Innovation of oxygen indicator for packaging leak detector: A review

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Abstract. Oxygen is one of the factors causing the food product damage. Therefore, vacuum packaging or modified atmosphere packaging (MAP) is an effective solution offered. However, there is always a risk of leakage in the package especially in the packaging process, in the distribution process, and by the insect or rodent damage. Therefore, an oxygen indicator that helps retailers and consumers to detect leaks and to prevent them from buying leaking products is created. Its working principle is to show a color change that reflects changes in the composition of the gas. The use of oxygen indicators is beneficial not only for consumers but also for manufacturers of products who use this indicator for loyal consumers to maintain the consumer credibility with their products. Furthermore, technological advances encourage researchers to improve several important aspects of oxygen indicators such as product safety application, product cost retrenchment, ease of manufacture, and environmental friendliness. This article reviews the development of oxygen indicators and the advantages and disadvantages of each type of oxygen indicator and provides information for researchers and the MAP industry on the types of oxygen indicators that are well developed in the future.

1. Introduction
Food products are easily damaged, and therefore packaging is made to protect goods and facilitate the product distribution process [1]. Oxygen is one of the causes to the food and beverage products damage. Oxygen results that cause the rancidity of unsaturated fats, darkened pigments of fresh meat due to aerobic bacterial and fungal growth, deterioration of fruits and vegetables, and changes in product aroma [2] encourages researchers to create packaging innovations. Food packaging designed without gas or air is called vacuum packaging [3], and modified atmosphere packaging (MAP) is a packaging technique that changes the composition of gas in the package according to the needs of the type of food product [4] where both methods are expected to maintain quality and improve shelf-life of food products.
During the process of handling, preparation and transportation there is always the possibility of packaged food products in contact with physical, chemical and biological agents [5]. An innovative, smart packaging system is designed to monitor the quality or the environmental conditions (food products) or the external conditions of packaged food products through information from the visual changes [6]. Monitoring is performed throughout the food supply chain (from raw materials to manufacturing, packaging, distribution, product use, and disposal) in order to reduce food waste, facilitate tracking, and improve the logistics of food products [7].

Leaks in the MAP package or in the vacuum package result in disadvantages from implementing the packaging innovations [8]. Smart packaging as a gas detector that is most commonly used is an oxygen indicator as the effect of oxygen is quite fatal to the quality of food products using the technology of MAP or vacuum [9]. The presence of oxygen in the package can be indicated by a color change on the oxygen indicator [10]. Applying the oxygen indicator helps producers, distributors, and consumers to check for product leaks. Because of its important use, many studies on oxygen indicators aim to solve various problems ranging from price, quality, safety, features, environmental friendliness and production processes.

2. Oxygen Indicator

Smart packaging is defined as the packaging that can work smartly in facilitating decision making to extend shelf-life, increase safety, improve quality, provide information, and warn about possible problems [9]. In its application, smart packaging is divided into two categories known as internal contact inside the food package and external contact outside the food package [9]. The examples of smart packaging that measures the conditions outside the package are time temperature indicators (TTI), radio frequency identification (RFID), integrity indicators, bar codes, and microwave maturity indicators. While the examples of smart packaging that measures the conditions inside the package are gas indicators, pH indicators, product freshness indicators, thermochromic inks, biosensors for identification of pathogens or toxins, etc.

Leak has always been the cause to the integrity damage of flexible plastics [11]. When the leak occurs, oxygen enters the package as a trigger for oxidative reactions and aerobic microbial growth that cause damage to food products [12]. An oxygen indicator is included as a solution to provide information about the oxygen concentration in the package [13]. The definition of indicator as a smart packaging is that it is a device in the package that conveys information to consumers about microbial activity, food quality, and/or other objects [5]. Information about the presence of oxygen from the oxygen indicator is presented in color changes resulting from chemical or enzymatic reactions [14]. Commercially available oxygen indicators are Ageless Eye® (Figure 1.), Vitalon®, and Samso-Checker® [15].

![Figure 1. Schematic representation of the leak indicators](image)

The first report on the oxygen indicators was introduced in the 1970s [17,18] inspired by the "Blue Bottle" experiment and popularized by Campbell [19]. The composition of the oxygen indicator includes redox dyes (such as methylene blue), basic compounds (such as sodium hydroxide and potassium hydroxide) and reducing compounds (such as reducing sugars) [20], as well as optional solvent preparations (such as water or alcohol) and bulking agents (such as zeolites, silica gel,
cellulosic materials, polymers) [21]. Indicators can be formulated as labels, printed coatings, and tablets, or they can be laminated in polymer films [22]. Research and development of indicative packaging is very often combined with O₂ absorber and modified atmosphere packaging (MAP) [17]. Indicators have aspects that must be fulfilled which are easy to use, easy to read, cheap, quick at working or very sensitive [18].

3. Innovation of Oxygen Indicator

There have been two kinds of innovations in the activation of oxygen indicators in recent years, namely by using UV light (Figure 2.) and pressure (Figure 3.). The reason for the development of innovation, because the UV activated oxygen indicator is an almost ideal indicator [12] and the pressure activated oxygen indicator uses the simple working principle of the oxygen indicator by separating the composition in two compartments.

![Figure 2. Illustration of UV activated oxygen indicator, which has the following general formulations: semiconductor (SC), sacrificial electron donor (SED), redox indicator (initial, high oxidized form: DOx, reduced photo, usually white, reduced form: D_red).](image_url)

![Figure 3. The reaction scheme for the oxygen indicator mechanism is based on redox dyes, reduced D_red (bleached) and D_Ox are the forms of oxidized redox staining (colored). The reducing agent is usually the reducing sugar in alkalis, metal ions (often to be Fe²⁺) or ascorbic acid.](image_url)

3.1. UV-Activated Oxygen Indicator

The following are Indicator innovations that are activated using UV light data taken from the last few years.

3.1.1. Novel photocatalyst-based colorimetric indicator for oxygen: Use of a platinum catalyst for controlling response times. The indicator is made from Pt-TiO₂, methylene blue, and glycerol as the object electron donor that is dispersed or dissolved in polymer media (sulfonated polystyrene, SPS). The platinum catalyst of 0.38 % weight yields 2 days of photo-bleaching at 4 °C in the refrigerator, 1.5 days at the room temperature, and 12 h at 21 °C with 1.52 wt% platinum. The indicator is very sensitive to relative humidity above...
30% and slows down if it is below -10 °C due to freezing of glycerol. It is re-useable for about 5 times of use. This indicator is also water-proof. This platinum-coated indicator can be used as an 'open-in-fridge-time' indicator with a controlled time delay (from opening to full color recovery) via the Pt level stored in TiO$_2$ [23].

3.1.2. Bioinspired Molecular Adhesive for Water-Resistant Oxygen Indicator Films. The basis of the development of this research is the ability to attach the amino acid composition of the proteins found among the plaque-substrates on the shells. Shells can stick to almost any hard surface in wet environments. Dopamine (DA) was identified as a simplified shell protein rich in 3,4-dihydroxy-L-phenylalanine and lysine as it contains catechol and amine functional groups. This adhesive is applied in the colorimetric oxygen indicator dye washing. Simple immersion of the film indicator in DA solution reduces the film's contact angle with water, from 105 degrees to 65 degrees and reduces ionin leakage from 70% to 50%. The indicator film that is resistant to dye washing will lose the dye or be activated by UVB irradiation for 5 min and get colored when it shows oxygen. This is a sign of successful oxygen indicator. The highest hydrophilicity is obtained at a pH level of 8.5 [24].

3.1.3. Novel Water-Resistant UV-Activated Oxygen Indicator for Intelligent Food Packaging. This is the first study to use an alginate polymer to prevent the dye escaping from the colorimetric oxygen indicator film on contact with water. The composition of the oxygen indicator film is ionin, glycerol, P25 TiO$_2$, and zein as redox dyes, and sacrificial electron donor activated by UVB (intensity = 2.5 mW/cm$^2$) in 5 min. The oxygen indicator immersed in water for 24 h results in a leak of $80.80 \pm 0.45$% and decreases when given a layer of alginate (1.25%) as a coating polymer to $5.80 \pm 0.06$%. Another advantage is that it is easy during the photo-bleaching process and is sensitive when it comes in contact with oxygen. The required color recovery time is 4 h [25].

3.1.4. Leaching-Resistant Carrageenan-Based Colorimetric Oxygen Indicator Films for Intelligent Food Packaging. In this study, a UV-activated oxygen indicator that is resistant to dye leaching is developed using carrageenan. Carrageenan is a naturally occurring sulfated polysaccharide which in this study is able to bind dyes substantially that can reduce the leak rate of the tested redox dyes (MB, AA and Th) into the water. The dye leakage from the carrageenan-based film decreases slightly as the concentration increases. The oxygen indicator in the form of a mixture of MB, TiO$_2$, glycerol and carrageenan is successfully bleached with the UVC light radiation (intensity = 5.5 mW/cm$^2$) in 4 min (the bleaching rate decreases as the polymer concentration increases). The required color recovery time is 8 h. This indicator has an irreversible response [26].

3.1.5. Titanium Dioxide Nanotube-Based Oxygen Indicator for Modified Atmosphere Packaging: Efficiency and Accuracy. In this research, titanium dioxide nanotubes (TiO$_2$) become semiconductor photocatalysts for oxygen indicators. The synthesized TiO$_2$ nanotubes are a mixture of rutile and anatase with a specific surface area of 190.35 m$^2$/g; and a 3.34 eV wide-bandgap. The indicator composition is a mixture of TiO2 combined with glycerol; methylene blue; and hydroxyethyl cellulose (HEC) which is then filtered on the polyethylene terephthalate (PET) film. The result obtained is the quickly responding indicator to activation that is not affected by natural light, making it efficient and accurate when applied to food packaging. The color recovery time is 10 min [27].

3.1.6. Visible Colorimetric Oxygen Indicator Based on Ag-Loaded TiO2 Nanotubes for Quick Response and Real-Time Monitoring of the Integrity of Modified Atmosphere Packaging. This study is successful in synthesizing Ag-TNT with hydrothermal reduction resulting in a
surface area of 227 m² g⁻¹ and a band gap of 3.30 eV. The composition of this indicator includes Ag-TNT / MB / HEC / glycerol which can block the response of the indicator to natural light (wavelength > 380 nm) and respond to UV rays quickly and effectively during activation. The color recovery time is 10 min [28].

3.2. Pressure-Activated Oxygen Indicator

A pressure-activated oxygen indicator is still very recently being developed. The following are two innovations of the oxygen indicator.

3.2.1. New pressure-activated compartmented oxygen indicator for intelligent food packaging. This is the first study to propose a packaged-activated oxygen indicator by using three main components such as methylene blue (MB), glucose, and NaOH which are then separated into two compartments (Figure 4). Optimal conditions are obtained from the separation of MB and glucose solution from NaOH stored at 4 °C, 20 °C and 45 °C, in which the indicator does not change the color. This indicator does not require anaerobic conditions in the manufacturing, storage and distribution processes. This is a new, simple and practical oxygen indicator. A stable recovery time is 24 h [29].

![Figure 4. Schematic diagram and working principle of oxygen indicators in the compartment. (a) unnatural components (b) natural components](image)

3.2.2. A Natural Component-Based Oxygen Indicator with In-Pack Activation for Intelligent Food Packaging. The use of natural ingredients and activation of the indicator is an innovation in this oxygen indicator. The natural ingredients used are redox dyes replaced with biocatalysts (laccase), natural substrates (guaiacol) and reducing agents replaced with natural amino acids (Cys). Laccase solution is dissolved into compartment I and the mixture of guaiacol and Cys solutions is dissolved into compartment II. The oxygen indicator is active after the compartment barrier breaks. The response to the rate of discoloration produced by the oxygen indicator is directly proportional to the oxygen concentration given. The color recovery time is 2 h. This indicator is expected to make a major contribution to healthier and safer food packaging [30].

4. Advantages and disadvantages

According to Mills, the ideal oxygen indicator is the indicator of a light-activated redox reaction. The drawback at that time is that the dye indicator dissolves into the water [12]. Thus, the oxygen indicator activated using the UV light has become the most often research in the recent years to address this problem. The innovation of speed indicators in response to photo catalysts uses titanium dioxide and nanotechnology as well as blocking the natural light response. Advanced technology in producing
these indicators is directly proportional to the costs incurred. The fastest response to the UV activated oxygen indicators is 10 min. There are no data on the provision of some oxygen concentration to the indicator activated by UV light, as we know that the packaging leaks on the market are usually very small and difficult to detect.

Pressure-activated indicators present a simple new low-cost solution for production. The improvement of this indicator innovation from the first generation is the use of natural ingredients, and if it is with the oxygen detection only up to 1 %, it is better to conduct the oxygen level test under the value. The safety of this indicator still needs to be improved because the indicator is a liquid that has a risk of contact with food products if there is a leak in the indicator packaging.

5. Conclusion
The oxygen indicator activated using UV and pressure is an indicator that still needs to be developed in the future. It is because both are activated after being in a MAP packaging environment. This oxygen indicator is cheap and irreversible, and easily visible to humans. All of these are ideal factors for an oxygen indicator. As environmentally friendly indicators are still rarely developed, combining the strengths and weaknesses of each of the presented research results can be a reference for further researchers.

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