THE USE OF OXYGEN INDICATORS - ELEMENTS OF INTELLIGENT PACKAGING FOR MONITORING OF FOOD QUALITY

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ABSTRACT. Background: Producers and researchers are looking at not only the methods of protection against ingress of oxygen into the package, but also want to provide consumers with guarantees of quality food they buy. Therefore, large-scale studies are conducted and implementation of intelligent packaging. The operation of these packages is the use of interactive, the most colorful indicators to assess the quality of the packaged product.

Methods: This article describes intelligent packaging technologies and presents research for different types of oxygen indicators.

Results and conclusion: Indicators for the detection of oxygen allows the consumer to provide some information on the suitability of the product for consumption. Apart from that, they are a simple tool that allows you to reduce the costs associated with loss replacement, repair damaged products or their disposal. Construction of indicator contained in the package is related to the specific product and factor to be controlled.

Key words: intelligent food packaging, oxygen indicators.

INTRODUCTION

Oxygen is an essential element for all living organisms and also plays an important role in many chemical industrial processes, including those in which an absence of oxygen is required. On the other hand, oxygen level in the package headspace can increase with time due to poor sealing, air permeation through the package materials, and the package tampered with or damaged during storage and/or transportation. As the result, the food can be contaminated with oxygen and spoiled. Whereas conventional oxygen detection methods require expensive instruments and trained operators, visual oxygen indicators are cheap and enable consumers to detect the presence of oxygen in the food package with naked eyes [Ahvenainen, 2003]. Therefore, it is no surprise that the removal of oxygen in the food packaging industry is of immense importance. Producers and researchers are looking at not only the methods of protection against ingress of oxygen into the package, but also want to provide consumers with guarantees of quality food they buy.

In order to maximise the quality and safety of foodstuffs, a prediction of shelf-life based on standard quality control procedures is normally undertaken. Replacement of such time-consuming and expensive quality measurements with rapid, reliable and inexpensive alternatives has lead to greater efforts being made to identify and measure chemical or physical indicators of food quality. The possibility of developing a sensor for rapid quantification of such an indicator is known as the marker approach [Kress-Rogers, 2001].
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Indicators as elements of intelligent packaging

Intelligent packaging (also more loosely described as smart packaging) is packaging that in some way senses some properties of the food it encloses or the environment in which it is kept and which is able to inform the manufacturer, retailer and consumer of the state of these properties. Although distinctly different from the concept of active packaging, features of intelligent packaging can be used to check the effectiveness and integrity of active packaging systems [Hutton 2003]. Intelligent packaging devices are capable of sensing and providing information about the function and properties of packaged food and can provide assurances of pack integrity, tamper evidence, product safety and quality, and are being utilized in applications such as product authenticity, anti-theft and product traceability [Summers 1992, Day 2001]. Also, intelligent packaging makes it possible to monitor specific parameters in the medium of the packaged product [Bilska 2011].

Intelligent packaging devices include sensors, time-temperature indicators, gas sensing dyes, microbial growth indicators, physical shock indicators, and numerous examples of tamper proof, anti-counterfeiting and anti-theft technologies. Information on intelligent packaging technology can be obtained from other reference sources [Summers 1992; Day, 1989, 2001]. Besides, intelligent packaging systems attached as labels, incorporated into, or printed onto a food packaging material offer enhanced possibilities to monitor product quality, trace the critical points, and give more detailed information throughout the supply chain [Rodrigues & Han, 2003]. Intelligent tags such as electronic labelling, designed with ink technology in a printed circuit and built-in battery radio-frequency identity tags, all placed outside the primary packaging, are being developed in order to increase the efficiency of the flow of information and to offer innovative communicative functions. Diagnostic indicators were first designed to provide information on the food storage conditions, such as temperature, time, oxygen or carbon dioxide content, and thus, indirectly, information on food quality, as an interesting
complement to end-use dates [Dainelli et al., 2008]. Indicators are called smart or interactive because they interact with compounds in the food. Microwave heating enhancers, such as susceptors and another temperature regulation methods, are sometimes regarded as intelligent methods as well.

OXYGEN INDICATORS-REVIEW

First reports concerning indicators of oxygen presence were delivered in the 1970s. The structure of an indicator attached to the packaging is connected to the character of the product and factor which should be monitored. Indicators which change their color are most frequently used. The change of the color is combined with activity of a selected factor and allows for evaluation of the quality of the packed product. Indicator should be easy to use and read, should be cheap, should work fast and be highly sensitive. Most of these indicators are based on colour change as a result of a chemical or enzymatic reaction. These indicators have to be in contact with the gaseous environment inside the package and hence are in direct contact with the food [De Jong et al., 2005]. Also, in the following section, presented examples of different types of oxygen indicators and their characteristics.

Lee et al. [2008] developed a new range of colourimetric oxygen indicators that are irreversible, reusable, and UV-light activated. Such "intelligent ink" oxygen sensors comprise a UV-absorbing semiconductor, such as TiO₂, a redox-indicator, such as methylene blue, a sacrificial electron donor, such as triethanolamine, and an encapsulating polymer such as hydroxyethyl cellulose; the ingredients are mixed together, with water as the solvent, to form an ink. The ink can be coated or printed subsequently onto a variety of substrates to produce a blue oxygen indicator film, which, when activated by UV light, becomes colourless. The activated, that is, UV-photobleached, film remains colourless unless, or until, exposed to oxygen, at which point the reduced methylene blue is reoxidised back to its original blue form. Generated in this reaction, electrons are the particles of semiconductor SC [e-], and the electrons reduce the dye to a colorless form Dox Dred. The reduced form of the dye quickly returns to its original color in the presence of oxygen. This cycle can be repeated inducing UV index [Mills, 2005]. Some commercial colorimetric oxygen indicators already exist, for example the Ageless Eye produced by the Mitsubishi Gas Chemical Company, but these indicators suffer from high retail costs and some ambiguity as package integrity indicators, due to their reversible nature. These indicator tablet turns from blue into pink within 2-3 hours after O₂ has reached a zero concentration at 25°C and into blue again in about five minutes when it is in contact with O₂. In 2009, Mills and Hazafy proposed nanocrystalline ncSnO₂-based, UVB-activated oxygen indicator. Instead of TiO₂, they used SnO₂ as a photosensitiser. These UV-activated colourimetric oxygen indicator comprising: polymer/SED/redox dye/photocatalyst, where polymer = HEC, donor = glycerol, dye = MB and photocatalyst = ncSnO₂. Also, the use of ncSnO₂ as a photocatalyst in the UV activated oxygen-sensitive inks opens up many possible avenues of application as it allows for a much more controllable UV-activation step.

Vu and Won prepared in [2013] novel water-resistant UV-activated oxygen indicator. This novel alginate-based UV-activated oxygen indicator, which is not only highly resistant to dye leakage, but also fast in the colour recovery. Alginate is a linear anionic polysaccharide containing blocks of [1,4]-linked b-D-mannurionate [M] and a-L-guluronate [G] residues from brown seaweeds and bacterial species, and has been applied to various areas including biomedicine, food, and biocatalyst due to its biocompatibility, low toxicity, low price, and mild gelation by addition of divalent metal ions such as Ca²⁺ [Fernández-Pan, Ignacio, & Caballero, 2011; Kanmani et al., 2011; Lee & Mooney, 2012; Mongkolkajit, Pulisirisombat, Limtong, & Phisalaphong, 2011; Rehm, 2010; Won, Kim, Kim, Park, & Moon, 2005]. They used alginate because most of the redox dyes used for oxygen indicators are cations, and discovered that alginate can form water-insoluble complex with a redox dye. In this indicator alginate was used as the coating polymer so that it can bind to a redox dye and thus prevent the dye from leaching into water.
The most common dye used in the indicators is methylene blue, which is typically white in the reduced state and blue in the oxidised state. Other redox dyes used in O₂ indicators are 2,6-dichloroindophenol [Shirozaki, 1990] and \(N,N',N',N''\)-tetramethyl-p-phenylenediamine [Lenarvor, et al.,1993]. A reducing compound is added to the O₂ indicator to reduce the dye and to keep it in the reduced state during the packaging process. Common reducing compounds for O₂ indicators are reducing sugars, but inorganic salts as well as reduction by irradiation have also been used. An alkaline compound is added to the indicator to maintain the pH on the alkaline side and thus prevent too rapid an oxidation reaction of the dye [Mattila-Sandholm, 1998; Perlman, 1985]. Inorganic compounds, such as sodium hydroxide, potassium hydroxide, calcium hydroxide and magnesium hydroxide, have typically been used for this purpose [Arin 2001; Yoshikawa, 1982].

Krumhar & Karel [1992] presented two-step colour reaction indicator. In the first reaction step O₂-sensitive material is oxidised and the formation of an acid or peroxide occurs. These components will cause a colour change in the specific colorant included in the system.

Sumitani et al., [2004], presented oxygen indicator based on an organic/inorganic hybrid compound consisting of methylene blue, a cationic surfactant and a reductant intercalated into saponite. Researches proposed a mixture of a blue colored dye, methylene blue, a reductant in the form of ascorbic acid or reducing sugar, and cetyltrimethylammonium ion intercalated into synthetic saponite became colorless in an atmosphere having an oxygen concentration of less than 0.1 vol%, and then returned to its blue color as a result of subsequent exposure to air. Besides, oxygen indicator, in the form of a thin film coated on paper prepared by adding a pigment, phloxine B, to the above organic/inorganic hybrid compound, exhibited a pink color at oxygen concentrations of less than 0.1 vol%, and a blue color at oxygen concentrations of higher than 0.5 vol%.

Others researchers proposed oxygen indicator, formulated from a combination of electrochrome, titanium dioxide and EDTA [Roberts et al., 2001]. They used polyviologen electrochromes which showed much faster reduction after exposure to UV light. Viologens are a family of electrochromic compounds which are pale in the oxidised form and highly coloured in the reduced form [Monk, 1998]. Besides, viologens have highly anodic redox potentials. Polyviologens retain the redox properties of the viologen parent compounds but are less susceptible to possible migration within food packaging [Factor, 1972 ; Simon, 1972]

Kaas R.L., in [2010], prepared oxygen indicator dye formulation utilizing methylene blue has been used to qualitatively demonstrate the oxygen barrier level of four side sealed pouches made with various barrier laminations before and after retort processing. Presented method can be used to assess barrier of the entire package and demonstrate areas of localized damage to the barrier. This indicator was prepared to quick and efficient means of assessing the barrier level of completed packages. Also, the formulation of oxygen indicator was based on methylene blue and glucose dissolved in water adjusted to pH of 11-12 with NaOH. Natural agar is added to gel the system and immobilize the indicator.

Lawrie et al., [2012] presented simple inkjet-printed, UV-activated oxygen indicator. In this indicator colloidal TiO₂ particles are made prior to inkjet-printing, allowing a water-based, UV activated, oxygen-sensitive ink for inkjet printing to be formulated that is suitable for printing by a DOD PIJ desktop printer. This colorimetric oxygen indicator does not contain a resin, consisting only of titania intimately mixed with MB and tartaric acid, and so is unlike any previous O₂-sensitive inks, such as the powder TiO₂/MB/glycerol/HEC inks. On the other hand, more recently, TiO₂ inks contributing added photocatalytic functionality [Arin et.al., 2011; Oh et.al., 2012; Manga et.al., 2010; Bernacka-Wojcik et.al., 2010] rather than simply colour, have been achieved, with the advantage of more uniform coverings spanning larger areas, in comparison to the more traditional spin, dip, or doctor blade coating techniques. These inkjet-printed TiO₂ thin films involve printing a TiO₂ sol-gel precursor [Dzik et.al., 2010; Čermá et.al., 2011] on glass, followed by high
temperature treatment of the printed layer to create a highly crystalline film of titanina.

Inkjet printing is now becoming increasing popular in the packaging industry. The most common applications of inkjet printing in the food packaging industry [Leach & Pierce, 1999] are: date-stamps, batch codes and any other variable information required on a package, with most food packages marked in some manner by inkjet printing. Inkjet-printing is becoming increasingly popular for functional [Magdassi, 2010] as well as standard, coloured-inks. Such functional inks include electrically conductive inks for flexible displays or sensors, [Wu et al., 2009, Courbat et al., 2010] ceramic inks for printing on tiles, [Magdassi, 2010] and inks which can be printed to form 3D structures. Inkjet printing itself falls under two broad classifications [Leach & Pierce, 1999; Magdassi, 2010] - continuous inkjet [CIJ] printing and drop on demand [DOD] inkjet printing. Of the two, DOD inkjet-printing is a much simpler and more environmentally-friendly system and is increasingly being used in the packaging industry to print directly on packages still on the packaging line, or on a web of polymer material similar to a flexo printing system. The most common DOD inkjet-printing method, used here, is piezoelectric inkjet [PIJ] printing whereby the oscillation of a piezo crystal [Magdassi, 2010; Kui & Tay, 2003] creates a pressure pulse, forcing an ink droplet out of the print head and onto the substrate.

SUMMARY

A numerous of literature reports on the oxygen sensor indicates a growing interest in this type of intelligent solutions. This is undoubtedly a significant role containing the food packaging. Packaging plays an increasingly important role in the whole food chain ‘from the field to the consumer's table’. Also, packaging has allowed us to have a wide variety of foods year round that would not be possible without the protection of the package. Foods now have a longer shelf life, resulting in less loss due to spoilage. For this undoubtedly contributes to use oxygen indicators. Oxygen indicators are used in intelligent food packaging, which monitors the condition of packaged food to give information on the food quality during transport and storage. Today, application of intelligent package leak-indicating systems in Europe has been limited to some time-temperature indicators. However, some food producers are increasingly seeking extra merchandising and safety features. The visible indicators are ideal in many cases, however, in the future it can be expected that an intelligent package can contain more complex invisible messages that can be read at a distance [Hurme & Ahvenainen, 2003].

To sum up, there are several reasons for the bright future of intelligent packaging with oxygen indicators:
− the significance of freshness and safety will increase,
− the demands of consumers will increase,
− globalisation and expansion of the marketing area make logistic chains longer placing more demands on traceability,
− the facilitation of in-house control for industry and retailing in the complete food supply chain
- intelligent packaging can also monitor product quality and trace the critical points in the food supply chain [Ahvenainen, 2003].

Besides, oxygen indicators should be inexpensive, easy to read and store, irreversible in response and provide instant assurance of package integrity, both on the packaging line and once it reaches the consumer. Ideal indicators should change a colour which is easily perceived by the untrained eye, without requiring any specialist analytical equipment [Mills, 2005].

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ZASTOSOWANIE WSKAŹNIKÓW TLENU - ELEMENTÓW OPAKOWAŃ INTELIGENTNYCH DO MONITOROWANIA JAKOŚCI ŻYWNOŚCI

STRESZCZENIE. Wstęp: Produenci i naukowcy zwracają uwagę nie tylko na zabezpieczeniu opakowania przed wnikańiem tlenu, ale również na zapewnieniu konsumentom odpowiedniej jakości żywności. W związku z tym na dużą skalę prowadzone są badania i wdrażanie opakowań inteligentnych.

Działanie opakowań inteligentnych opiera się na zastosowaniu interaktywnych wskaźników, które poprzez zmianę barwy pozwalają ocenić jakość zapakowanego produktu.

Metody: W artykule opisano inteligentne technologie pakowania żywności oraz przedstawiono badania nad różnego rodzaju wskaźnikami tlenu.

 Wyniki i podsumowanie: Wskaźniki do wykrywania obecności tlenu dają konsumentowi informację o przydatności produktu do spożycia. Poza tym, są prostym narzędziem, które pozwala na zmniejszenie kosztów związanych z wycofywaniem przeterminowanych produktów. Budowa wskaźnika umieszczanego w opakowaniu jest związana z konkretnym produktem i kontrolowanym parametrem.

Słowa kluczowe: inteligentne opakowania żywności, wskaźniki tlenu

DIE ANWENDUNG VON SÄUERSTOFF-ANZEIGERN ALS ELEMENTEN DER INTELLIGENTEN VERPACKUNGEN ZUR ÜBERWACHUNG VON LEBENSMITTEL-QUALITÄT

ZUSAMMENFASSUNG. Einleitung: Produzenten und Wissenschaftler zielen in ihrem Wirken darauf hin, die Verpackungen nicht nur vor dem Eindringen des Sauerstoffes zu schützen, sondern auch den Konsumenten die entsprechende Qualität von Lebensmitteln zu gewährleisten. Im Zusammenhang damit werden im großen Umfang Untersuchungen geführt und effektive Einführungen von intelligenten Verpackungen betrieben. Die Funktionsbetätigung der intelligenten Verpackungen stützt auf die Anwendung von interaktiven Anzeigern, die durch Veränderung von Farben die Qualität des verpackten Produktes zu beurteilen erlauben.

Methoden: Im Beitrag wurden intelligente Technologien für das Verpacken von Lebensmitteln beschrieben und Untersuchungen von verschiedenartigen Sauerstoff-Anzeigern dargestellt.


Codewörter: intelligente Verpackungen für Lebensmittel, Sauerstoff-Anzeiger

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