Anthocyanins – Applications in Smart Packaging

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ABSTRACT

Smart packaging systems have widely been used in raw and processed food products for quality analysis and quality management ensuring food safety. Active packaging and intelligent packaging technologies are two different forms of smart packaging. Active packaging applies gas emitters, gas and moisture absorbers, scavengers, chelating agents and so on in/on the packaging for maintaining and extending the shelf life of the food products. Whereas, intelligent packaging systems uses different indicators as tool for detecting and communicating the food quality to the consumers. Extensive research has been conducted to find out a sustainable and safe solution for the packaging industries, where a single component can serve the dual purpose. Anthocyanins are one of the active compounds which have been extensively explored for their application in active and intelligent packaging systems. Anthocyanins are plant constituents which impart the bright and attractive orange, red, purple, and blue colors to most fruits and vegetables, and flowers. The antioxidant and antimicrobial properties help in improving the product shelf life, and the pH sensitive pigment is used as quality indictor in packages. This review article focuses on recent studies that deal with the use of anthocyanin for smart food packaging applications, giving a thorough understanding of the benefits of anthocyanin-based natural dyes for shelf-life indicator when applied to package material specific to foods. The potential of anthocyanin opens the path to technological developments for commercialization of the technology for different food commodities.

Keywords: *Active packaging, anthocyanin, food safety, food quality, intelligent packaging, smart packaging*

1. Introduction

Until recent past decades, for determining the quality and freshness of food, traditional physiochemical methods were prevalent. Microbiological and molecular methods such as total plate count, and detection of ATP metabolite concentration were used to evaluate food quality and safety. However, with the advent of smart packaging the entire process of determining the quality of food product progresses. With the help of smart packaging, determining the quality or freshness of food has become a low hanging fruit.[1]

Researchers have been striving hard every day to come up with such newer technologies, for instance, pH sensitivity and color changing function of anthocyanins have been explored in making color indicator smart packaging films to trace the freshness of food such as meat and milk. Besides, the antimicrobial and antioxidant activities of anthocyanins play major role in active packaging systems.

2. Smart Packaging

Smart packaging is considered as an umbrella term, including various functionalities, depending on the packaging of food, pharmaceutical, beverages and so on. Active packaging and intelligent packaging are two different forms of smart packaging. It provides a total packaging solution or one stop solution. On one hand it gives information about the product and its environment, which indicates the intelligent packaging and on the other hand it acts upon these changes which is known by the name of active packaging.[2]

According to Vander roost et al., "Smart packaging is a combination of both active and intelligent packaging." It provides a solution to monitor and control the environmental conditions of the package and prevents any changes occurring. This type of packaging can be used in a variety of food applications like fresh food, beverages, ice-cream, dairy products and animal products.[3]

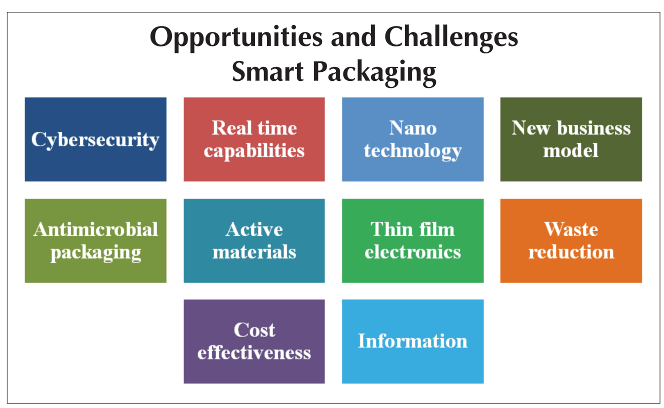

Figure 1: Opportunities and challenges of smart packaging[5]

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There is a wide potential for smart packaging in the market which can also be said as 'value- added' benefits. It is also found out that these packaging can be utilized to detect inefficacies in food supply chain and to monitor product quality.[4] However, these technologies face challenges in their path of commercialization (Figure 1).

2.1 Active packaging

Active packaging was initially introduced as an alternative to traditional packaging methods. Increasing consumer demands and emerging market trends led to its introduction in the market. The technology which is used in active packaging, intentionally releases or absorbs different compounds from the food or the headspace which is left in the food packet. Moreover, these emitters lessen the effects of microbes or any other deteriorative action from the microbes or any other involuntary actions. Which, in turn, prolongs the shelf life of the food product. Active packaging is dominated by scavengers for oxygen, ethylene, moisture and emitters.[6]

2.1.1 Scavengers

Scavenging technology is embedded within the package structure nowadays. And, hence, it provides an integrated approach where ethylene, moisture and oxygen scavengers are the most popular one in the commercial products..[7]

a) Oxygen scavengers

These oxygen absorbers help in controlling the microbial growth. Iron, ascorbic acid and other substrates are mainly used as oxygen scavenger.[8]

b) Ethylene scavenging products

It enhances the product shelf life by mitigating the ripening process and senescence. These commanding products are mainly found in packages and sachets. Various clays and chemical compounds are used as ethylene scavengers such as zeolite, bentonite, coral, ceramics, glycol, polyethylene, polystyrene, potassium permanganate, silver nitrate, benzene, aluminium oxide activated charcoal, silica gel, and kieselguhr.[8]

c) Moisture scavengers

Moisture scavengers absorb moisture or any liquid weeping or oozing out from food, thereby helps in keeping aesthetics of the product and also extend the shelf life of the food product for instance, Dry-Loc by Novia, Meat Pad by McAirlaid's.[9]

2.1.2 Emitters

Emitters lessen the harmful and deteriorative effects of microbial growth, oxidation or uncontrolled ripening by direct contact with food. A number of emitters can be used for instance, antimicrobial carbon dioxide emitters, antimicrobial nano-sized metals etc. Other compounds that can be used in active packaging are spices, essential oils, and plant extracts.[10]

2.2 Intelligent packaging

Intelligent packaging materials are those that monitor the internal and external environmental conditions of the food package.[11] With time different measures were taken by the scientist in order to ensure safe and quality food. As time passes, the demand for preserved, ready to eat, less time consuming and minimally processed foods has increased in the market. In order to cater that section of society scientists and researchers came up with different intelligent packaging systems which are consumer friendly, non-destructive, and noninvasive.[12]

This type of packaging includes the use of following three technologies:

i) Indicators, which indicate and communicate the food quality.

ii) Data carriers, such as radio frequency identification tags (RFID), or barcodes which help in storage, transportation and distribution of products.

iii) Sensors, which help in quantification of food analytes.[11]

2.2.1 Indicators

Indicator sensors in intelligent packaging are reliable and consumer friendly tools for providing reliable and authentic information pertaining to the food conditions, the environment and the packaging integrity. In order to fabricate indicator sensors number of indicator solutions and carriers are being used in industries. For instance, pH responsive anthocyanins infused chitosan-based intelligent film was developed for detection of food spoilage. This system has changed the traditional communication functions of packaging into intelligent communications with use of interactive and colorful indicators which also allow evaluation of the current product quality. Most commonly available types of intelligent packaging in the market are time temperature indicators, freshness indicators, and indicator for leaks.[13]

Time and Temperature Indicators: These are the most commonly used indicators in intelligent packaging. Time-temperature indicators are used to monitor the current temperature of the packed products and are able to detect or capture even a small fluctuation in temperature beyond the safe storage limit, which is further indicated by a color change in the product packaging. These indicators have found wide application in chilled and frozen products where irreversible discoloration of label reveal defrosting and temperature deviation, thus communicating product quality and safety.[14]

2.2.2 Data Carriers

Data carriers are the automation devices that are used for maintaining transparency in the food supply chains. It does not have to do anything with food quality. Barcodes and RFID tags are most commonly used as data carriers in food supply. Barcodes are a series of parallel spaces and lines which extend to give 12-digit number. They are used due to their low price and easy to use nature which can be read by optical barcode scanners and the data is then sent to the devices where the information is stored and processed. RFID tags, the most advanced form, include 3 components- it is made of a microchip connected to an antenna, a reader for emitting radio signals and a middleware that bridges the RFID hardware and enterprise applications.[11]

2.2.3 Sensors

Sensors are the devices that helps to detect or locate information whenever signal is given. They consist of a receptor which is the sensing part. The information is obtained by absorption which is then detected by inducing either redox potential, pH, temperature or light etc. Then this information is transferred into the transduction element, which help to carry the information to the signal processing electronics which is then displayed onto signal display unit.

An ideal sensor should have the following properties:

- specificity for the target
- sensitivity
- quick response time
- can be used for a longer period of time
- small size

Recently 2 different kinds of sensors are found in intelligent devices in packaging: biosensors and gas sensors.[11]

Gas sensors are the devices that responds to the gas analytes present in the surroundings. Biosensors are the analytical device that are sensitive to biological reaction happening in their surroundings. Their receptor detects specific target analyte and the transducer converts biological signals to quantifiable data.[15]

Intelligent packaging is very different from active packaging materials in a way that active packaging works to extend the shelf life of the food products while intelligent packaging communicate about food quality. Moreover, intelligent packaging can be used to keep a check on active packaging by sensing and sharing the changes made by active packaging with the stakeholders. So, both of these works synergistically to lead to a concept known as SMART PACKAGING.[11]

2.3 Challenges of Smart Packaging

2.3.1 Antimicrobial packaging is gaining popularity these days due to its benefit to the food quality but future research should be done to explore naturally present bioactive compounds, antimicrobial and bio-preservatives that are also biodegradable.[4]

2.3.2 Development of thin-film electronics is a challenging part that needs to be researched upon. It is found that this can be used for temperature tracking in perishable products.[3]

2.3.3 Waste generation from these type of packaging materials is harmful for the environment, so proper disposal systems should be made for these.[4]

2.3.4 The customers are demanding more and more information due to the development of such packaging systems, which is posing a big challenge for food production sector.[4]

2.3.5 Use of smart technologies add the cost to the packaging and the product. Thus, research should be done to find a cost-effective implementation tool.[4]

3. Anthocyanins – Potential Application in Food Packaging

New developments in food packaging are in progress and are quite focused on diminishing the solid waste stream. The necessities of the consumers include, high-quality expediency food and above all assurance of food safety and better information of the food product. pH changes with food spoilage have been exploited in developing visual pH indicators. pH indicators have two principal components 1) a pH sensitive dye and 2) a solid matrix for immobilizing the dyes. Chemical dyes such as bromophenol blue and chlorophenol red are sensitive dyes which are used in pH indicators. However, various studies have utilized the pH sensitive natural pigments as indicator dyes, among which anthocyanins are widely researched. Natural dyes are preferred for their non-toxicity, easy preparation, and environment safety.

Anthocyanins are the glyosidic form of the anthocyanidins and are produced by the phenylpropanoid pathway. These water-soluble pigments are found in leaves, stems, flowers, and fruits of many plants. The six types of anthocyanidins found in foods are cyanidin, delphinidin, pelargonidin, peonidin, petunidin, and malvidin.[16,17] Anthocyanins are formed by a flavylium cation backbone which is hydroxylated in different positions (generally on carbons C3, C5, C6, C7 and C3', C4′, C5′), yielding different anthocyanidins.[18]

The most frequently occurring monomeric anthocyanins, are the glycosides of cyanidin, delphinidin, malvidin and pelargonidin.[19] These compounds show different colors (red, blue and purple) depending on their accumulation. At low pH values, anthocyanins are present as flavylium cations, and as uncharged quinones at neutral pH. At alkaline conditions, all anthocyanins are found to be slightly stable, undergoing different degradation pathways with subsequent discoloration.

3.1 Stability of Anthocyanins

Anthocyanin is responsible for red, purple and blue pigmentation of flower, fruits, and vegetables. The color and stability of the pigment is a function of many factors like chemical structure and concentration of the anthocyanin, pH, temperature, oxygen, light, enzymes, metallic ions, other flavonoids, and phenolics, sugars, ascorbic acid, and sulfites. Due to the highly reactive nature of anthocyanins, they degrade or react with other constituents present in media to form colorless or brown colored compounds.[20]

The presence of an oxonium ion makes the anthocyanins vulnerable to nucleophilic attack by compounds like sulfur dioxide, ascorbic acid, hydrogen peroxide and even water. Presence of oxygen and various enzymes also causes the loss of anthocyanin at high- temperature processing. Stability of anthocyanins is due to acylation with various organic acids, pigmentation, self-association and/or metal chelation. Additionally, pH also shows a marked effect on anthocyanin stability that further effects the color. Studies have also depicted the effect of polyphenol oxidase (PPO) inactivation on thermal stability of anthocyanin where blanching leads to complete PPO inhibition and enhanced extraction of anthocyanins.

4. Application with polymers

Anthocyanins have found their application in smart packaging system in conjugation with polymers. Binding and encapsulation of the pigments with various carbohydrate, protein and fat polymers help in controlled release of the compounds with high specificity while increasing the stability of anthocyanins. Different approaches can be used to combine the pigment with polymers, few are discussed as follows.

4.1 Casting process

Using casting process, a PVA/starch film was prepared with incorporation of anthocyanin.[21] The film was able to monitor pH changes and inhibited the growth of undesirable microbes in pasteurized milk. These color-based pH indicators in packaging can be widely used to detect microbiological growth. Chitosan film having anthocyanin as a natural pH-colorimetric indicator were made through the incorporation method.[22] The film is a good alternative detector for a safe and quality product package, providing information with change in pH during the transport and storage. Another pH-sensitive film through solvent casting of polymer solutions containing corn starch, glycerol, and anthocyanin extract had been also developed.[23] The film showed pH-based color change from pink to purple and blue. Natural dyes cannot tolerate the high temperatures thus it is coated onto the material after forming or are added to cast films in polymer processing. Some authors have also used compression molding along with casting for making gelatin-based films incorporated with anthocyanin.[24]

4.2 Encapsulation

It is widely used method to protect the environmental sensitive phytochemicals like anthocyanins. Several encapsulating agents like maltodextrin, gum Arabic, glucose, starch, whey proteins are used as a wall material. Numerous techniques are used for microencapsulation including spray-drying, microfluidization, coacervation – phase separation process, solvent evaporation process, interfacial polymerization, pan coating process, air suspension process, and multi orifice centrifugal process. Encapsulation is a very efficient way to introduce these compounds into products. Encapsulated bioactive compounds provide flexibility with its use and have an improved stability.[25] An active biodegradable film was developed with encapsulated anthocyanins that showed excellent antioxidant property for olive oil package.[25] Encapsulation techniques are being widely used to reduce interactions of food with environmental factors such as temperature, light, moisture, and oxygen.

4.2.1 Spray-drying

Spray-drying is the most preferred method for the microencapsulation of sensitive bioactive compounds like anthocyanins. Different polysaccharides such as tapioca starch, maltodextrin, inulin, gum Arabic, citrus fiber, glucose syrup and soy protein isolate are used as the encapsulating agents in the process. Encapsulation using this method provides the stability to the compounds by preventing the degradation by oxygen, temperature, and light. Previous studies have explained the stability of anthocyanins as a factor of process conditions such as type and concentration of carries agents, technique applied, time-temperature combination etc.

5. Anthocyanins for active and intelligent food packaging

The use of anthocyanins (a natural dye) in the food packaging industries has been explored because of their high antimicrobial, antioxidative and indicative properties. The concept of smart packaging is basically extending the shelf life and maintaining the sensory properties of food product. Usually, low levels of anthocyanins are found in the food tested. Thus, accurate analytical methods are required to estimate the concentration of anthocyanins that is needed to stabilize the food in order to simulate the number of anthocyanins that should migrate from the packaging into the food. For investigating the same a study was also conducted where the performance of combination of lysine, proline and anthocyanins as wet colorimetric indicator of CO_2 was tested for anthocyanin stability. The combination exhibits basic pH and an azure color and upon CO_2 exposure it had showed intense purple color. The developed indicator is stable for several weeks.[26]

5.1 As an antioxidant material for active packaging application

A lot of studies recommended that the anthocyanin related antioxidant activity provide protection to fruits and vegetables against many of the degenerative and chronic diseases. The anthocyanidins and anthocyanins have shown a way more superior antioxidant activity than vitamins C and E. Anthocyanins are capable of confining free radicals through the donation of phenolic hydrogen atoms which also provides anthocyanins anti-carcinogenic activity. Studies have provided a linear correlation between the antioxidant activity and the anthocyanin concentration in blackberries, red raspberries, black raspberries and strawberries.[27,28] Anthocyanins and anthocyanidins possess free radical scavenging ability to scavenge harmful oxidants such as reactive oxygen and nitrogen species (ROS and RNS).[27,28] The flavylium skeleton of anthocyanins involves radical electron delocalization on sp2 orbitals of the oxonium moiety. The para- and ortho-phenolic groups are important groups for the formation of semiquinones and for the stabilization of one-electron oxidation products.[20,28] 3, 5, 7 and 3′and 4′ substituents, respectively are important for the formation of different electronic delocalized and oxidized structures.[20,28,29,30]

5.2 As an antimicrobial agent for active packaging application

There is very less information available about the antimicrobial activity of the pure anthocyanins. Generally, anthocyanins are active against many microbes. Gram-positive bacteria usually are more vulnerable to the anthocyanin action than Gram-negative microbes. Antimicrobial activity of anthocyanin-containing fruits is because of multiple mechanisms and synergies that occur due to the presence of compounds including anthocyanins, weak organic acids, phenolic acid and many more.[31]

5.3 As an indicator for intelligent packaging application

Now-a-days food packaging is not only used for shielding the food, but it also plays a very important role in communicating the food safety. One such application of smart packaging is the pH-sensing film. Many pH sensing films are made from artificial color which restricts their applications in the food packaging because these dyes are carcinogenic or mutagenic. These can have a damaging effect on aquatic life as well as on human beings. Therefore, natural dyes which are extracted from plants serves as a good alternative for use in biodegradable packing materials. Many studies have been conducted in this field. In one such studies the extracted natural dyes from the flower of Bauhinia Blakean Dunn were immobilized in chitosan in order to make a pH sensing film that showed the color change from red to green in the pH range 2-9. Similarly, anthocyanins have also being used for making such pH sensing films. Anthocyanins from purple sweet potato were used to develop a film using agar potato starch.[32] A polyelectrolyte complex (PEC) matrix was developed using chitosan and pectin for entrapping a bioactive compound (anthocyanin) for obtaining a useful pH indicator device.[33] pH changes are a significant reason for notifying spoilage in many food products, therefore many efforts have been made for improvement of visual pH indicators as one type of smart food packaging system because of the advantages like small size, great sensitivity, and lower costs. A smart label for pH monitoring using bacterial cellulose (BC) nanofibers with red cabbage anthocyanins (*Brassica oleracea*) has also been made.[34] The label has diluted anthocyanin which show a clearer response to pH variation.[35] A pH- responsive film based on chitosan and curcumin has also been developed for detecting spoilage above pH 8.[36]

Similarly, a simple indicator label using the colorimetric method for monitoring shrimp freshness has also been developed. A film was prepared using black chokeberry (*Aronia metacarpal*) pomace extract along with chitosan. The immobilized dye in chitosan films showed to the pH-based color change between pH 1 to 10. Acetic acid is an important chemical reagent in food industry, it mostly functions as acidity regulator. The green label had been prepared from the extract of chitosan and purple sweet potatoes for smart packaging systems. [37]

6. Conclusion

Smart packaging is a combination of both active and intelligent packaging, which can be used very effectively to communicate food quality and to act on any changes occurring within the environment. Intelligent packaging alone is not very effective for improving the shelf life of the products; therefore, these are combined with active packaging to make a two-in-one beneficial smart packaging system. Referring to the findings mentioned in this paper, anthocyanins serve the role of both active and intelligent systems. These pigments can be used as pH indicators due to their ability to change color in different pH range. Further, anthocyanins possess antioxidative properties and limited antimicrobial properties. Which make these compounds an ideal natural alternative to synthetic dyes and preservatives in smart packaging system. However, the instability and complexity in extraction, development and application restricts the commercial utilization of the pigments. Therefore, extensive research is required for developing an efficient waste valorization system, improved sensor technologies, thin film electronics, and relevant data system for sustainable future applications.

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