

Nirmal, N.P., Mereddy, R. & Maqsood, S. (2021). Recent developments in emerging technologies for beetroot pigment extraction and its food applications. *Food Chemistry*, **356**, 129611.

Oun, A.A., Roy, S., Shin, G.H., Yoo, S. & Kim, J.T. (2023). pH-sensitive smart indicators based on cellulose and different natural pigments for tracing kimchi ripening stages. *International Journal of Biological Macromolecules*, **242**, 124905.

Pandiselvam, R., Mitharwal, S., Rani, P. *et al.* (2023). The influence of non-thermal technologies on color pigments of food materials: an updated review. *Current Research in Food Science*, **6**, 100529.

Parlak, M., Sahim, O.I., Dundar, A.N. *et al.* (2024). Natural colorant incorporated biopolymers-based pH-sensing films for indicating the food product quality and safety. *Food Chemistry*, **439**, 138160.

Poudel, R., Dutta, N. & Karak, N. (2023). A mechanically robust biodegradable bioplastic of citric acid modified plasticized yam starch with anthocyanin as a fish spoilage auto-detecting smart film. *International Journal of Biological Macromolecules*, **242**, 125020.

Priyadarshi, R., Ezati, P. & Rhim, J.W. (2021). Recent advances in intelligent food packaging applications using natural food colorants. *ACS Food Science & Technology*, **1**, 124.

Qin, Y., Liu, Y., Yong, H., Liu, J., Zhang, X. & Liu, J. (2019). Preparation and characterization of active and intelligent packaging films based on cassava starch and anthocyanins from *Lycium ruthenicum Mur*r. *International Journal of Biological Macromolecules*, **134**, 80.

In this study anthocyanins were extracted from *Lycium ruthenicum Murr* and incoporated into cassava starch. The effect of anthocyanins content on the physical,structural, antioxidant and pH-sensitivity properties of starch-annthocyanins films were investigated. The inclusion of anthocyanins on the starch polymer improved the physico-chemical properties of the starch-polymer composite. The composite films further exhibited remarkable colour variation with quality changed of packaged pork. This work is relevent to this current study because it highlighted compability of natural pigments with biopolymers and also the potential application of plant-based pH-sensitive pigments as real food freshness monitor.

Ran, R., Chen, S., Su, Y. *et al.* (2022). Preparation of pH-colorimetric films based on soy protein isolate/ZnO nanoparticles and grape-skin red for monitoring pork freshness. *Food Control*, **137**, 108958.

Ran, R., Wang, L., Su, Y. *et al.* (2021). Preparation of pH-indicator films based on soy protein isolate/bromothymol blue and methyl red for monitoring fresh-cut apple freshness. *Journal of Food Science*, **86**, 4594.

Renita, A.A., Gajaria, T.K., Sathish, S. *et al.* (2023). Progress and prospective of the industrial development and applications of eco-friendly colorants: an insight into environmental impact and sustainability issues. *Foods*, **12**, 1521.

Rodríguez-Mena, A., Ochoa-Martinez, L.A., Gonzalez-Herrera, S.M., Rutiaga-Quiñones, O.M., González-Laredo, R.F. & Olmedilla-Alonso, B. (2023). Natural pigments of plant origin: classification, extraction and application in foods. *Food Chemistry*, **398**, 133908.

Roy, S. & Rhim, J.W. (2021). Anthocyanin food colorant and its application in pH-responsive color change indicator films. *Critical Reviews in Food Science and Nutrition*, **61**, 2297.

Sani, M.A., Tavassoli, M., Hamishehkar, H. & McClements, D.J. (2021). Carbohydrate-based films containing pH-sensitive red barberry anthocyanins: application as biodegradable smart food packaging materials. *Carbohydrate Polymers*, **255**, 117488.

Schumann, B. & Schmid, M. (2018). Packaging concepts for fresh and processed meat – recent progresses. *Innovative Food Science and Emerging Technologies*, **47**, 88.

Shao, P., Liu, L., Yu, J. *et al.* (2021). An overview of intelligent freshness indicator packaging for food quality and safety monitoring. *Trends in Food Science and Technology*, **118**, 285.

Sharifi, K.A. & Pirsa, S. (2021). Biodegradable film of black mulberry pulp pectin/chlorophyll of black mulberry leaf encapsulated with carboxymethylcellulose/silica nanoparticles: investigation of physicochemical and antimicrobial properties. *Materials Chemistry and Physics*, **267**, 124580.

Shen, N., Ren, J., Liu, Y. *et al.* (2023). Natural edible pigments: a comprehensive review of resource, chemical classification, biosynthesis pathway, separated methods and application. *Food Chemistry*, **403**, 134422.

Shi, S., Xu, X., Feng, J., Ren, Y., Bai, X. & Xia, X. (2023). Preparation of NH_3- and H_2S-sensitive intelligent pH indicator film from sodium alginate/black soybean seed coat anthocyanins and its use in monitoring meat freshness. *Food Packaging and Shelf Life*, **35**, 100994.

Singh, T., Pandey, V.K., Dash, K.K., Zanwar, S. & Singh, R. (2023). Natural bio-colorant and pigments: sources and applications in food processing. *Journal of Agriculture and Food Research*, **12**, 100628.

Sobhan, A., Muthukumarappan, K. & Wei, L. (2021). Biosensors and biopolymer-based nanocomposites for smart food packaging: challenges and opportunities. *Food Packaging and Shelf Life*, **30**, 100745.

Soltani, M., Mohi-alden, K. & Omid, M. (2021). A critical review on intelligent and active packaging in the food industry: research and development. *Food Research International*, **141**, 110113.

Szadkowski, B., Rogowski, J., Maniukiewicz, W., Beyou, E. & Marzec, A. (2022). New natural organic–inorganic pH indicators: synthesis and characterization of pro-ecological hybrid pigments based on anthraquinone dyes and mineral supports. *Journal of Industrial and Engineering Chemistry*, **105**, 446.

Tanwar, R., Gupta, V., Kumar, P., Kumar, A., Singh, S. & Gaikwad, K.K. (2021). Development and characterization of PVA-starch incorporated with coconut shell extract and sepiolite clay as an antioxidant film for active food packaging applications. *International Journal of Biological Macromolecules*, **185**, 451.

Wang, L., Yang, C., Deng, X. *et al.* (2023). A pH-sensitive intelligent packaging film harnessing *Dioscorea zingiberensis* starch and anthocyanin for meat freshness monitoring. *International Journal of Biological Macromolecules*, **245**, 125485.

Wang, Q., Jiang, Y., Chen, W. *et al.* (2022). Development of pH-responsive active film materials based on purple corncob and its application in meat freshness monitoring. *Food Research International*, **161**, 111832.

Wu, Z.Y., Zhang, F., Kuang, Z., Fang, F. & Song, Y.Y. (2022). Fast and sensitive colorimetric detection of pigments from beverages by gradient zone electrophoresis on a paper based analytical device. *Microchemical Journal*, **179**, 107499.

Xu, H., Chen, L., McClements, D.J. *et al*. (2022). Progress in the development of photoactivated materials for smart and active food packaging: photoluminescence and photocatalysis approaches. *Chemical Engineering Journal*, **432**, 134301.

Yan, J., Cui, R., Qi, Y., Li, L. & Yuan, M. (2021). A pH indicator film based on chitosan and butter fly pudding extract for monitoring fish freshness. *International Journal of Biological Macromolecules*, **177**, 328.

Yao, X., Yun, D., Xu, F., Chen, D. & Liu, J. (2022). Development of shrimp freshness indicating films by immobilizing red pitaya betacyanins and titanium dioxide nanoparticles in polysaccharide-based double-layer matrix. *Food Packaging and Shelf Life*, **33**, 100871.

Ye, K.X., Fan, T., Keen, L.J. & Han, B.N. (2019). A review of pigments derived from marine natural products. *Israel Journal of Chemistry*, **59**, 327.

Yu, D., Cheng, S., Li, Y., Su, W. & Tan, M. (2023). Recent advances on natural colorants-based intelligent colorimetric food freshness indicators: fabrication, multifunctional applications and optimization strategies. *Critical Reviews in Food Science and Nutrition*, 1–25.

Yu, F., Fei, X., He, Y. & Li, H. (2021). Poly (lactic acid)-based composite film reinforced with acetylated cellulose nanocrystals and ZnO nanoparticles for active food packaging. *International Journal of Biological Macromolecules*, **186**, 770.

Zeng, P., Chen, X., Qin, Y. *et al*. (2019). Preparation and characterization of a novel colorimetric indicator film based on gelatin/polyvinyl alcohol incorporating mulberry anthocyanin extracts for monitoring fish freshness. *Food Research International*, **126**, 108604.

Zhang, J., Zhang, J., Huang, X. *et al*. (2023). A visual bi-layer sensor based on agar/TiO_2/butterfly bean flower anthocyanin/κ-carrageenan with photostability for monitoring Penaeus chinensis freshness. *International Journal of Biological Macromolecules*, **235**, 123706.

Zhang, X., Zhao, Y., Shi, Q. *et al*. (2021). Development and characterization of active and pH-sensitive films based on psyllium seed gum incorporated with free and microencapsulated mulberry pomace extracts. *Food Chemistry*, **352**, 129333.

Zhao, L., Liu, Y., Zhao, L. & Wang, Y. (2022). Anthocyanin-based pH-sensitive smart packaging films for monitoring food freshness. *Journal of Agriculture and Food Research*, **9**, 100340.

Zheng, L., Liu, L., Yu, J., Farag, M.A. & Shao, P. (2023a). Intelligent starch/chitosan-based film incorporated by anthocyanin-encapsulated amylopectin nanoparticles with high stability for food freshness monitoring. *Food Control*, **151**, 109798.

Zheng, L., Liu, L., Yu, J. & Shao, P. (2022). Novel trends and applications of natural pH-responsive indicator film in food packaging for improved quality monitoring. *Food Control*, **134**, 108769.

Zheng, T., Tang, P. & Li, G. (2023b). Development of a pH-sensitive film based on collagen/chitosan/ ZnO nanoparticles and mulberry extract for pork freshness monitoring. *Food Chemistry*, **402**, 134428.

Zielinski, A.A.F., Sanchez-Camargo, A., Benvenutti, L., Ferro, D.M., Dias, J.L. & Salvador Ferreira, S.R. (2021). High-pressure fluid technologies: recent approaches to the production of natural pigments for food and pharmaceutical applications. *Trends in Food Science and Technology*, **118**, 850.