Color Changing Plastics for Food Packaging

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INTRODUCTION

Changes in consumer preferences and demand for safe and high quality food products have led to innovative developments and modifications to different types of packaging materials. Packaging plays an important role in the food industry because it helps to protect the product against environmental effects, communicates with the consumer as a marketing tool, provides the consumer with greater ease of use and time-saving convenience, and contains products of various sizes and shapes.[20] The quality and safety of a food products could be affected at various points during its distribution and transportation. Thus, any mishandling of the food product can have a significant impact on its safety and overall quality, especially if the integrity of the package is not maintained.[10]

For many consumers, the freshness and quality of a food is determined by the "use by" or "sell by" date that is printed on the package. Thus, these dates should be seen as a "good-faith promise of the freshness of the product".[10] In the United States, product dating is not generally required by government regulations (except for infant formula and some baby foods) and there is no uniform system for the current practice.[18] The recent outbreaks associated with the use of packaged cut vegetables, is an indication that product dating alone is insufficient for alerting consumers to the dangers of a contaminated product.

This dependence on the packaging to obtain information on the safety and or quality of a product is designed to allow consumers to make more intelligent purchasing decisions. This could be a tool for increasing sales if consumers are aware of the presence and purpose of new innovations on the package. Packages with the ability to detect changes occurring in the environment and respond by changing its properties or by producing a signal are referred to as active or intelligent packaging. These are sometimes referred to as smart packaging.

A package system is considered to be “active” if it actively changes the condition of the package product to extend its shelf life or improve food safety or sensory properties, while maintaining the quality of the food.[19] On the other hand, a package is “intelligent” if it has the ability to monitor the product, senses the environment inside or outside the package, and communicates with consumers.[9] In terms of food safety and quality issues, intelligent packaging systems can be helpful to communicate with consumers and provide information about the conditions of the food through a direct visual change.[7] Time-temperature indicators, gas leakage indicators, toxin indicators and spoilage detectors/freshness indicators are different types of intelligent packaging systems.[3] If the method an intelligent packaging uses to communicate with consumers is not easily recognized, the usefulness of the device is limited. One method of communicating that seems to work well with consumers is a change in color in response to a change within the product itself. This change in color should be sufficiently intense that it is easily recognized by consumers, processors or government regulatory personnel.

The incorporation of color changing plastics into food packaging materials is a method to alert consumers to the conditions inside a food package. These plastics can facilitate the identification of products that are progressing towards spoilage, or that have loss their quality and wholesomeness.

COLOR CHANGING PLASTICS

One of the emerging technologies with potential to revolutionize the packaging industry is the use of color changing plastics. These would be packaging with the ability to alert consumers of a potential problem with a food product by producing a color change as a visual warning. “Chromogenic” materials are those that change their optical properties in response to an external stimulus.[8] This could be triggered by change in temperature (thermochromic materials), irradiation from light (photochromic materials) and through the application of an electric potential (electrochromic materials), as examples.[1]

Polymer Opal firms

An example of a color changing material is polymer opal films developed by scientists at the University of Southampton in the United Kingdom and the Deutsches Kunststoff-Institut (DKI) in Darmstadt, Germany. These polymers contain crystals that are made of repeating units but have a large contrast in their components’ optical properties. This causes a range of frequencies to occur and this causes variations in the light that is reflected from these regions. These are called photonic band gaps. Thus, materials made with this would have colored and dark areas. The polymer opal films developed in Germany and UK had crystals having small regularily assembled particles but having areas of irregularities. In addition to this, tiny carbon nanoparticles were wedge between the crystalline spheres. Thus, incident light did not only reflect at the interfaces between the crystalline spheres and the surrounding materials, it was also scattered by the nanoparticles embedded between the spheres.[16]

Since nanoparticles are nanometers in dimension and have a high surface to volume ratio, the films produced are capable of having an intense color. The appearance of these colors could be influenced by changes in the manner in which the spheres are arranged and the placement of the nanoparticles. If flexible films are made with this material, stretching them will cause orientation of the lattice structure and changes to the distance between the spheres. This will cause a change in color to appear.

Assume that a flexible package made with this material is used to package a shelf-stable food. If this food becomes contaminated with gas forming bacteria, the sealed package will become bloated and pressure will build against the material. This could cause a stretching of the film and result in it changing its color. This would thus alert a customer to an unsafe packaged product.

Because of the potential to produce films with intense colors, this technology can be an alternative to the use of chemical dyes. Since many chemical dyes are toxic and/or environmentally unfriendly, the use of polymer opals eliminates issues such as the migration of toxic chemicals from food contact materials to packaged products. ***Figure 1*** illustrates the arrangement of the spheres of a polymer opal film. Compression of the film (a) changes the lattice arrangement and produces changes to the light reflection and thus the color change seen in (b) and (c).

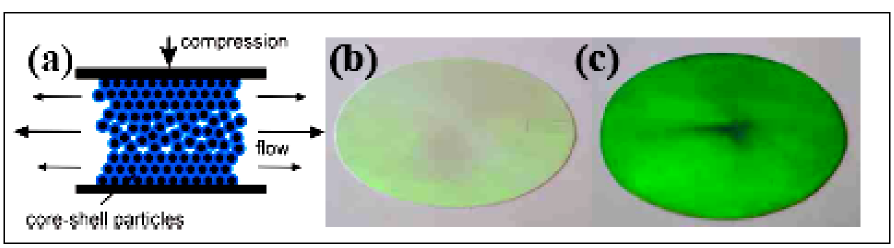

Figure 1: (a) Compression shear-assembly of polymer opal. (b-c) Optical images under natural lightning of 10 cm diameter polymer opal films, which are (b) undoped and (c) doped with 0.05% by weight carbon nanoparticles.[13]

Electrochromic Polymers

An electrochromic material is capable of undergoing reversible changes in its optical absorption properties when small ions are inserted electrochemically into its crystal structure. Therefore, an electrochromic device can be viewed "as an electrical battery with its charging state manifested as optical absorption".[1] According to Sotzing (2006), these polymers are capable of changing color if there is a change in the environment.[16] This technology seems very promising because these materials could be used as sensors in the food and security industries.[13]

Conjugated polymers are an interesting class of electrochromic materials due to their color tunability and high optical contrast.[14] Color changes in these are caused when they are impacted by an external stimulus capable of changing their λ_{max} and $\pi - \pi^*$ transitions. These changes are dependent on the nature of the energy gap between the molecules in the conjugated polymer's orbitals. These changes are all influenced by the nature of the conjugation. Thus, changes to the structure of the repeating units in the polymeric chain by processes such as oxidation or an electrical potential, will cause changes to the color of the polymer.

If a conjugated electrochromic polymer is exposed to an electrical potential and it is sufficient to oxidize the polymer, it will change its color. If a similar material is used to package a processed meat product, for example, the package will change color if exposed to a given quantum of light. The result will be a protection of the food from color loss. To create the electrical potential it would be necessary to laminate the conjugated polymeric film with inorganic oxides which could serve as an ion storage device. For example, Ma et al. (2007), created this ion storage device in sunglasses research by using indium tin oxide and vanadium oxide in sunglasses research.

Direct Incorporation of Color Indicators

Color indicators for fermented products, such as *kimchi* (fermented vegetable products in Korea), could be useful for monitoring the degree of fermentation that these products experience prior to consumption.[5] Oriental cabbage and radish are some of the vegetables used to prepare *kimchi*. They are salted after prebrining, blended with various spices and other ingredients and then fermented. Commercial *kimchi* products go through a continuous natural fermentation process during storage and distribution, yet their ripeness/over-ripeness cannot be detected by general testing methods without opening the packaging to access the product.[6] In 1999, Hong and Park evaluated the possibility of incorporating color indicators (bromocresol purple or methyl red) into polymeric films (polypropylene resin + calcium hydroxide as a CO_2 absorbent). These color indicating films were attached to the inside of sealed *kimchi* packages. The results obtained allow the researchers to detect the degree of ripening of the *kimchi* without the need to open the package. This color change occurred because bromocresol purple is yellow at pH 5.2 and changes to purple at approximately pH 6.8. On the other hand, methyl red is red at pH 4.2 and changes to yellow at approximately pH 6.2. As *kimchi* ripens it produces excessive organic acids and its pH falls.[6] Thus, once the pH falls below a given value, it will change the color of the indicator and this will signal that over ripening and quality loss have occurred. The direct incorporation of these additives into films used to package *kimchi* is a color indicating device that could help consumer to determine the quality of *kimchi* without opening the package.

Spoilage detectors/freshness indicators

These indicators are placed inside sealed package and are designed to alert consumers to chemical changes occurring within the product. They are sensitive to specific by-products that originate from deterioration reactions in the food.[3] Pacquit and collaborators (2007) used this approach to develop a smart packaging that was able to monitor the microbial breakdown of products in the headspace of packaged fish. This was done using pH indicator dyes that are sensitive to volatile amines associated with fish spoilage. This pH sensitive dye was entrapped within a polymeric matrix, and when the spoilage volatile compounds were released, visible color changes were observed as a response (see ***Figure 2***). ***Figure 3*** illustrates the working of this device for the detection of fish spoilage. The results indicated that a fast and sensitive detection of spoilage compounds in fish can be achieved by colorimetric methods.

Figure 2: Color changes to a bromocresol green (BCG) sensor in response to a fish spoilage.

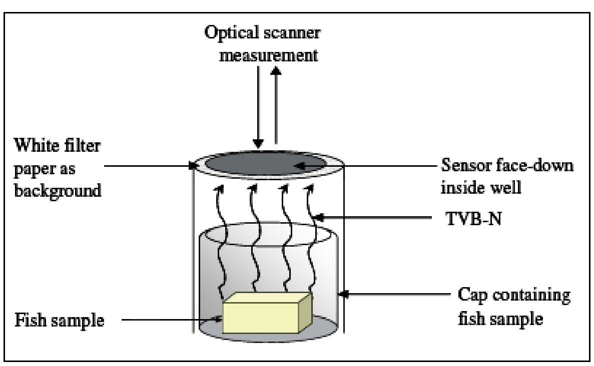

Figure 3: Diagram showing how the fish spoilage detector works (based on Byrne et al., 2002).

In an additional study, scientists at the Food and Drug Administration's National Center for Toxicological Research (NCTR) identified volatile amines as a potential link to certain seafood spoilage. Miller and collaborators at the NCTR subsequently developed a food quality indicator disk capable of detecting the level of volatile amines emanating from spoilt seafoods .[10] When put to the test, a gradual color change was observed in the disk as the seafood decomposed. According to Miller, the insertion of these indicators into packaged seafood products can help FDA inspectors to identify fish products that are unsafe for consumption and this helps to make the inspection process more effective.[10] Consumers are also beneficiaries of this technology since they will be alerted to presence of an unsafe product.

Time - temperature indicators

Variations in temperature is one factor that affects the freshness of food products. Although a product is processed, packed and shipped at the optimum temperature for prolong shelf life, during shipment and storage prior to retail sale, quality may be lost due to temperature fluctuations. To ensure that temperature abuse did not occur, time-temperature indicators on packages can provide consumers with an assurance and a sense of the product's quality.

Time-temperature indicators (TTI) are small measuring devices capable of showing a time-temperature-dependent relationship as an irreversible color change.[3] Fresh Check® indicator is an example of a TTI. This can be affixed to a package as a self-adhesive device and appears as a circle surrounded by a dark ring (see ***Figure 4***). Consumers are advised not to consume the product if the center circle is darker than the outer ring. The center circle changes color gradually upon accumulated temperature exposure and gives consumers an indication of the freshness of the food product.[4] This technology is based on the polymerization of diacetylenic monomers, whose rate is dependent on temperature.[9] As the environmental temperature rises, diacetylenic monomers polymerize and change to a darkened material. The application of this technique also works for heat processed foods. If these foods are under-processed the color indicator will not show a certain hue. This would be an indicator to processors that the product should either be discarded or reprocessed.

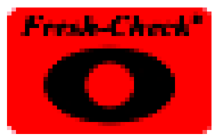

Figure 5: Fresh-Check® Time-Temperature Indicators

Color Changing Additives

Another example of a color changing package is a technology developed by Smart Lid Systems, (Sydney, Australia). This is a color changing coffee cup lid. This innovation has won several awards including a "WorldStart Packaging Award" in 2008 and the "Best of Show" Award at the Ameristar Awards Ceremony in 2007.[17] The smart lid is infused with a color changing additive which allows it to change from a coffee bean brown to a bright red color when exposed to an increase in temperature. If the red color is too intense, it indicates to consumers that the coffee in the cup is too hot for comfortable drinking (***Figure 5***). If the lid is cocked and not positioned correctly, the brown color will not be distributed evenly and this will indicate that a potential for spillage exists. The change in color starts at 38ºC and it reaches full intensity at 45ºC. This color changing additive is safe in food contact surfaces since it meets the requirements of the United

States Food and Drug Administration (FDA) regulations relating to direct food contact materials additives.[17]

Figure 5: Color changing disposable beverage lids showing increasing redness from left to right.[17]

CONCLUSION

Color changing plastics can be considered an innovative technology that can benefit not only consumers but manufacturers, retailers and regulatory agencies. In collaboration with scientists and experts from different fields (such as bioengineers, chemists, food scientists, among others), the safety, security and quality of food products can be improved. In addition, consumers can get the benefit of having the assurance that the foods they purchase are of good quality and safe from harmful chemicals and microorganisms. Food processors can also use these indicators as signals that a deviation in their operations has occurred and this allows them the opportunity to make corrective actions. Government regulators can also use these devices as an aid in being more efficient in doing inspections and when investigating outbreaks caused by contaminated or spoilt foods.

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