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Recent Advances in Intelligent Food Packaging Applications Using Natural Food Colorants

Ruchir Priyadarshi, Parya Ezati, and Jong-Whan Rhim*

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ABSTRACT: This review covers the latest research done in biopolymer-based pH-responsive color indicators integrated with natural colorants for real-time monitoring of packaged food quality. The pH-dependent color change of various natural food colorants and the structural change of colorants at different pH values were described. Recent developments in the fabrication of pH-responsive color indicator films prepared by immobilizing natural food colorants obtained from various plant sources into different biopolymer substrates are discussed. Their applications on different food types, including meat, seafood, and dairy products, have been reviewed. They show clear and noticeable color changes with variation in the pH of the food that indicates the degree of deterioration over time. Subsequently, besides the problems faced by natural food color-based indicators, the discussion of commercial pH indicators has also been highlighted.

KEYWORDS: *intelligent packaging, biopolymers, natural colorant, pH-responsive, halochromic indicator, food freshness monitoring*

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1. INTRODUCTION

Packaging is one of the essential food production processes and plays an important role in ensuring food quality and safety. It protects food from the external environment and prevents breakage or leakage, facilitating distribution and marketing and reducing economic losses. The packaging also has a communication function that provides details such as date of manufacture, shelf life, nutritional facts, and method of use and storage. The recent increase in consumers' preference for high-quality fresh food, lifestyle changes, and marketing competition presents challenges to producing delicious, fresh, ready-to-eat foods with guaranteed safety and quality and increasing demand for new developments in packaging technologies.[1] Nevertheless, the lack of desirable food protection to the external environment and the want of food safety and quality monitoring and food freshness labeling have been limiting factors for traditional food packaging technology. The continuously evolving food market requires the design and development of various new packaging technologies to maintain food quality, overall food safety, and organoleptic characteristics and calls for the ability to monitor the quality of packaged foods easily. Intelligent or smart packaging methods are typically used to attach or incorporate labels or tags to indicate or identify changes in packaged food quality. According to the European Food Safety Authority (EFSA), intelligent materials are "materials or articles which monitor the condition of the packaged food or the environment surrounding the food".[2] Intelligent packaging refers to a type of packaging that can monitor the condition of the packaged food or the environment inside the packaging such as temperature, pH, moisture level, gaseous composition, and spoilage metabolites, to provide information about chemical, biochemical, physical, and microbiological quality to the consumers. It is an extension of traditional packaging responsible for communication with consumers based on their ability to detect and record changes occurring in food or the packaging environment.[3] Another advantage of intelligent packaging is that it contributes to improving Hazard Analysis and Critical Control Points (HACCP) and Quality Analysis and Critical Control Points (QACCP) systems.[4] Thus, it can detect food quality changes in real-time on-site, identify potential health risks, and reduce their occurrence, ultimately maintaining food quality and ensuring food safety. In addition to increasing food quality and safety, intelligent packaging is expected to play an important role in reducing food waste. It is estimated that the European Union alone generates about 88 million tons of household food waste each year.[5,6] On the other hand, nearly 10% of the food wasted is related to shelf-life dating.[6] Currently, most processed foods typically use a "Best before" or "Use by" date system. However, since these dates are based on past experience and assumptions, many food products are often discarded even if they are still suitable for consumption.[7,8] In addition to household food waste, a large amount of food is wasted under the current management system, where the entire product lot is disposed of based on sampling test results of some products in the lot according to standard quality control protocols.[7] Intelligent packaging, especially intelligent packaging based on visual color change indicator materials, can play an essential role in solving these problems

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and reducing food waste. Application of the color-changing indicator labels can change the trend of assigning a static "best before" or "use by" date to the products and bring in the "Dynamic Shelf Life" concept, even among products of the same lot.[7,8] This promising potential of intelligent packaging increases the economic impact. The intelligent packaging market is valued at $17.5 billion in 2019 and is expected to reach $251.6 billion by 2025, with an average annual growth rate of 6.78% during this period.[9] During this forecast period, Asia Pacific is expected to record the highest compound annual growth rate (CAGR), so it is expected to be the fastest-growing region for the development and utilization of smart packaging.[10]

Intelligent systems can be classified into sensors, indicators, and radio frequency identification (RFID) systems.[11] Among them, the pH-responsive color-changing materials belong to the indicator category. An indicator is a substance that can provide a characteristic optical change, such as a color change, for determining the presence or concentration of another substance or a reaction between two or more substances, which provides qualitative or semi-quantitative information about a food product.[1] The pH-responsive freshness indicators provide information on product quality by identifying chemical changes caused by microbial growth.[12] In the past decade, the development and production of pH-responsive color-changing indicators have gradually expanded. These pH-responsive color-changing indicators are non-invasive and non-destructive and offer the advantage of inexpensive ingredients and fast reaction. The important thing is that the pH indicators have a relatively simple working principle, i.e., they react with the metabolites produced by food spoilage and change color, which can be determined visually. There is no need for sophisticated tools such as handheld electronic detectors that pass data to computer systems to process and obtain understandable information about food quality, such as those required by RFID systems.[10] Almost all of the indicators commonly used now consist of synthetic dyes such as bromothymol blue, bromocresol green, bromocresol purple, methyl red, cresol red, chlorophenol, and xylenol.[13] However, these synthetic dyes have long been known to be toxic and carcinogenic to human health, so they are not suitable for food applications.[13] Therefore, scientists are continually looking for natural alternatives to synthetic dyes, and plant-based natural pigments have been proposed as the best option so far.

In the past decade, there has been a surge in research into natural pigments such as anthocyanins, curcumin, shikonin, alizarin, betalain, and more.[13,14] Among these pigments, red-violet anthocyanins are the richest and most widely studied pigments for their ability to change color due to pH changes.[13] Anthocyanins are obtained from various parts of several plant species, including leaves, stems, rhizomes, roots, fruits, flowers, and seeds.[13] Curcumin is a yellow pigment commonly found in the rhizomes of the species *Curcuma* longa.[15] Alizarin and shikonin are red pigments obtained from the roots of plants belonging to the families *Madder* and *Boraginaceae*, respectively.[16,17] Likewise, as the name suggests, reddish-purple betalains are obtained from the root tubers and leaf stalks of *Beta vulgaris* or red beet.[18] Betalains have also been found in some less commonly used plant sources such as inflorescences of *Amaranthus caudatus* and cactus fruits of *Opuntia* and *Hylocereus* genera.[18,19] Most of the natural pigments are generally found in plant organs suitable for direct human consumption. However, they can also be procured from agro-waste and waste produced by the food processing industries, such as leaves, husk, and peels of fruits and vegetables.[14,20] Thus, various natural pigments obtained from plant sources provide a possible green alternative to synthetic dyes for intelligent food packaging applications.

This review covers the use of natural plant pigments that show color changes in response to pH. The basic chemistry of pH-responsive color change for various natural pigments and the color change behavior of pigments within different biopolymer matrices are discussed. In addition, in light of recent research, we also discuss the issue of using color indicators in intelligent packaging applications. This review covers the description of the intelligent halochromic indicators based on natural colorants, their advantages and limitations, the perspectives, and challenges of updating food applications.

2. OVERVIEW OF PH INDICATORS

pH, along with changes in packaged foods' external and internal properties, is one of the vital signs of food spoilage. Its value is related to microbial activity, endogenous enzymes, and protein decomposition, which depend on the type of food (meat, fish, milk, poultry, etc.) and storage conditions. Metabolites released by microbial growth (i.e., organic acids, amines, hydrogen chloride, sulfur compounds, carbon dioxide, etc.) change the pH of the food or the environment around the food, as illustrated in Figure 1. These changes can be considered signs of food spoilage and can be detected with visual indicators.

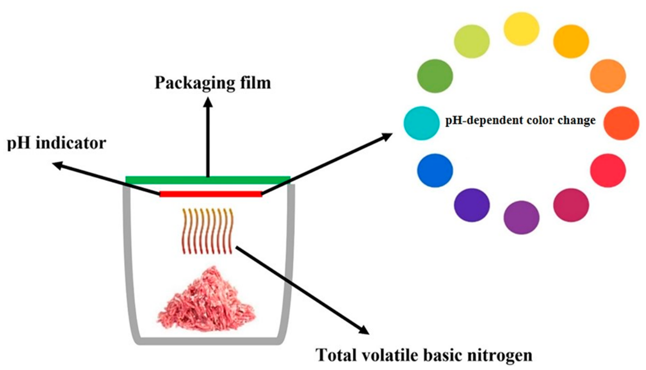

Figure 1. Illustration of color changes in the indicator films in response to variation in the food pH due to the production of volatile compounds.

In this regard, a package containing a pH indicator provides visual information on the freshness of a product to consumers by detecting and recording changes in pH value according to quality changes. Typically, the pH indicators are primarily composed of pH-sensitive dyes and solid supports that act as an entrapment matrix and immobilize dye molecules.[21] In general, three primary methods are proposed for the preparation of indicators. First, the physical adsorption: dye immobilized on solid support based on ion exchange. Second, the covalent binding procedure: dye attached to a hydrophilic matrix, for example, glass or cellulose. Third, the physical entrapment: dye trapped in polymer-based support.[22] Besides, Hasan et al. and Rotariu et al. prepared electrochemical potentiometer biosensors to control the pH of an electrolyte solution and detect the presence of the ion in food and beverages.[23,24] It is well known that the performance of pH indicators in terms of sensitivity, reversibility, stability, and

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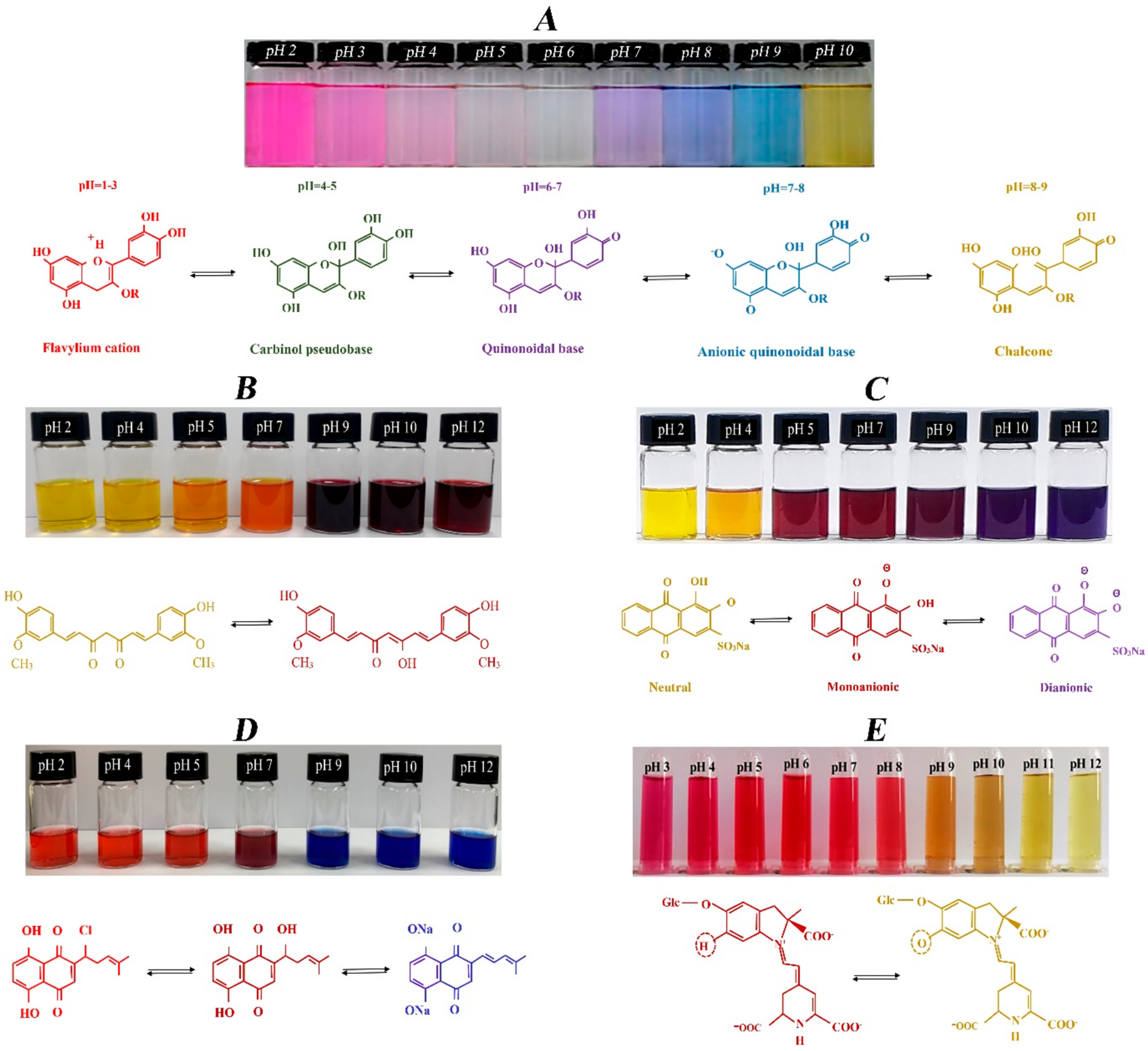

Figure 2. Color changes in response to pH variation of (A) anthocyanin, (B) curcumin, (C) alizarin, (D) shikonin, and (E) betalains.

response time depends on the type of dye, solid support, and immobilization procedure. Total volatile basic nitrogen (TVB-N), consisting of ammonia, trimethylamine, and dimethylamine, is a mixture of major alkaline compounds resulting from protein breakdown by putrefactive bacteria and is commonly used as an analyte detected by an indicator to evaluate the quality of meat products and seafood.[25−27] These compounds can increase the pH of the food samples.[28] On the other hand, the production of ethanol or organic acids from glucose fermentation can lower the pH of food samples. In addition, carbon dioxide (CO_2) gas is another end product of a microbial activity that lowers the pH of food by contributing to hydronium ion production. In other words, different bacterial populations release metabolites such as lactic acid, acetic acid, ammonia, carbon dioxide, etc., which react with indicators integrated inside the food package to reveal visual information through color change.[29] Usually, pH indicators act as chemical detectors and indicate specific odor components in the air, such as alkaline gases or CO_2. Meanwhile, it reacts to hydrogen ions (H^+) or hydronium ions (H_3O^+) in solution. The mechanism of the color change of pH-sensitive dye is due to the resonance effect caused by either acidic or alkaline compounds. The acidic compounds lead to the delocalization of the negative charge on hydroxyl groups, while the alkaline compounds result in their deprotonation.[30]

Indicator labels generally consist of two main components: one is a dye that exhibits a pH-responsive color change, and the other is a solid substrate that immobilizes the dye molecules. Various synthetic dyes and natural colorants have recently been immobilized on various solid substrates to develop pH-sensitive indicators.[25,27,31,32] These two components of the pH-responsive indicators have been discussed in detail in other sections.

An essential part of the pH indicator is the halochromic dye. The halochromism, or the pH-responsive color change in different natural colorants, is shown in Figure 2. The dye is chosen based on its ability to meet fundamental requirements such as establishing intense interaction with analytes and the resulting color change. The main thing is that the color change of the indicator must be reliable and reproducible.[33] For the preparation of pH indicators, pH-sensitive dyes are divided into two main groups: synthetic dyes and natural colorants.

2.1. Synthetic Dyes. A variety of synthetic pH-sensitive dyes showing red (methyl, chlorophenol, phenol, cresol), blue (xylenol, thymol, bromothymol), purple (m-cresol purple, bromocresol purple), yellow/orange (dimethyl, methyl), and

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green (bromocresol) colors have been used.[34,35] Acid−base indicators to detect pH changes were developed using methyl orange, neutral red, and bromocresol green. The developed indicators were tested in contact with gases, semisolids, and liquids at pH 2, 6, and 11. The indicator could reversibly change color at different pH values.[35] For the intelligent packaging of cooked crabs, a pH-sensitive chromophore based on azo-anthraquinone on cellulose fiber felt was developed.[36] The indicator displayed purple and red color when exposed to alkaline and acidic environments, respectively. It was able to show sensitive, real-time, and visible color changes from red to green at pH 1-4 and from green to purple at pH 5−12. The indicator also showed an immediate and rapid color change visually detectable from green to dark purple with the naked eye 1.5 h after the cooked crabs began to deteriorate, and turned black after 4 h when the food sample has completely deteriorated. They concluded that color indicators could monitor the quality of food products in real-time and enhance packaging appearance. In another study, Kuswandi et al. developed a dual-sensor label embedded in the package to check beef freshness.[37] Since a single sensor has limitations in real-time deterioration detection; they used bromocresol purple and methyl red as pH indicators for the dual sensor preparation to overcome this drawback. As meat deterioration occurred, the pH indicators exhibited the spoilage onset at pH 6.23 through a color change from red to yellow and from yellow to purple, for methyl red and bromocresol purple, respectively, at room and chilling temperatures. For the manufacture of color indicators, synthetic dyes have been favorably used in pH-sensitive indicators due to their advantages such as low cost, stability, versatility, and intensity. However, apparent negative effects such as biological and environmental incompatibility and the carcinogenic and toxic effects of synthetic dyes have changed legal and consumer trends, which are shifted toward the use of natural colorants.[38] The promising prospects of natural colorants such as nontoxicity, reproducibility, environmental friendliness, and sufficient availability have prompted researchers to use them as pH-responsive color-changing dyes.[39]

2.2. Natural Colorants. *2.2.1. Anthocyanins.* Anthocyanins are water-soluble food colorants and additives responsible for the red or purple color of various fruits, vegetables, and flowers.[40] These pigments are among the most widely studied natural colorants in the food industry due to their ability to change color depending on pH variations over a wide pH range. Chemically, anthocyanins belong to a family of polyphenol-based flavonoids composed of glycosylated polyhydroxy and polymethoxy structures having two aromatic rings connected by a linear three-carbon chain. Anthocyanins are composed of aglycone anthocyanidins, namely 2-phenyl benzopyrylium cation or flavylium 3-glucosides. The color change properties of anthocyanins as a function of pH depend on structural modifications resulting from the amphoteric nature of anthocyanins.[41] At low pH, anthocyanins exist as flavylium cations, which exhibit the most intense red color. At pH 4−5, the flavylium cation's rapid hydration generates colorless species of carbinol pseudobase and chalone, as a result of which the red color intensity decreases. The quinoidal anhydrobase is formed due to further deprotonation of the flavylium cation, which exhibits a purple hue at pH 7, followed by deep blue ionized anhydrobase at pH 8. With further increase in pH, substituent groups of anthocyanins are degraded, resulting in the formation of light yellow chalcone through the central ring fission of the anhydrobase.[42] The color and stability of anthocyanins are greatly affected by various factors such as pH, light, temperature, metal ions, enzymes, antioxidants, oxygen, hydroxyl or methoxyl groups, UV radiation, and copigmentation. Investigations about the color stability of anthocyanins at various pH values showed that the formation of flavylium cation at low pH makes anthocyanins highly soluble in water. Therefore, these compounds are more stable in acidic conditions. On the other hand, anthocyanins break down and become unstable under alkaline conditions with more pronounced color changes.[43] The halochromism of anthocyanins is shown in Figure 2(A).

2.2.2. Curcumin. Curcumin is a bioactive natural compound derived from turmeric (*Curcuma longa*) rhizomes. Turmeric contains four curcuminoid derivatives—curcumin, demethoxycurcumin, bisdemethoxycurcumin, and cyclocurcumin—giving it a yellow-orange color. Among them, curcumin, also known as diferuloylmethane, is the most crucial component.[44] Curcumin is a low molecular weight, nontoxic, and hydrophobic diphenol compound, insoluble in water and ether but soluble in methanol, ethanol, and dimethyl sulfoxide. It has attracted interest in the fabrication of composite films for packaging applications because it provides additional functional features such as enhanced mechanical strength, UV protection, antioxidant properties, and antibacterial activity.[31] In addition to its functional properties, curcumin also exhibits a noticeable pH-responsive color change. The color change of curcumin is due to the change in its predominant structure under different pH conditions. Curcumin has an ordered crystal structure which is comprised of a seven carbon chain consisting of an α,β-unsaturated β-diketone moiety, which is attached to two aromatic rings having ortho-methoxy phenolic -OH groups.[45] It has been reported that the molecular configuration of curcumin is dependent on the pH of the solution, polarity, and temperature. At neutral and alkaline pH, the α,β-unsaturated β-diketone moiety in the curcumin structure is a breakdown point and acts as a hydrogen donor site leading to hydrolysis and degradation of curcumin. The transfer of intramolecular hydrogen atoms in the β-diketone chain occurs in the curcumin structure, which exists as a keto-enol tautomer form depending on the solvent properties. It exists in the bis-keto form at acidic or neutral pH, and the enolic form predominates at basic pH.[46] In the pH solution range 1−7, the dominant bis-keto form of curcumin displays a yellow color with very low water solubility. On the other hand, its high stability may be related to the conjugated diene structure. Under neutral or basic conditions, curcumin decomposes rapidly due to the loss of protons from the phenolic group, and the enolic form predominates. As the pH is adjusted to alkaline conditions, the destruction of curcumin leads to the formation of trans-6-(4-hydroxy-3-methoxyphenyl)-2,4-dioxo-5-hexenal as the primary degradation product while feruloyl methane, ferulic acid, and vanillin are its minor degradation products, leading to a noticeable color change to red. At the same time, the solubility and stability of curcumin are increased as alkalinity is increased. The functioning of the enolic form is based on the donation of H atoms from C−H bonds of the central carbon atom to the neighboring oxygen atoms, which is mainly due to the weak delocalization of unpaired electrons.[47] The halochromism of curcumin is shown in Figure 2(B).

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2.2.3. Alizarin. Alizarin, a natural colorant belonging to the anthraquinone dye, is derived from the roots of *Rubia tinctorum* L., also known as Mordant Red 11 and Turkey Red. Hydroxyanthraquinones are the primary compounds in Mordant Red, including alizarin (1,2-dihydroxy-anthraquinone), purpurin, pseudopurpurin, lucidin, xanthopurpurin, and rubiadin.[48] Alizarin is a phenolic alcohol-soluble compound with an orange-brown color, commonly used as a dye in textile fabrics and art since ancient times. Chemically, alizarin consists of two hydroxyl substitutions at possible positions attached to three coplanar six-membered carbocyclic rings. The proton transfer process in the molecular structure of alizarin leads to intramolecular hydrogen bonding between the hydroxyl group and the adjacent carbonyl oxygen atom.[27] The color changes of alizarin result from the formation of neutral, monoanionic, and dianionic forms under acidic, neutral, and alkaline conditions, respectively. At pH 2−4, ionization of the phenolic hydroxyl group in the benzene rings and the presence of nitro and azo groups of azobenzene dye give rise to uncharged molecules that show yellow color.[49] Raising pH to 5−7 leads to dissociation of the phenolic hydroxyl group due to the resonance effect, resulting in the formation of monoanionic molecules in the solution, which appears red. Further increasing the pH to 9−12 causes the second dissociation of phenolic hydroxyl groups resulting in the accumulation of dianionic molecules and increasing the intensity of the purple color.[50] The halochromism of alizarin is shown in Figure 2(C).

2.2.4. Shikonin. Another group of natural colorants is naphthoquinone pigments, also known as shikonin, which are generally derived from the dried roots of *Lithospermum erythrorhizon* Sieb. Et Zucc., belonging to the *Boraginaceae* family. The main structure of a naphthoquinone compound consists of two parts: a naphthazarin moiety and a chiral six-carbon side chain. The naphthazarin core is essential because of its high chemical reactivity. It is readily susceptible and polymerized in the presence of oxygen, light, heat, or treatment with acids or bases.[51] However, a little investigation into naphthoquinone compounds has been studied for their potential as dyes in intelligent packaging applications. It is believed that the naphthoquinone moiety acts as a breakdown point and induces hydrolysis and degradation of naphthoquinone structure at neutral and alkaline pH. Only a few studies have been reported on the effects of pH on stability and color changes of naphthoquinone substances in an aqueous medium to use pH-responsive color-changing films. Dong et al. and Huang et al. specifically studied the color response of naphthoquinone compounds as an indicator of meat product freshness.[52,53] They demonstrated that the spoilage affects the colorimetric label of naphthoquinone pigments, and their color was consistent with the spoilage threshold of the total viable count and TVB-N content in the fish sample. Dong et al. reported the highest stability of these compounds with a rose-red color obtained at neutral pH around 5−9 and showed a sharp change from blue-violet in the dilute alkaline to dark blue in the strong alkaline conditions in the pH range 10−12. They demonstrated that the significant color change depended on the transformations of the chromophore molecular structure, which is unstable and degrades at alkaline pH conditions.[52] The halochromism of shikonin is shown in Figure 2(D).

2.2.5. Betalains. Betalains are another group of natural food colorants with red-purple-crimson colors found in beet and pitaya plants. Betalains, also known as chromoalkaloids, are water-soluble compounds because of nitrogen in their basic structure.[54] Betalains can be classified into two subgroups. The first consists of red/purple betacyanins containing betalamic acid (the chromophore) and cyclo-3,4-dihydroxyphenylalanine (cyclo-DOPA). The second subgroup comprises the yellow-orange betaxanthins, consisting of the condensation products of betalamic acid and amino acids or amines.[55] These natural colorants are widely used as additives in various food products such as meats, dairy products, poultry, soft drinks, etc. Betalains are approved by the FDA for their safety and absence of any toxic and allergic effects.[56] Structural stability at acidic and neutral pH (pH 3−7) has contributed to the commercialization of betalains as a natural food colorant for various low acidic and neutral foods. On the other hand, betalains are most vulnerable under certain conditions such as alkaline pH, light, temperature, water activity, enzymes, and oxygen. Interestingly, betalains can undergo structural changes and exhibit color changes at high pH values. In distilled water, the natural pH of betalains is 3.85, which gives it a red color, and hence, their solution shows the same color in the pH range 3−7.[57] When the pH value is increased to 8−9, the color of the solution changes to orange, while at pH 10−12, it turns yellow confirming the gradual degradation of betacyanins into colorless cyclo-DOPA 5-O-(malonyl)-β-glucoside and yellow betalamic acid in alkaline solutions.[58] Betalains have not been used much for the development of colorimetric indicators, and only two reports are available on the use of betalains to monitor the freshness of shrimp and fish.[56] Betalains are extremely promising pigments that can be introduced as an indicator for intelligent packaging due to their pH-sensitive properties. The halochromism of betalains is shown in Figure 2(E).

Numerous studies have revealed the efficacy of natural colorants in the fabrication of pH indicators, indicating a high potential for food packaging application. These colorants are natural and eco-friendly and exhibit antioxidant activity, contributing to the prevention of lipid oxidation when packaging food products with high-fat content, such as meat products. However, natural colorants have some stability issues, such as degradation during storage under harsh temperatures and light conditions. Due to this fact, despite a recent increase in patent applications and granted patents, the synthetic dyes find only 5% of the total market value in packaging applications, whereas there is still no market for the natural pigments.[59]

2.3. Solid Support. The pH-responsive indicators usually consist of two basic components: a dye and solid support. Dyes are the main components that change color with changes in pH. A solid support is defined as the base material (usually a polymer matrix) to which the dye is immobilized.[60] Solid support materials can be applied alone or in combination to immobilize pH-sensitive dyes for sensing applications. In principle, the properties of solid support, such as an accessible microstructure and adequate surface properties, are necessary to improve the uniform diffusion of the dye without reaction between the matrix material and the colorant. Besides, the hydrophobic matrix contributes to reducing the effects of humidity.[30] The most commonly used solid supports are synthetic polymers and biopolymers. Synthetic polymers are highly versatile materials derived from petroleum derivatives that provide excellent physical, chemical, and mechanical properties, ultimately leading to a protective barrier against external stimuli, environmental conditions, and microbial/

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Table 1. Application of Natural Colorant Incorporated Biopolymer-Based pH-Sensing Films for Indicating the Freshness of Various Food Products

Food	Film base	Natural colorant	Colorant source	Ref
Pork	Chitosan	Anthocyanin	Purple sweet potato	74
Pork	Chitosan/PVA	Anthocyanin	Red cabbage	75
Chicken	Chitosan/Pectin	Anthocyanin	*Hibiscus rosa-sinensis*	76
Pork	Chitosan/Starch/PVA	Anthocyanin	Roselle calyx	77
Sausage	Agar/Tapioca starch	Anthocyanin	Red cabbage	78
Pork	Agar/Potato starch	Anthocyanin	Purple sweet potato	79
Pork Lard	κ-carrageenan/Hydroxypropylmethylcellulose	Anthocyanin	*Prunus maackii* juice	80
Chicken	Cassava starch	Anthocyanin	Blueberry residue	81
Pork	Cassava starch	Anthocyanin	Grape skin	82
Pork	Regenerated cellulose	Naphthoquinone	*Arnebia euchroma*	52
Chicken	Starch/Gelatin	Anthocyanin	Red radish	83
Pork/Fish	Chitosan	Anthocyanin	*Bauhinia blakeana* Dunn. flower	84
Pork/Seafood	Cassava starch	Anthocyanin	*Lycium ruthenicum* Murr.	85
Pork/Fish	PCL/PEO nanofibers	Anthocyanin	Acai *(Eutrepe olereceae)*	86
Beef/Chicken/Shrimp/Fish	Pectin	Anthocyanin	Red cabbage	87
Pork/Shrimp	κ-carrageenan	Curcumin	*Curcuma longa*	88
Shrimp	Chitosan	Curcumin	*Curcuma longa*	89
Shrimp/Fish	Chitosan	Anthocyanin	Black rice bran	90
Fish	Chitosan/Corn starch	Anthocyanin	Red cabbage	91
Fish	PVA	Anthocyanin	Mulberry extract	92
Fish	Furcellaran Gum	Anthocyanin	Beetroot Elderberry Blueberry Green tea Yerba mate	93
Fish	Agar	Naphthoquinone	*Arnebia euchroma* root	53
Fish	Tara gum/Cellulose	Anthocyanin	*Vitis amurensis* husk	94
Fish	Starch/PVA	Anthocyanin	*Hibiscus sabdariffa*	95
Fish	Glucomannan/PVA	Betalains	Dragon fruit peel	56
Fish	Bacterial cellulose nanofiber	Anthocyanin	Black carrot	41
Fish	Cellulose acetate nanofibers	Alizarin	Roots of Madder family plants	96
Fish	Chitosan	Alizarin	Roots of Madder family plants	50
Shrimp	Pectin	Curcumin	*Curcuma longa*	31
Fish	Starch/Cellulose	Alizarin	Roots of Madder family plants	27
Shrimp/Milk	κ-carrageenan	Anthocyanins	*Lycium ruthenicum* Murr.	97
Fish/Milk	Gellan gum/Gelatin	Anthocyanins	Red radish	98
Milk	Chitosan	Anthocyanin	Purple and black eggplant	42
Milk	Chitosan/PVA	Anthocyanin	Red cabbage	99
Milk	Chitosan/cellulose	Anthocyanin	Black carrot	100
Milk	Tara gum	Anthocyanin	Grape skin	101
Milk	Starch/PVA	Anthocyanin	Purple sweet potato	102
Milk	Starch	Anthocyanin	Carrot	103
Cheese	Polyvinylpyrrolidone/CMC/Bacterial cellulose/Guar gum	Anthocyanin	Red cabbage	104

physicochemical damage. However, the overuse of synthetic petroleum-based polymers raises global concerns as well as serious environmental problems due to the accumulation of nondegradable wastes from petroleum-based plastics.[61] Growing awareness of the food industry and consumers and increasing environmental awareness of this reality is driving the demand for ecofriendly materials that reduce waste. Thus, this has led to the replacement of petroleum-based polymers with biopolymers that are becoming increasingly popular in a relatively short time. The development of biodegradable and ecofriendly biopolymers using renewable resources has a high acceptance rate among consumers and is receiving considerable attention in packaging design.[62]

Biopolymers are natural polymers obtained from plant and animal sources with long-chain molecular subunits that degrade in the environment meet the stated criteria for replacing petroleum-based nonbiodegradable polymers. Biopolymers such as polysaccharides, proteins, lipids, and mixtures have been used for potential applications such as packaging materials. Polysaccharide-based biopolymers such as chitosan, starch, agar, carrageenan, cellulose derivatives, and proteins such as gelatin and corn zein are the most widely studied due to their excellent film formability and suitable structure as solid support materials for the fabrication of pH indicators.[63,64] Besides, many useful biopolymers can be obtained from agricultural industry by-products, an added benefit of following the zero waste principle.[20] For example, by-products of the seafood industry such as gills, skins, trimmings, and crustacean shells can be used for chitin and chitosan production.[65,66] On the other hand, fruit and vegetable processing wastes such as

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seeds, husks, stems, debris, and pomaces are a rich source of pectin and cellulose.[67,68] In addition, plentifully available algal seaweeds can be used to produce biopolymers such as alginate, carrageenan, and agar with high potential in food packaging applications.[69−71] The vital properties, such as nontoxicity, biocompatibility, and biodegradability, and film formation make biopolymers a suitable alternative for active and intelligent packaging development. However, their relatively low integrity, barrier properties, and mechanical properties have limited practical applications. Various methods have been addressed to avoid this shortcoming of biopolymers, such as mixing two or more biopolymers or combining biopolymers with functional fillers to provide additional functionality to the biopolymer film.[72] By adding pH-sensitive colorants to biopolymers, intelligent packaging systems can provide other features that indicate food quality and safety. Therefore, biopolymer-based packaging can provide pH indicating function, making it a better choice for real-time quality monitoring of packaged foods.

3. APPLICATION OF PH INDICATOR FILMS

The most widely used method for evaluating food quality is using chemical or microbial analysis. However, these methods are typically used on a laboratory scale and take time to obtain analysis results, making it difficult for producers, retailers, or consumers to quickly determine the quality attributes of packaged foods in the supply chain. Changes in food quality begin as soon as the foods are processed and packaged and continue to occur during distribution and storage.[73] The advent of pH indicator packaging has made it possible to visually determine the quality attributes of packaged foods throughout the supply chain. Table 1 summarizes the recent reports on the application of pH indicator films to various foods.

3.1. Meat and Meat-Based Products. Fresh meat is a perishable food and is very susceptible to physiological changes. Most meats deteriorate within 3 to 4 days after the slaughter, even refrigerated. Meat contains essential nutrients such as amino acids, sugars, and nucleotides suitable for microbial growth. As decay progresses, these compounds produce biological amines, ammonia, hydrogen sulfide, indole, and organic acids by microbial metabolism, causing strong odors, off-flavors, and discoloration.[105] Therefore, the meat industry needs powerful yet simple tools to determine the quality of packaged meats and predict shelf life and degree of spoilage.

Natural colorant-based pH indicators have been employed to detect the change in food pH due to the production of these volatile microbial metabolites, displaying an irreversible color change.[84] Zhang, Lu, and Chen (2014) prepared a chitosan-based indicator by adding pH-sensitive *Bauhinia blakeana* flower extract.[84] The chitosan film-based indicator changed color from red to green with increasing pH, making it a convenient, nondestructive indicator for pork spoilage monitoring. Red cabbage anthocyanin was used with agar/tapioca starch-based films to determine the shelf life of beef sausages.[78] The pH change due to sausage deterioration was monitored daily for 3 days. Initially, the bright purple indicator film (pH = 5.80) turned to light purple (pH = 5.85), dark purple-blue (pH = 6.12), and purple-green (pH = 7.12) after 24, 48, and 72 h of exposure, respectively. Vo et al. also used the red cabbage anthocyanins incorporated into chitosan/PVA blend films for monitoring pork freshness.[75] The indicator film was initially translucent sea green, corresponding to a neutral pH, and exhibited a significant color change over 24 h when in contact with a piece of pork slice at ambient temperature. The film exhibited a sequential color change to pink at the 12-hour exposure time, turned yellow-green at the 24-hour exposure, indicating that microbial action formed an initial acidic and then alkaline environment on the meat surface. Dudnyk et al. prepared red cabbage anthocyanins incorporated pectin films for monitoring the freshness of various meat and seafood products.[87] The color of the indicator film changed dramatically from purple to yellow, with increasing pH upon exposure to volatile amines released due to microbial growth. Othman et al. prepared hibiscus flower extract-based chitosan-corn starch films for monitoring chicken breast freshness.[76] The films displayed a color change from purplish-gray to dark gray and green as the pH increased due to the accumulation of amines and ammonia due to the spoilage of meat by mesophilic bacteria. Another study on chicken meat was performed by Lucchese et al., who used anthocyanins extracted from blueberry residues to prepare cassava, a starch-based pH indicator film.[81] The indicator film was used to monitor the chicken spoilage during storage at 6 °C for 10 days. Similar work was performed by Choi et al., who extracted anthocyanins from purple sweet potato and incorporated them into agar-potato starch films used for real-time monitoring of packaged pork.[79] The films changed color from red to green with increasing pork pH as a result of spoilage. Roselle anthocyanin incorporated biopolymer blends were prepared by Zhang et al. for monitoring the packed pork freshness.[77] Three different biopolymer mixtures were fabricated—starch/PVA, starch/chitosan, and PVA/chitosan—and their sensitivity to ammonia vapor was determined. The roselle anthocyanin incorporated starch/PVA film displayed the highest sensitivity toward ammonia vapor and hence was used as a pork freshness indicator at 25 °C. The film initially had a red color, gradually turned to green at 60 h, and finally turned to yellow at 72 h of storage, indicating that the pork spoilage is progressing over time. Yong et al. developed pH-sensitive packaging films using different chitosan films incorporated with purple rice extract (PRE) or black rice extract (BRE) for monitoring pork freshness.[106] Films with PRE showed a noticeable color change when the pH increased from the initial value of 6.15 to 6.33. On the other hand, no significant color change was observed for the BRE integrated film. The results suggested that purple rice anthocyanins were better and more sensitive to pH-dependent color changes. Qin et al. developed pH-sensitive packaging films based on cassava starch and *Lycium ruthenicum* anthocyanins and tested their effectiveness for monitoring the freshness of packaged pork.[85] The films showed a distinctive color change within the pH range 2−13. When the pork samples' pH increased from 5.96 to 7.45 over 48 h, the initially pink-colored film changed to dark purple/gray after 24−32 h and then turned greenish-yellow, indicating degradation of pork quality over time. Dong et al. used naphthoquinone dye extracted from *Arnebia euchroma* to fabricate colorimetric films of regenerated cellulose.[52] The films were used to determine the freshness of packaged pork at 20, 4, and −20 °C for 5 days. A distinct color change of the film from rose-red to purple and then to bluish violet was observed with increasing pH due to the volatile basic nitrogen, indicating the spoilage of pork. Chayavanich et al. fabricated pH-sensitive films using starch/gelatin and red radish anthocyanin.[83] The film changed color from orange at pH = 2 to purple at pH = 10 and showed purple-gray shade at pH > 12. The film was used for packaging of chicken meat and the freshness was monitored over a period of 48 h. The film changed color from red to gray-purple at any temperature, which was due to the deprotonation of anthocyanins by volatile ammonia compounds generated during the deterioration process.

3.2. Fish and Seafood Products. Fish and seafood, which are highly perishable products, are known to break down through three mechanisms: enzymatic breakdown, microbial spoilage, and lipid oxidation. Microbial spoilage is the primary and most important cause of degradation in seafood quality. Like meat products, when seafood products undergo microbial degradation, microbial metabolism products such as volatile basic nitrogen, trimethylamine, sulfur compounds, esters, aldehydes, and ketones are produced, which are responsible for the characteristic odor of fish and seafood spoilage.[107] Of these metabolic chemical by-products, volatile basic nitrogen and trimethylamine are the most widely used target compounds for decay and shelf-life indicators. These compounds accumulate in the packaging headspace, and the pH of the indicator film changes due to its alkaline nature.

A lot of research has recently been done to develop pH-sensitive materials using biopolymers combined with natural colorants for intelligent packaging of fish and seafood products. *Brassica oleraceae* (red cabbage) extract incorporated chitosan-corn starch pH indicator films were fabricated by Silva-Pereira et al. for determining the freshness of fish fillets.[91] The fish spoilage was assessed over 7 days at room temperature (25 °C) and refrigeration temperature (4−7 °C). For fish stored at room temperature, the initial transparent film showed no color change for up to 16 h, after which the color began to turn blue and finally yellow after 72 h, indicating complete spoilage. On the other hand, in the case of refrigerated fish fillets, the spoilage proceeded somewhat slowly. After 72 h, the film turned blue, and after 7 days, it turned yellow, indicating complete decay. Ma et al. used *Vitis amurensis* husk extract, a by-product of white wine processing, for a pH indicating colorant by incorporating it into a tara gum-cellulose nanocrystal film.[94] The film was used to determine fish spoilage, which showed that the color changed from pink to yellow-green with increasing pH values. In another study, poly(vinyl alcohol)-chitosan nanoparticle films conjugated with mulberry extract were fabricated to monitor fish quality.[92] The color of the film changed from red to green as the pH increased due to fish spoilage. The same authors prepared curcumin incorporated tara gum-poly(vinyl alcohol)-based pH sensing films and tested their efficacy to monitor shrimp spoilage.[108] The color indicator film was yellow at first but turned brown when it was subjected to a high concentration of ammonia, and when the film was then exposed to an acidic environment, it turned yellow again, showing reversibility of color change. Wu et al. developed smart films for seafood freshness monitoring by adding curcumin (Cur) to a chitosan (CS)/oxidized chitin nanocrystal (O-ChNCs) matrix.[89] When this film was used in seafood packaging, a noticeable color change from yellow to red was seen as the food sample's pH value increased. The pH sensitivity was tested over the pH range 3.0−10.0. Wu et al. also tested black rice bran anthocyanins using the same polymer nanocomposite matrix for similar applications.[90] The black rice bran anthocyanin solutions showed color variations from red to grayish green in the range pH 2.0−12.0, and the films with 3% anthocyanin (w/w of nanocomposite polymer matrix) were suggested to show the best color difference when used for monitoring freshness of packaged shrimps. Liu et al. developed a curcumin-integrated κ-carrageenan film for shrimp freshness monitoring.[88] The film had a yellowish color in the pH range 3.0−7.0, but as the pH increased from 7.0 to 8.0, a distinctive change in redness was observed with the sharp increase in the Hunter *a*-value from −5.47 to 21.87, and the visible color changed from light yellow to dark brown, indicating the spoilage of shrimp. Liu et al. also developed κ-carrageenan-based color indicator films incorporated with *Lycium ruthenicum* Murr extracts for the same application.[97] The films showed a significant color change during the storage of shrimp from light gray (0 h) to bluish green (36 h) and finally to yellow (72 h).

Moradi et al. developed an intelligent pH-sensing indicator based on bacterial nanocellulose and black carrot anthocyanins.[41] They used it to monitor the freshness/spoilage of rainbow trout and carp fillet during the storage at 4 °C. The indicator showed a distinctive color difference from red to gray in the pH range 2−11 and was visible with the naked eye. The pH-sensing indicator showed a distinct color change that could differentiate between fresh (dark carmine), most edible (attractive pink), and decay (jelly bean blue and khaki) stages of the two fish fillets. The initial pH values of rainbow trout and carp fillets were 6.36 and 6.24, respectively, gradually increased during storage at 4 °C, and reached 7.09 and 7.22, respectively, at the end of the storage. The increase in the pH value of fish products is due to the microbial metabolites and the action of endogenous enzymes. Huang et al. developed an indicator film for monitoring fish freshness based on agar incorporated with *Arnebia euchroma* root extract.[53] The enantiomeric naphthoquinone colorant present in *Arnebia euchroma* root extract is pH sensitive and exhibits a noticeable color difference with pH change. The film was used as a freshness label to monitor the freshness of Wuchang bream (*Megalobrama amblycephala*) fish. The color indicator label was initially pink, turned purple at 16 h, and finally turned bluish-violet after 24 h at 25 °C.

Ezati et al. prepared a chitosan-based pH indicator film by adding alizarin.[50] The indicator film showed a visible color response to pH change due to the release of ammonia vapor in the package headspace caused by fish spoilage. The color of the indicator film changed vividly from slightly yellow to purple in the pH range 4−10. The film indicated the onset of fish spoilage by showing a color change from khaki to light brown as the pH of the packaged fish changed. Ezati et al. also used alizarin combined with starch-cellulose paper to track the freshness of rainbow trout fillet.[27] The alizarin-starch-cellulose indicator (ASC) showed a color change from yellow to purple in the range 2−11 and retained the color stability after two months of storage at 4 °C. Also, the color change of the indicator coincided with the TVB-N content of fish fillets. In another study, Ezati et al. prepared a pectin-based indicator film combined with curcumin and used it for shrimp packaging.[31] The film showed a very distinct color change from yellow to orange as the shrimp quality changed. Besides, this film showed high antibacterial and antioxidant properties due to the functionality of curcumin.

3.3. Milk and Dairy Products. Milk and other dairy products such as cheese, butter, and yogurt are essential foods, especially for vegetarians. Milk is obtained from several species of cattle, and each milk has a unique composition. For example, cow milk is made up of 89% water, 5% carbohydrates, 4% protein, 3.5% fat, and the rest of the vitamins and minerals. However, this composition changes with the species and the immediate environment in which the species lives. This composition determines the properties of the processed product and the type of packaging required. There are also different varieties for each of these products with varying attributes on the market. So, packaging milk and dairy products are the most challenging task for packaging researchers. Most milk and dairy products are distributed, handled, and stored at refrigerated temperatures. Therefore, intelligent packaging is of paramount importance in determining the shelf life and quality of products during distribution and until consumption. Much research has been done on the intelligent packaging of milk and dairy products over the past decade, but only a few have used natural pH indicators.

Pereira et al. prepared an indicator material for monitoring milk spoilage by adding anthocyanin pigments obtained from red cabbage to chitosan-PVA film.[99] Milk spoiled when the temperature rose above its freezing point, and the pH of the milk decreased from 6.7 to 4.6. The indicator color changed from dark gray to dark pink, indicating that the milk was spoiled. In another piece of research, Ma et al. prepared tara gum-cellulose nanocrystal-based films incorporated with grape skin anthocyanins.[101] The film changed color from bright red to dark green as the pH changed from 1.0 to 10.0. When the film was used to evaluate milk spoilage at ambient temperature for 48 h, it turned dark red as the pH decreased from 6.48 to 2.94, indicating the spoilage of milk. Liu et al. also prepared pH-responsive films based on starch-PVA by adding anthocyanins extracted from a purple sweet potato to monitor pH changes in pasteurized milk.[102] Visual differences were observed when stored for 48 h at room temperature, and the color of the indicator film turned red over time, which is associated with milk spoilage. Zhai et al. developed an edible pH-sensitive film using gelatin, gellan gum, and red radish anthocyanin extracts for intelligent food packaging applications.[98] The indicator film showed a color change from orange-red to yellow in the pH range 2−12. After storage at 25 °C for 48 h, the film became redder with the R-value increasing from 232 to 253 as the acidity of the milk increased from 14.78 °T to 25.67 °T, indicating the spoilage of the milk. Liu et al. also tested the κ-carrageenan films incorporated with *Lycium ruthenicum* Murr extracts for monitoring milk spoilage.[97] The indicator film was initially gray when exposed to fresh milk (pH = 6.71) and changed to dark pink (pH = 3.24) after 48 h of storage, indicating the spoilage of the milk. Yong et al. used purple and black eggplant extracts as anthocyanin sources to prepare chitosan-based pH-sensitive films.[42] The anthocyanin contents of purple eggplant extract and black eggplant extract were 93.10 and 173.17 mg/g, respectively. Due to the difference in anthocyanin content, the film containing black eggplant extract showed a more noticeable color change than the film containing purple eggplant extract. The film changed color from green-blue at high pH to purple as the pH was decreased and was found to be suitable for milk freshness monitoring. Black carrot anthocyanin was used as a halochromic indicator in the chitosan/cellulose matrix by Tirtashi et al. to monitor the freshness of milk.[100] The color of black carrot extract was investigated using various pH buffers. The black carrot extract color turned pink at pH 2−6, purple at pH 7, blue at pH 8−10, and gray when pH increased to 11. The indicator film was used to monitor the freshness of pasteurized milk with initial pH = 6.6 and TA = 16 °D. The pH and TA values rose to 5.7 and 26.5 °D after 48 h storage at 20 °C. The corresponding color change of the indicator film is from blue to lilac in 24 h, and purple rose after 48 h storage to indicate the degree of spoilage of the milk. Another pH sensing material was prepared using starch and carrot anthocyanins to monitor the freshness of milk.[103] The color of the film changed from dark blue for fresh milk (pH = 6.5, TA = 17 °D) to purple for spoiled milk (pH = 5.7, TA = 28 °D) after 48 h storage at 20 °C. Recently, Bandyopadhyay et al. prepared multi-component hydrogel films composed of polyvinylpyrrolidone-carboxymethyl cellulose-bacterial cellulose-guar gum (PVP-CMC-BC-GG) and red cabbage anthocyanins for the monitoring of cheese quality.[104] The pH indicator film initially turned slightly pinkish when placed on the cheese for the first time due to the interaction with the lactic acid and other organic acids present in the cheese. The pH indicator turned red in the presence of acid due to the conversion of anthocyanin to red flavylium form and turned green in the presence of base due to the formation of carbinol pseudobase. The film showed a distinct color change with changes in cheese quality during storage.

4. COMMERCIAL INDICATORS FOR MONITORING FOOD FRESHNESS

The advent of research in the field of pH indicator packaging materials dates back to the 1950s. Nevertheless, the number of commercially available products on the market is relatively small. Moreover, no natural colorants used to manufacture intelligent colorimetric pH sensing products have been reported to date. Almost all commercial products available use synthetic dyes for this purpose. Various halochromic indicators are currently commercially applied to determine the freshness of short shelf-life products such as fish, meat, and poultry. Figure 3 shows some of the indicator labels commercially available in the market.

The Fresh Tag® colorimetric indicator was introduced in 1999 by COX Technologies (Plainfield, IL) and was perhaps the first commercialized pH indicator for food applications. It was used to monitor the freshness of packed chicken and

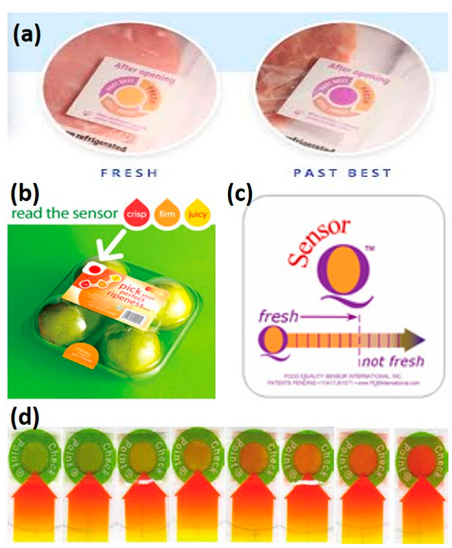

Figure 3. Commercially available colorimetric indicator labels in the market: (a) Fresh Tag, (b) RipeSense, (c) SensorQ, and (d) CheckPoint. Reproduced with courtesy of the creator companies.

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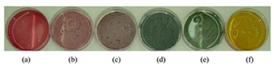
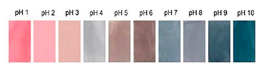
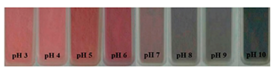
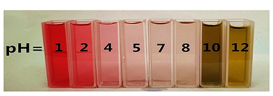
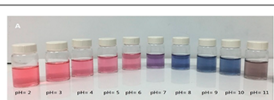
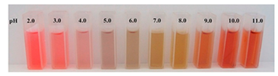
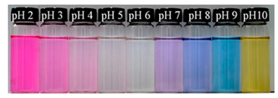
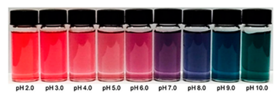
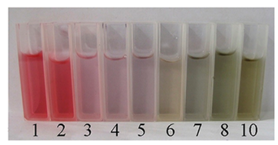
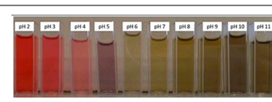
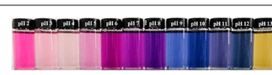
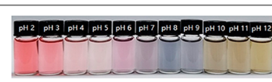
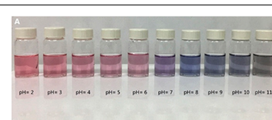
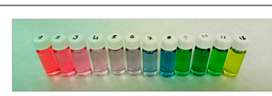
Table 2. pH-Dependent Visible Color Change of Anthocyanin Obtained from Various Natural Sources[a]

Colorant source	pH-dependent visible color variation	Ref
Purple sweet potato		74
Purple rice (A) / Black rice (B) extract		106
Grapes		109
Black chokeberry		110
Purple fleshed sweet potato extract		111
Bauhinia blakeana Dunn. flower		84
Purple (A) and black (B) eggplant		42
Black soybean seed coat		112
Purple potato		113
Black rice bran		90
Red cabbage		75
Mulberry extract		92
Black carrot		100
Black plum peel extract		114
Roselle calyx		77
Beetroot		
Elderberry		93
Blueberry		
Purple onion peel		115
Purple sweet potato		116
Lycium ruthenicum		97
Red radish		98
Red cabbage		117
Purple sweet potato		79
Grape skin		101
Vitis amurensis husk		94
Red cabbage		118
Blueberry residue		81
Lycium ruthenicum		85
Hibiscus sabdariffa		95
Black carrot		41
Red cabbage		119

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seafood products by detecting volatile amines produced during their deterioration process. As volatile amines were built in the package's headspace, the pH increased, changing the color of the indicator from yellow to dark blue. However, this indicator has no longer been commercialized since 2004. Another biogenic amine sensor was marketed by Food Quality Sensor International (Lexington, MA) under the brand name SensorQ. The indicator was attached and applied inside the meat and poultry packaging to visually indicate the freshness of the product to consumers. This indicator detected changes in pH due to the formation of volatile amine compounds due to the microbial degradation of the packaged food products. The orange color of the sensor indicates that the product is fresh or that microbial growth is insignificant. When the concentration of bacteria inside the package exceeds the threshold level, the indicator color becomes tan, indicating that decay occurs. CheckPoint® was another pH based food quality indicator label developed by Vitsab International AB, Sweden. The indicator is initially in an inactivated state and composed of two mini-sachets. One of the sachets contains fat absorbed by vinyl chloride powder, suspended in an aqueous mixture of the pH-sensitive colorimetric compound. The other sachet contains lipolytic enzymes. The two sachets are separated by a barrier layer that breaks down over time, and the enzymes and fats react to form decanoic acid. The acid, in turn, reacts with the pH-sensitive compound, changing its color from dark green to light yellow. Various types of indicators with varying activation time and functions working at different temperatures were manufactured using different combinations of enzymes, substrates, and their concentrations. RipeSense® is the first intelligent sensor label developed by New Zealand-based companies RipeSense and Hort Research. The label changes color to indicate the ripening of the fruit. The sensor shows the ripeness of the fruit by changing its color in response to the gas or aroma emitted as the fruit ripens. The aromas released from the fruits are esters, which are derivatives of fatty acids and hence are acidic. The colorimetric sensor label is initially red, then gradually turns orange as the fruit ripens and finally turns yellow. This allows consumers to check only the color of the sensor label and choose fruit based on maturity.

5. CHALLENGES AND PROSPECTS OF THE PH INDICATING PACKAGING SYSTEM

In recent years, intelligent packaging using pH-sensitive color indicator films or labels has emerged as a convenient way to detect or judge the freshness and quality of packaged food in real-time. In particular, as interest in food safety and environmental preservation increases, the demand for indicator films using natural biopolymers and natural colorants that are ecofriendly and biocompatible instead of petroleum-based plastics or synthetic dyes in the intelligent packaging field is increasing. However, as described in the previous section, there are still few color indicator products made from natural pigments and natural biopolymers that are ecofriendly and safe. There are many limitations and challenges associated with the development of this technology, hindering commercialization.

Most spoilage in food is primarily due to the growth of microorganisms. Microbial action forms acidic or basic metabolic products and can be detected using a pH-sensitive color change indicator film. The color change of the indicator film should be proportional to the concentration of these metabolic products, which depends on the degree of spoilage. However, most indicators have limitations on the concentration of metabolites to be considered for the detection of deterioration. The most significant metabolic products are total volatile basic nitrogen (TVB-N) in meat and seafood-based products and organic acids, such as lactic acid, pyruvic acid, acetic acid, etc., in milk and dairy products. Therefore, to date, most of the research on natural colorant-based pH-sensitive films has been limited primarily to meat, seafood, and dairy products and fruits and vegetables.

The effectiveness of natural colorant-based pH sensors is also a challenge. In general, most natural colorants are not efficient enough to detect quality changes in the early stages of food spoilage. In the early stages of spoilage, the concentration of these metabolites is so low that no noticeable color change of the pH-responsive color indicator film can be seen. Moreover, the pH of most foods changes in the range 5.0–7.0 when spoiled. In other words, it tends to be slightly acidic or slightly basic. However, most natural colorants rarely exhibit noticeable color changes in the small pH range around neutral. On the other hand, their color change is pronounced at very low or very high pH values. Also, the ability of natural colorants to change color depends on the source from which they are extracted. Table 2 shows the pH-responsive color change of anthocyanin colorants derived from various sources. Liquid products such as milk and juice face another limitation of the use of indicators. Most biopolymers and natural colorants used in the manufacture of pH-sensing films are hydrophilic and therefore tend to degrade upon prolonged exposure to liquids. A method of coating the indicator with a hydrophobic film may be used to solve this problem, and in this case, the sensitivity of the indicator is inevitably lowered. Also, since most pH-sensing films work in direct contact with food, there is a high likelihood that substances added to the indicator will migrate into the food, leading to legal issues, limiting the commercial use of these sensors.

6. CONCLUSIONS AND FUTURE PERSPECTIVES

In recent years, the use of color indicators for real-time monitoring of food quality has gained tremendous popularity in smart and intelligent food packaging applications. These products make it easy to reasonably control the quality control of food products across the entire supply chain, from producer to end consumer. Among the various intelligent packaging technologies, colorimetric sensors are easy to use as they enable consumers to visually check the quality of their food products without the need for complex analytical methods. Many currently used color indicators use synthetic dyes that change color according to pH changes. However, synthetic dyes pose serious safety concerns because synthetic dyes can leak from sensor labels and migrate to packaged food products. Recently, to replace synthetic chemical dyes, indicators have been developed using various natural colorants such as anthocyanins, betalains, curcumin, shikonin, and alizarin. These colorants have already proven safe, making them a reasonable and robust candidate to replace synthetic dyes. The natural colorant-based color indicators have been successfully used for the intelligent packaging of meat products (beef, pork, and poultry), seafood and fish products (shrimp and fish fillet), and milk and dairy products (milk and cheese). However, there are few research reports on the application of intelligent packaging for fruits, vegetables, and agricultural-based food products to date. Also, the pH sensitivity of most natural colorants is somewhat inferior to chemical dyes, which is one of the things that need to be improved. Emphasizing all the

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limitations of intelligent pH-responsive indicator films based on natural colorants for intelligent food packaging applications, future developments in this research field should increase the pH sensitivity of color indicating materials. There are also limitations of target analytes, such as detection thresholds of the indicators that need to be addressed. This requires research to find new target analytes that can respond more immediately and accurately to indicate food quality. Since most foods are spoiled by microbial action, more research is needed to detect common microbial markers. When bacterial contamination occurs in food products, the bacterial enzymes are released on the food surface, responsible for spoilage. Further research is needed on the development of colorimetric materials that respond to microbial enzymes released on the surface of food so that changes in food quality can be detected in the early stages of food contamination. Such materials have been used to detect microbial contamination in biomedical devices at an early stage by providing a colorimetric signal. When bacterial action begins in food, the pH decreases to slightly acidic, so more sensitive pH-responsive materials that can detect these minor pH changes must be developed. It is crucial to develop an indicator with a unique color change function in the neutral pH range, to determine the quality change in the early stages of most packaged foods. Therefore, it is necessary to consider narrowing the pH sensitivity of the indicator within the pH range 5.0−7.0. This will expand the application of a single pH sensing substance to a wide range of food products. Nonetheless, natural colorant-based pH-responsive color indicator materials have tremendous potential for future sustainable smart packaging applications. Natural colorant-based food quality indicators are expected to expand to the commercial level soon as the volume of research currently underway in this area increases and the increased interest in intelligent packaging by consumers and producers.

AUTHOR INFORMATION

Corresponding Author

Jong-Whan Rhim − *Department of Food and Nutrition, BioNanocomposite Research Institute, Kyung Hee University, Seoul 02447, Republic of Korea;* orcid.org/0000-0003-1787-5391; Email: jwrhim@khu.ac.kr

Authors

Ruchir Priyadarshi − *Department of Food and Nutrition, BioNanocomposite Research Institute, Kyung Hee University, Seoul 02447, Republic of Korea*

Parya Ezati − *Department of Food and Nutrition, BioNanocomposite Research Institute, Kyung Hee University, Seoul 02447, Republic of Korea*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsfoodscitech.0c00039

Author Contributions

Ruchir Priyadarshi: Conceptualization, writing manuscript, collecting and analyzing data. Parya Ezati: Conceptualization, writing manuscript, collecting and analyzing data. Jong-Whan Rhim: Conceptualization, funding acquisition, supervision, reviewing and editing.

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Notes

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