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Anthocyanin – A Natural Dye for Smart Food Packaging Systems

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Abstract Interest in the use of smart packaging systems for food products has increased in recent years. Therefore, food researchers are focusing on the development of new indicator based smart packaging technologies by using anthocyanin-based natural dye. Anthocyanins are one of the plant constituents known as flavonoids and responsible for the bright and attractive orange, red, purple, and blue colors of most fruits, vegetables, flowers, and some cereal grains. Indicators of natural dyes such as anthocyanins could express the quality and shelf life of perishable food products. However, the sensitivity and stability for their use in smart food packaging should be established to reach the market proposals. This review article focuses on recent studies related to use of natural dyes based on anthocyanin for smart food packaging applications. This study offers valuable insight that may be useful for identifying trends in the commercialization of natural dyes or for identifying new research areas. This review also provides food and packaging scientists with a thorough understanding of the benefits of anthocyanin-based natural dyes for shelf life indicator when applied to package material specific foods and hence can assist in accelerating commercial adoption.

Keywords Anthocyanin, Natural dyes, Active packaging, Indicator, Food, Smart packaging

Introduction

Food packaging is used to protect food from environmental contamination and other influences such as odors, shocks, dust, temperature, physical damage, light, microorganisms, and humidity. It is key to ensuring the quality and safety of food, while also extending shelf-life and decreasing food losses and wastage[1-7]. In the 20th century, many advancements in packaging technology appeared smart packaging systems including intelligent packaging (gas indicators, microwave doneness indicators) and active packaging (oxygen scavengers, moisture absorbers, and the controlling release of antimicrobial agents). These innovations further improved food quality, food safety, and shelf-life[8-12].

Smart package performance can be attained via the applications of indicators, sensors, barcodes, and radio-frequency identification (RFID) systems. Indicators inform the changes occurring in a food product or its environment through visual or other changes. The commonly used indicators in the meat industry freshness indicators. Colorimetric indicators are used to monitor the quality and safety as well as sense the spoilage in meat-based products by measuring the changes in color by means of cameras or other image-capturing devices or in some instances by the naked eyes[13-15]. All these technologies should be cheap, non-toxic, stable, sensitive, irreversible, and easy to introduce in the packaging system and so could effectively monitor the condition of food, packaging and the environment. In the fresh produce sector, Indicators contributed a significant role in reducing food loss, and waste in the supply chain by improving product protection, temperature, and environmental controls. Furthermore, it mitigates consumer's confusion about the safety of food products; therefore, food package manufacturers must consider all these factors to optimize sustainability[16].

The number of published studies on food spoilage indicators is still limited. However, several trials report that freshness indicators are designed to respond to chemicals released by food as a result of spoilage where an oxidative process is usually caused by microorganisms, which break down food carbohydrates, proteins, and fats to a wide variety of low-molecular-weight molecules. For example, some natural pigments from vegetable sources, anthocyanins have great potential as indicators in smart packaging systems. These flavonoids are widely spread in nature comprising the largest group of water-soluble plant pigments. They have been isolated mainly from

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flowers and fruits. Color expression of anthocyanins is strongly influenced by its structure, pH, co-pigmentation, temperature, UV radiation, and presence of oxygen providing different colors that range from salmon-pink through red and violet to nearly black. The color instability of anthocyanins makes these pigments especially useful to monitor food quality and therefore can be used as an indicator of food spoilage in the packaging applications. Anthocyanins are responsible for the carmine, magenta, mauve, indigo blue and pink as present color in the flowers, fruits, vegetables and etc. Anthocyanins belong to a large group of compounds collectively known as flavonoids, which are a subgroup of an even larger group of compounds known as polyphenols. Major anthocyanins from different plant sources are presented in Table 1. Chemically, anthocyanins occur as glycosides of flavylium (2-phenyl benzo pyrylium) salts, but differ from them by structural variations in the number of hydroxyl groups, the degree of methylation of these hydroxyl groups, the nature and number of sugar moieties attached to the molecule, and the position of the attachment, as well as the nature and number of aliphatic or aromatic acids attached to the sugars. Being polar in nature, anthocyanins are soluble in polar solvents such as methanol, ethanol, and water. This is the reason why most of the extraction processes are designed to use such solvents. These solvents are being acidified to stabilize anthocyanins in the flavylium cation. Anthocyanins show structural variations, which are mainly due to differences in the number of -OH moieties in the molecule, the degree of methylation of -OH moieties, the nature and the number of the sugar moiety attached to the aglycone molecule, and the specific position of these attachments. In addition, anthocyanins also vary in their quantity depending upon the source.

While there has been great interest and developments in the field of smart packaging[17,18], comparatively very little attention has been paid to the source of color indicators like anthocyanin. Hence this review paper aims to provide an overview of anthocyanin- a natural dye used for smart packaging applications, especially for indicators. We first discuss the driving forces of anthocyanin in food packaging, their extraction, and purification methods of anthocyanin for the use with a polymer, and then provide an overview of regulatory aspects, future perspective for the moisture absorbers.

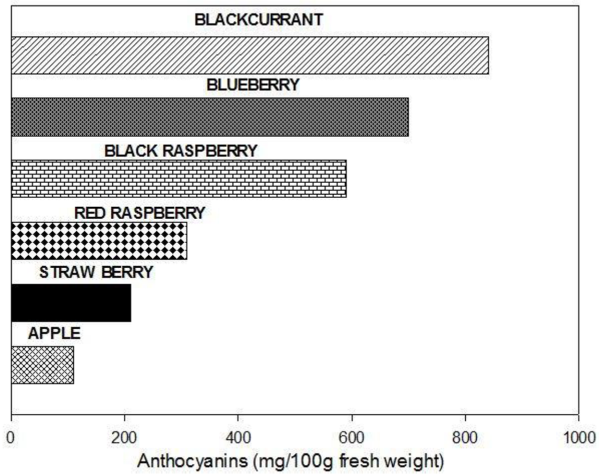

Fig. 1. The anthocynin contents of different fruits.

Study of Anthocyanins in Food Packaging Systems

1. Potential of food packaging application with driving forces of anthocyanins

Anthocyanins are natural based, non-toxic, water-soluble pigments that provide the purple, blue and red color of many plants and fruits. The anthocyanin contents of different fruits are shown in Fig. 1. The structural transformations of anthocyanins are associated with a color change in the function of pH. Food safety and quality extend ahead of just the food item itself when the food products come into contact with packaging materials. Stringent international and national policy such as EU regulation no. 1935/2004 and the comparable FDA requirements in the U.S. have been aimed at ensuring that unwanted substances do not transferred to food items. These standards are being adopted worldwide to safeguard the integrity of food contact materials such as food packaging, kitchenware, and food appliances. New developments in food packaging are in progress. The key driving forces for these changes comprise consumer demands, industrial antagonism and regulatory aspects. Environmental apprehension and efforts to diminish the solid waste stream are essential. The necessities of the consumers include gently preserved, high-quality expe-

Table 1. Major anthocyanins from different plant sources

Source	Anthocyanins
Apple, elderberry, blackberry, pear. Peach, fig, cherry, red, onion, red cabbage, gooseberry	Cyanidin
Banana, red cabbage, strawberry, potato,	Pelargonidin
Pomegranate, black gram, purple carrot, eggplant, green bean	Cyanidin and delphinine
Plum, sweet cherry, purple sweet potato	Cyanidin and peonidin
Mango	Peonidin
Bilberry, red grape	Petunidin and malvidin

diency food as well as greater assurance of food safety and better information of the food product.

Since pH changes are an important factor to inform spoilage in many food products, numerous efforts have been made toward the development of visual pH indicators as one type of smart food packaging technologies, due to several advantages including small size, great sensitivity, and low costs. Generally, visual pH indicators consist of a pH sensitive dye and a solid matrix to immobilize the pH dye[19]. Chemical reagents such as bromophenol blue and chlorophenol red[20] are pH-sensitive dyes that can be utilized to develop pH indicators, although the use of synthetic chemical compounds is avoided due to their potentially harmful effects to human beings for food applications. Recently, several studies have reported the potential of natural pH sensing dyes from different source as shown in Table 2. Many anthocyanins can be applied for food packaging systems since natural dyes are rarely toxic, easy to prepare, and pollution free[21].

2. Extraction methods for anthocyanin

The qualitative and quantitative study of anthocyanin from plant resources typically relies on the assortment of the suitable extraction process. Extraction is the primary step of any natural bioactive compound plant study and plays an important part on the final result and outcome. The common extraction process for anthocyanin from red cabbage is shown in Fig. 3. The extraction processes for sample preparations are mostly affected by the matrix properties of the plant part, sol-

Table 2. Sources of anthocyanin-based natural dyes for indicator applications

Classification	Source	Image	Nature			References
			Acidic	Initial	Alkaline	
Flower	Butterfly Pea		Red	Blue	Blue	Suebkhampet and Sotthibandhu[61]
	Red rose		Pink	Red	Yellow	Okoduwa et al.[62]
	Allamanda cathartic		Brown	Brown	Yellow	
	Hibiscus (*Hibiscus rosa-sinensis*)		Pink	Blood red	Pale yellow	
	Roselle red flower		Dark pink	Pink	Yellow	Suppadit et al.[63]
Fruit	Pomegranate seed		Light orange	Dark Brown	Light Brown	Tilekar et al.[64]
	Wax myrtle (berry)		Pink	Light pink	Orange	Kanda et al.[65]
	Grape		Pink	Light purple	Green yellow	

Table 2. Sources of anthocyanin-based natural dyes for indicator applications (Continued)

Classification	Source	Image	Nature			References
			Acidic	Initial	Alkaline	
Vegetable	Turmeric		Yellow	Yellow	Orange	Syafinar et al.[66]
	Red cabbage		Red	Blue	Orange-yellow	Kanda et al.[65]
	Purple carrot		Red	Pink	Orange yellow	Reyes and Cisneros-Zevallos[67]
	Purple sweet potato		Pink	Pink	Green	Choi et al.[68]
	Black bean (shell)		Red	Violet	Green yellow	Kanda et al.[65]
	Black Gram		Pale pink	No color	Yellow	Chidan Kumar et al.[69]
Leaves	Rhoeospathacea		Pink	Pink	Green	Pimpodkar et al.[70]

vent, temperature, pressure and time. Several extraction procedures can use for the extraction of anthocyanin from plant materials. Non-conventional extractions have been developed during the last 50 years as environmental friendly method according to decreased use of artificial and inorganic chemicals, reduced operational time, and improved yield of extract.

1) Soxhlet extraction

A soxhlet extraction can be carried out when low solubility compound needs to extract from a solid combination. The procedure places a specific piece of glassware in-between a flask and a condenser. The refluxing solvent constantly washes the solid extracting the preferred compound into the flask. Santos et al.[23] used soxhlet extraction for anthocyanin extraction from jabuticaba skins. In this work, dried plant parts were put into thistle of Soxhlet extractor and then used methanol/ethanol as a solvent. The temperature of the apparatus was maintained well under the boiling point of the used solvent. Several cycles of solvent were run to extract all the compounds from plant parts.

2) Supercritical fluid extraction (SCFE)

Supercritical fluid extraction (SCFE) is a two-step procedure, which uses an opaque gas as typically carbon dioxide more than its significant temperature (31^{o}C) and significant pressure (74 bar) for extraction. The natural product is pulverized and charged into the extractor. Carbon dioxide is fed to the extractor all the way through a high-pressure pump (105-350 bar). The extract charged carbon dioxide is sent to a separator (61-120 bar) through a pressure reduction valve. At the reduced temperature and pressure conditions, the extract precipitates out in the separator. The extract free carbon dioxide stream is introduced several times for effective extraction of all the dye material from the natural product. SCFE is better extraction method over the conventional solvent extraction of natural dyes. First of all, it uses a clean, harmless, cheap, nonflammable, safe, environmentally friendly, nonpolluting solvent-carbon dioxide (CO_2). Secondly, the energy costs linked with SCFE are lower than the conventional technique[24].

3) Subcritical water extraction (SW)

Many plants used for extracting natural colorant by subcritical water extraction. Dissolved oxygen was removed using nitrogen before the extraction. Deoxygenated water used in an HPLC pump involuntary for a steady flow of 1-3 mL/min. A 10.4 mL extraction cell operational with 0.5 m frit at the inlet and outlet was associated with a 1 m cooling loop (in ice water) outside of the oven. A pressure control valve placed connecting the cooling loop and the collection vial. The extraction was carried out efficiently. The SW extracts had comparable or higher levels of anthocyanins than extracts obtained using conventional hot water or 60% methanol. Subcritical water at 100 to 110°C appears to be an excellent alternative to organic solvents to extract anthocyanins and another phenolic from the dried red grape skin and possibly other grape processing byproducts[25].

4) Ultrasound-assisted extraction (UAE)

UAE can be carried out by a combination of desiccated along with the ground sample in methanol or any solvent in a flask, which was then placed in an ultrasonic bath for 30 min. In the beginning, the temperature of extraction was 20-40°C. It became 60°C after one hour of extraction. Anthocyanins and phenolic compounds were extracted from grape peel using UAE. The extraction process was optimized concerning solvent, extraction temperature and time.

5) Solvent-free microwave-assisted extraction (SFMAE)

Grigoras et al.[26] investigated solvent free microwave assisted extraction an amount of approximately 50 g of fresh sweet cherries. This was introduced in a 250 mL glass vessel without any solvents and submitted to microwave irradiation at 1000 W for four cycles of 45 sec each. Extracted juice recovered in the vessel after each irradiation cycle was removed and collected in a vial. The gathering of the four extracts collected after the four cycles constitutes the crude extract which is centrifuged (7000 rpm) for 5 min at 10°C. The supernatant was immediately frozen at -80°C to be lyophilized. A thin red layer of the dry extract was obtained[24].

6) Pressurized fluid extraction (PFE)

Pressurized fluid extraction is similar to soxhlet extraction, apart from that the solvents are used in close proximity to their supercritical region. The high temperature in this physical region enables high solubility and high diffusion rate of lipid solute in the solvent. In maintenance of the solvent with lower temperature than its boiling point, the high pressure enables a high penetration of the solvent in the sample. Thus, PFE permits high extraction efficiency with a low solvent volume (15-40 mL) and a short extraction time (15-20 min). This procedure is also known as "accelerated solvent extraction"[26]. The use of PFE can improve sample throughput by reducing extraction time and minimizing or eliminating the use of toxic solvents. Arapitsas et al.[27] investigated that pressurized hot water containing 5% of ethanol was used as an extremely efficient extraction solvent for anthocyanin extraction from red cabbage.

7) Pulse electric field (PEF)

PEF can increase mass transfer during extraction by destroying the membrane structure of plant materials for enhancing extraction and decreasing extraction time. The principle of PEF is to destroy cell membrane structure for increasing extraction. During the suspension of a living cell in an electric field, an electric potential passes through the membrane of that cell. Based on the dipole nature of membrane molecules, electric potential separates molecules according to their charge in the cell membrane. After exceeding a critical value of approximately 1 V of transmembrane potential, repulsion occurs between the charge carrying molecules that form pores in weak areas of the membrane and causes a drastic increase of permeability. PEF treatment application on grape skin before maceration step can decrease the period of maceration and get better the constancy of bioactive (anthocyanin and polyphenols) throughout vinification[28].

3. Purification methods for anthocyanins

Chromatographic techniques have primarily used for purification of anthocyanins. Crude anthocyanin nature solvent has been selected[24] and used in chromatography for purification purposes. During the purification process, adsorption is most commonly implemented for the removal or low concentrations of non-degradable organic compounds from concentrated compounds. When molecules in a liquid attach themselves to the surface of solid substance adsorption takes place. Adsorbents have an extremely high inner surface area that permits adsorption. Some scientists studied adsorption in this process for anthocyanin purification. 2 mL of Amberlite XAD7HP/Amberlite XAD4/Amberlite IRC 80/Amberlite IRC 120 and Dowex 50WX8 was contacted with 30 mL of a centrifuged extract of red cabbage in a 50 mL conical flask while agitating on a vibratory shaker. After reaching adsorption equilibrium, the resins were washed with deionized water and then desorbed with 30 mL of ethanol solution[29].

4. Identification methods for anthocyanin

Identification of anthocyanin has a very important role in the quality evaluation of crude process food. Characterization of anthocyanins can be carried out by a variety of methods developed so for. Some commonly used techniques include high-performance liquid chromatography (HPLC), thin layer chromatography, nuclear magnetic resonance (NMR) spectroscopy, mass spectroscopy, electrospray ionization (ESI) mass spectroscopy, and liquid chromatography-mass spectrometry (LC-MS). Spectroscopy is the prime technique used for identification due to its simplicity and low cost. Anthocyanin spectrum characteristic provides useful information regarding its stability. Additionally, HPLC with photodiode array detector (PDA) has been also used in the anthocyanins identification and quantification. Mass spectrometry (MS) and nuclear magnetic resonance (NMR) of H and C have become the preferred techniques for anthocyanins identification. Recently, hyphenated techniques such as HPLC coupled to MS APCI-MS, FAB-MS, and ESI-MS have become very powerful tools for the anthocyanins identification. The anthocyanins were separated and identified on the basis of their respective M+ (cation) using LC/ES-MS. Barnes et al.[30] used HPLC-UV and HPLC-ESI-IT-TOF-MS for identification of anthocyanins from blueberries. In the past two decades, numerous ionization methods have been developed for non-volatile or thermodynamically unstable samples such as the anthocyanins. These techniques avoid the volatilization and subsequent ionization. They supply energy to the solid sample or liquid in different ways, so that the direct formation of gaseous ions is produced. As a consequence, it is possible to obtain very simplified spectra. Among these desorption sources, it is found FAB, ESI, and MALDI, which are considered smooth ionization sources because they cause very low fragmentation and allow exact molecular weight determinations. NMR technique has been used for the anthocyanins structural elucidation[31].

5. Stability of anthocyanin

Since anthocyanin is extracted from natural resources and responsible for red, purple and blue pigmentation of flower, fruits, and vegetables, its color and stability can be affected many factors such as the chemical structure and concentration of the anthocyanin, temperature, pH, light, oxygen, enzymes, metallic ions, other flavonoids, and phenolics, ascorbic acid, sugars, sulfites. Because of highly reactive nature of anthocyanin, it can readily degrades or react with other constituents in the media to form colorless or brown colored compounds (Fig. 2). The existence of an ox-onium ion contiguous to carbon

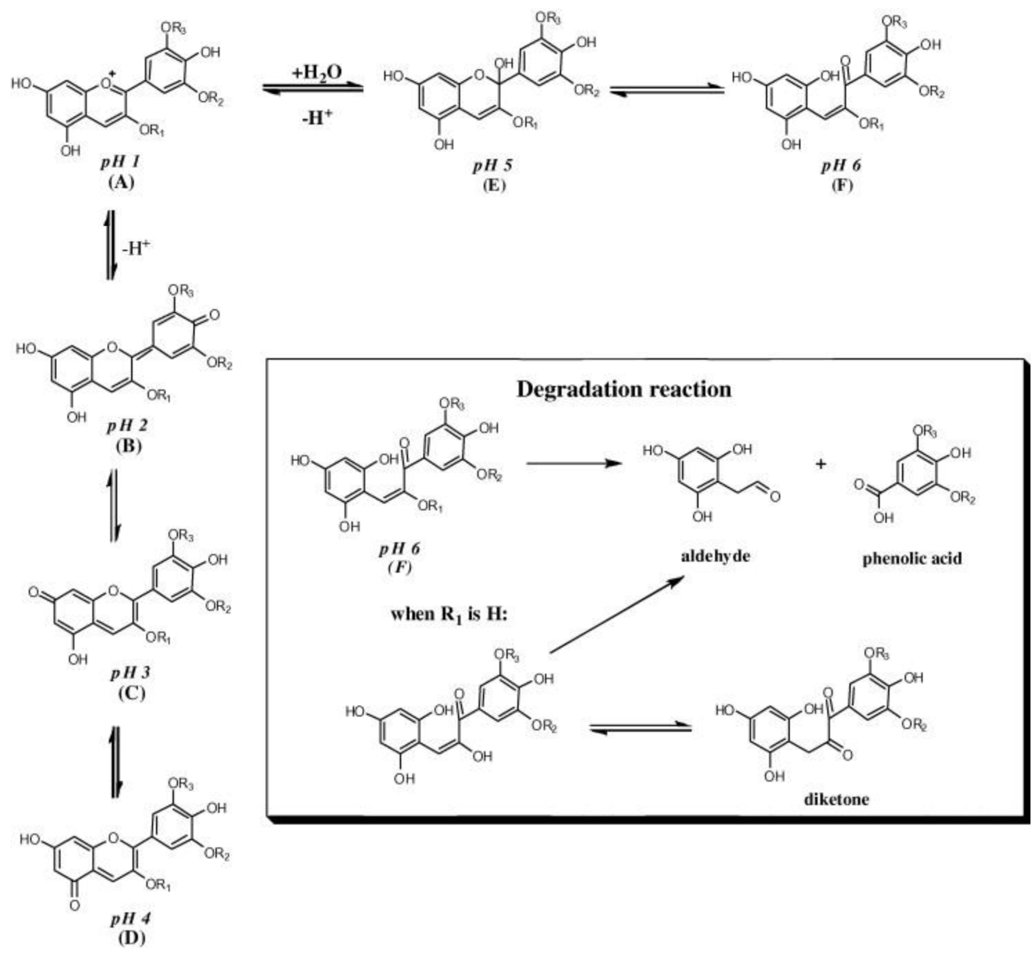

Fig. 2. Scheme of reaction of anthocyanin degradation.

2 makes the anthocyanins predominantly vulnerable to nucleophilic attack by such compounds as sulfur dioxide, ascorbic acid, hydrogen peroxide and even water. Presence of oxygen and various enzymes causes the loss of anthocyanin pigmentation during high-temperature processing. A definite degree of pigment stabilization could be conferred by acylation with various organic acids, pigmentation, self-association and/or metal chelation. In addition, pH has a marked effect on anthocyanin stability on the color of media[32]. Wang and SY[33] studied the degradation kinetics of anthocyanin extracted from black berry juice concentrate and found that during storage. Anthocyanins in the 65.0°Brix blackberry juice concentrate degraded more rapidly than that in 8.90°Brix blackberry juice with the activation energies of 65.06 kJ/mol and 75.5 kJ/mol, respectively. Deylami et al.[34] studied the effect of polyphenol oxidase (PPO) inactivation on thermal stability of anthocyanin extracted from mangos teen pericarp. PPO inhibition as the first step for stabilization of anthocyanins of mangos teen pericarp was studied. Blanching can be achieved to complete PPO inhibition and also enhanced anthocyanin extraction efficiency.

6. Application with polymers

1) Casting process

Incorporation of natural additives into polymers has been commercially applied in drug and pesticide delivery, household goods, textiles, surgical implants and other biomedical devices. Recently researcher also tries to incorporate anthocyanin based natural dye directly into polymer matrix as casting approaches. The recent research studies for incorporation of anthocyanin in polymer matrix are given in Table 3. Many natural biopolymers such as starch, chitosan, pectin, konjac glucomannan have been widely used in food packaging due to their low toxicity, biocompatibility and biodegradability. Liu et al.[35] prepared PVA/starch film using direct incorporation with anthocyanin. The film is capable to monitoring pH changes and inhibiting undesired microbial growth in pasteurized milk. Color based pH indicators offer a potential use as indicators of microbial metabolites as a microbiological growth could induce a pH change. Chitosan film containing anthocyanin as a natural pH-colorimetric indicator were made as direct incorporation method by Yoshida et al.[21]. Chitosan anthocyanin film could offer an efficient alternative to trace down food packaging giving a safe and quality product package due to the pH variation information during the transport and storage. Prietto et al.[36] developed a pH-sensitive film from solvent casting of polymer solutions containing corn starch, glycerol, and anthocyanin extract (from red cabbage or black bean) prepared at pH 5. The color of the developed films changed from pink to purple and blue as a function of the pH.

Because nature dye cannot tolerate the high temperatures, it often coated onto the material after forming or are added to cast films in polymer processing. Cast edible film, for example, has been used as a carrier for anthocyanin and applied as coatings onto packaging materials. Example includes that

Table 3. Recent research studies on the use of an anthocyanin-based indicator for smart food packaging applications

Source	Polymer matrix	Method of incorporation	Food application	Authors
Hibiscus	Chitosan & Corn Starch	Dispersion	-	Othman et al.[71]
Black chokeberry	Chitosan	Casting dispersion	-	Halász, & Csóka[52]
Red cabbage	Zein	Electrospinning	-	Prietto et al.[36]
Edible plant	Iota-carrageenan	Immobilized	Seafood (Squid)	Ahmad et al.[72]
Red cabbage	Polyethylene glycol	Casting	Poultry Meat	Ghosh and Katiyar[73]
Blueberry	Corn Starch	Immobilization	-	Luchese et al.[55]
Red cabbage	Cellulose	Immersed	-	Pourjavaher et al.[48]
Flower petals	Titration based Indicator	Pure Extracted material	-	Poonam et al.[74]
ClitoriaTernatea flower	-	Pure Extracted material	-	Biswas and Dasmohapatra[75]
Rose flower & red cabbage	Agarose	Dispersion	Buffalo meat	Shukla et al.[76]
Grape powder	Chitosan/Pectin	Casting	-	Maciel et al.[47]
Red Cabbage	Polyvinyl alcohol	Casting	-	Pereira et al.[77]
Purple sweet potato	Glycerol	Casting	-	Ishak et al.[78]
Jaboticaba flour	Modified Starches	Casting	-	Lucchese et al.[79]
Grape	Chitosan	Casting	-	Yoshida et al.[21]
Grape	Cassava starch	Casting	Pork	Golasz et al.[80]
Cabbage	Chitosan	Coating on card paper	-	Maciel et al.[41]
Grape and Spinach Extract	Cassava starch	Casting	-	Veiga-Santos et al.[81]

Saliu et al.[37] studied anthocyanin based CO_2 indicator. For making the indicator label fabrication, a coating containing the indicator dye was prepared by adding to distilled water polyethylene glycol-400, ethyl cellulose and the aqueous indicator solution. The mixture was homogenized and degassed in a solitec ultrasonic water bath. The coating was casted onto an optically transparent polyester support (poly-ethylene terephthalate) to obtain a film and then dried at room temperature for 5 hrs. Some authors also used compression molding with casting for making gelatin based film incorporated with anthocyanin[38].

2) Encapsulation

Microencapsulation may be a useful method to protect the environmental sensitive food ingredients such as anthocyanins until they reach the target object. Maltodextrin is often used as a wall material for microencapsulation. Several techniques are also used for microencapsulation including spray-drying, coacervation – phase separation process, pan coating process, solvent evaporation process, air suspension process, interfacial polymerization, and multi orifice centrifugal process. The incorporation of anthocyanins into food and medical products is a challenging task due to their low stability toward environmental conditions during processing and storage. However, these compounds can endow antioxidant properties to the products in which they are added. Encapsulation is an efficient way to introduce such compounds into these products. Encapsulated bioactive compounds are easier to handle and offer improved stability. Stoll et al.[39] investigated two different wall materials, gum arabic, and maltodextrin, on the microencapsulation of anthocyanins extracted from grape pomace and their effect on active biodegradable film properties. E silva et al.[40] developed an active biodegradable film with encapsulated anthocyanins which shows excellent antioxidant property for olive oil packaging.

Encapsulated bioactive compounds are easier to handle and offer improved stability. Encapsulation techniques have already been in wide use to reduce interactions of food and medicinal components with several environmental factors such as temperature, light, moisture, and oxygen. Encapsulation of anthocyanins by techniques other than spray-drying still remains an unexplored area and is therefore a promising area of research.

3) Spray-drying

Spray-drying is a commonly applied method for the microencapsulation of extracted plant phenolics such as anthocyanins. Polysaccharides such as maltodextrin, inulin, gum arabic, tapioca starch, citrus fiber, and other materials of glucose syrup and soy protein isolate are mainly used as matrix materials. Starches is used for containment of flavor essences and other components by spray-drying in a manner that can provide oxidative protection. The use of natural polymers as a coating material can enhance anthocyanin stability and help in controlled release of these functional ingredients in the human body for more efficient nutraceutical usage. By means of spray-drying method, the encapsulated plant phenolics are stabilized against degradation due to the impact of oxygen and light during dry storage. Previous studies show that encapsulation condition such as gelling agent and technique applied can directly influence anthocyanin degradation.

7. Anthocyanins for active and intelligent food packaging

The application of anthocyanins natural dye on polymeric materials in the food packaging sector has been investigated due to their high potential properties. The concept of smart packaging is extending the shelf life and maintains the sensory properties of food product. Generally, very low levels of anthocyanins are found in the food or food simulants tested. Therefore, accurate analytical methods are essential to determine the migration of monomers or additives from food contact materials to food or food simulants. Also, it is important to know the amount of anthocyanins required to stabilize the food in order to simulate the amount of anthocyanins that should migrate from the packaging into the food. Francesco Saliu et al.[41] investigated the performance of a combination of lysine, polylysine and anthocyanins as wet colorimetric indicator of CO_2. Lysine/poly-lysine/anthocyanins aqueous solutions exhibit basic pH and an azure color. Upon CO_2 exposure it shows intense purple color. Developed indicator is stable for several weeks in the cold storage condition (0-5^oC), capable to respond to small variation of gaseous CO_2 (up to 2.5%) and detect direct and reverse transitions. Since all the employed ingredients are food grade available, the system displays a great potential to be used as a device that enable a real-time and by naked eyes evaluation of the freshness of food products, giving an indication of the total amount of CO_2 produced during the spoilage of foods.

1) As an antioxidant material for active packaging application

The compounds which are easily oxidize are often the excellent antioxidants. A number of studies have recommended that the anthocyanin content and their related antioxidant activity contribute to the fruits and the vegetables shielding effect against degenerative and chronic diseases. Some plants and fruit extracts with high phenolic compounds content have been reported to act as mutagenesis and carcinogenesis inhibitors. The anthocyanidins and anthocyanins have shown a superior antioxidant activity than vitamins C and E. These compounds are capable to confine free radicals by donation of phenolic hydrogen atoms this is the reason for its anti-carcinogenic activity. It has also been reported, a linear correlation between the values of the antioxidant capability and the anthocyanins content in blackberries, red raspberries, black raspberries and strawberries. In addition, it has been described that the berry extracts possess a high scavenging activity towards reactive oxygen species chemically generated. The antioxidant activity of berries is directly proportional to the anthocyanins content[31].

2) As an antimicrobial agent for active packaging application

Anthocyanins are mostly plentiful in different fruits, especially in berries. The valuable effects of these compounds for human health have been recognized from at least the 16th century. Despite the enormous number of papers devoted to the different biological effects exerted by anthocyanins, only a limited number of studies is focused on the antimicrobial activity of these compounds. Anthocyanin content of berry fruits varies from 7.5 mg/100 mg fresh fruit in redcurrant (Ribes rubum) up to 460 mg/100 g fresh fruit in chokeberry (*Aronia melanocarpa*). After consumption, anthocyanins are intensively metabolized in the intestines and liver. Glucorination, methylation and sulfation are the most emblematic metabolic reactions. Antimicrobial activity of crude extracts of plant phenolic compounds against human pathogens has been intensively studied to distinguish and develop novel healthy food ingredients as well as medical and pharmaceutical products. However, there is very slight information obtainable about the antimicrobial activity of the pure anthocyanins. Generally, anthocyanins are active against different microbes. However Gram-positive bacteria usually are more vulnerable to the anthocyanin action than Gram-negative ones[42]. Mechanisms underlying anthocyanin activity include both membrane and intracellular interactions of these compounds. Antimicrobial activity of berries and other anthocyanin-containing fruits is likely to be caused by multiple mechanisms and synergies because they contain various compounds including anthocyanins, weak organic acids, phenolic acids, and their mixtures of different chemical forms. Therefore, the antimicrobial effect of chemically complex compounds has to be critically analyzed.

3) As an indicator for intelligent packaging application

At the present time food packaging is not just for shielding the food, but it also plays significant role for communicating either product is good for consumption or not. The reprehensive packaging application of smart packaging is pH-sensing film. But most of pH sensing films are prepared from artificial color which limits the uses of pH-sensing film in the food packaging due to consumer expectations for food safety. Because artificial dyes are carcinogenic or mutagenic, this might cause potential damage to aquatic life and human beings. Therefore, natural dyes extracted from plants are alternatives for use in biodegradable packing materials. Zhang et al.[43] extracted natural dyes from the flower of *Bauhinia blakeana* Dunn were immobilized in chitosan to prepare a colorimetric pH sensing film which shows the color change from red to green in the pH range 2-9. A pH-sensing film from grape skin (EGS) incorporated into taragum/cellulose nanocrystal matrix (CNC). EGS UV-vis spectra in the range of 1-10 were studied and color changed from bright red to dark green. EGS/CNC based film can be applied in activation test on milk which shows change in the coloration of the film[44]. Anthocyanins extracted from purple sweet potato have a higher stability to temperature and light, in comparison to dyes extracted from other plants. Choi et al.[45] developed a film using agar potato starch and natural dyes extracted from purple sweet potato (*Ipomoea batatas* L.). Both agar and potato starch are solid matrices used to immobilize natural dyes of anthocyanins. Silva-Pereira et al.[46] investigated chitosan/corn starch based

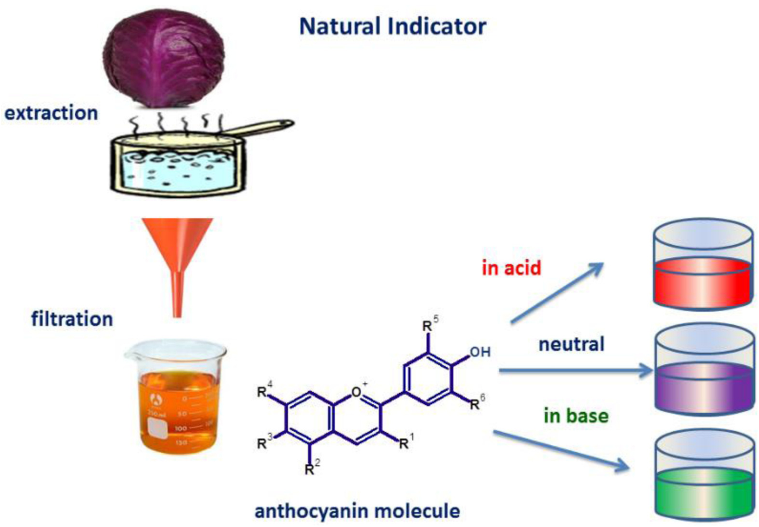

Fig. 3. Scheme of extraction process for anthocyanin from red cabbage.

film with red cabbage extract as visual indicator of fish deterioration. Fish fillet used to study the spoilage detection sensor. The result showed that change in color during spoilage of fish due to pH change.

Further, Maciel et al.[47] investigated polyelectrolyte complex (PEC) matrix formed between chitosan and pectin to entrap a bioactive compound (anthocyanin) obtaining a useful pH indicator device. The proposed system is advantageous due to its simple manufacture and visual change in color, offering an alternative for indicating pH variations in food products. This device has potential applications in food packaging. Since pH changes are a significant reason to notify spoilage in many food products, numerous efforts have been made toward the improvement of visual pH indicators as one type of smart food packaging system. Several advantages include small size, great sensitivity, and low costs. Pourjavaher et al.[48] characterized a smart label for pH monitoring based on bacterial cellulose (BC) nanofibers doped with anthocyanin's extracted from red cabbage (*Brassica oleracea*). The label containing diluted anthocyanin's showed a clearer response to pH variation. Novel colorimetric films were developed by Zhai et al.[49] for real-time monitoring of fish freshness based on starch/polyvinyl alcohol (SPVA) incorporated with roselle (*Hibiseus sabdariffa* L.) anthocyanin's (RACNs). The colorimetric films presented visible color changes over time due to a variety of basic volatile amines. These colorimetric indicators fixed in the headspace of the packaged fish presented specific color changes upon reaction with the TVB-N in the form of gas sensors. In this way, these packaging systems had great potential to indicate the real-time fish freshness. Pereira and Andrade[50] successfully prepared a pH-responsive film based on chitosan and curcumin. The developed film for pH changes was suitable for food packaging spoilage indicator for pH higher than 8. Listyarini et al.[51] developed a simple indicator label using colorimetric method for monitoring shrimp freshness. This indicator label was made from natural dye extract of Ruellia simplex flowers which immobilized on cellulose paper by dip coating method. The color of the indicator label when detecting the fresh shrimp was pink color. After the shrimp spoilage began, the color of the label changed to purple and then became yellow when it reached badly spoilage. Halasz and Csoka[52] studied the black chokeberry as natural dye indicator. Back chokeberry (*Aronia Melanocarpa*) pomace extract was mixed with chitosan to prepare colorimetric pH indicator films. The immobilized dye in chitosan films responded well to the pH change and showed a high color difference from pH 1 to 10.

Measuring concentration of acetic acid in food ingredient is a complex process at household level. With the help of natural dye based indicator we can easily measure the acetic acid. Acetic acid is an important chemical reagent which commonly used in chemical industry. In food industry, acetic acid mostly functions as acidity regulator the green label is made from the extract of chitosan and purple sweet potatoes as smart materials. The extraction color of the purple sweet potatoes changes from red to purple for pH buffer condition from 2 to 7[53]. *Artemisia sphaerocephala* Krasch. gum (ASKG)-based films responded to exposure to NH_3 as their color changed from brown to brownish red under a certain relative humidity. ASKG could be used as a packaging material and that purple onion peel extract-containing ASKG films express potential as smart packaging materials and gas-sensing labels[54]. Luchese et al.[55] prepared a biodegradable film using cassava starch, glycerol, blueberry residue. The color difference of this indicator was evaluated after its application in buffer solutions (pH = 4, 5, 6 and 7), simulants (saline, sucrose and protein solutions) and foodstuffs (orange juice, corn oil and chicken pieces). Kurek et al.[56] prepared the chitosan based smart films using blueberry and blackberry pomace extracts as active agents at different concentrations (1, 2 and 4% w/v). With changing pH from 2 to 10, films with blueberry changed from rose to blue green and with blackberry from red to dark violet. Novel films based on κ-carrageenan (Car) incorporated with curcumin (Cur) were developed for freshness monitoring of foods. A low amount of Cur (no higher than 3%) could be well-dispersed in Car matrix. Their properties was successfully used to monitor the spoilage of pork and shrimp during storage. As a pH colorimetric indicator, the Cur incorporated Car films may have a great potential in the freshness monitoring of food[57]. Wei et al.[58] demonstrated that gellan gum and purple sweet potato can form stable composite films. The composite films demonstrated high antioxidant activity and underwent a colorimetric transition along with the pH change caused by the volatile basic compounds released from the digested proteins during the growth of *E. coli*.

8. Safety and regulatory aspects

Anthocyanin in smart food packaging systems are rising and hopeful technologies that will progressively be applied in the years to extend shelf-life and improve the quality, safety and integrity of packaged foods. In recent years, many shelf life indicator systems have been developed. New concepts can be expected the smart packaging system such as anthocyanin based indicators which will become commercially available in the near future. However, for innovative food packaging technologies to be successful, they must comply with regulations[59]. The food-contact application of smart packaging systems may have an effect on various European regulations for packaged food such as regulations for food-contact materials, food additives, biocides, modified-atmosphere packaging, and hygiene of food- stuff, labelling and packaging waste. As all smart systems can be considered to be food-contact materials, the EU framework directive (Directive 89/109/EEC) appears to be of primary importance. Therefore, it is worthwhile to investigate the possibilities to adapt this directive to regulate smart packaging in Europe.

The increasing development of smart packaging technologies challenges the current regulatory framework, which must now address new technical considerations to ensure the safety, quality, and stability of food products. Although the legislation applied to traditional packaging can be adapted to active packaging[60], specific laws and guidelines should be introduced to clarify the legal uses of novel technologies in food packaging. In the United States, current FDA regulatory programs include the food additive petition (FAP) program, generally recognized as safe (GRAS) notification program, and food contact substance (FCS) notification program, which provide an authorization process for direct food additives, GRAS substances, and indirect additives, respectively. Migratory smart packaging should follow the FAP program or GRAS notification because this technology releases antioxidants into food as an intended technical effect. Anthocyanin based antioxidant packaging needs to follow the FCS notification program because the active agent is unlikely to migrate to the food. Japan is also leading the way in the development and use of smart packaging for food, and active packaging concepts have penetrated markets in Australia. The development of active packaging in the EU market is limited. Most of the products on the market in the United States, Japan, and Australia cannot yet be introduced in Europe because of inadequate and more-stringent EU legislation. The regulation of smart packaging in the EU is still evolving, and certain inherent constraints in the law (such as the overall migration limit) result in a set of hurdles for the regulation to keep up with rapidly developing technological innovations. The new smart packaging directive introduced in 2009 across Europe (EC Regulation 450/2009) is expected to bring much-needed clarity and pave the way for the launch of new products in the European market.

Future trends

Research in the field of anthocyanin for smart food packaging is very dynamic and develops in relation with the search for environment friendly packaging solutions. Nanotechnologies are projected to play a main role taking into account all additional food safety considerations and filling the presently existing gap in knowledge. They will be involved in the development of triggered/controlled release of active agents and for targeted indicators. New non-migratory materials for innovative functions such as in-package food processing are also a promising field of development. The next technological revolt would be bioactive, biodegradable, and bio nanocomposite. It is likely to be the smartest development yet to be used in modern packaging innovations. A big challenge in this research area of the quality indicators is to find the indicators that are sensitive (ppm - ppb levels) and exact. Most of the current pH-based indicators lack these properties. The next level of smart packaging will be the bio-smart packaging. A novel set of this technology can be designed to give response to a number of issues related to the feasibility, stability and bioactivity of functional ingredients as well as biosecurity for the food industry. The anthocyanin based bio-smart packaging will open new frontiers and opportunities for preserving the quality of food products and in monitoring the status of product quality, respectively.

Conclusion

Anthocyanins for packaging technologies are developing in recent years which are being integrated to the smart food packaging systems to meet the requirements of food supply chain. This review highlights the huge potential of anthocyanin and concludes that challenges in the use of natural dyes in packaging materials discussed. Adoption of suitable indicator by the food industry can be useful for safety, monitoring and providing information of food product in the package. Research on the anthocyanin can result in further improvement of the existing packaging system. Application of natural dyes contributes to the improvement of the quality of consumer life. Scale up and industrialization of the anthocyanin for food packaging application could be challenging and therefore should be taken into consideration at early development state for successful commercialization.

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