LogForum

> Scientific Journal of Logistics <

2015, 11 (1), 7-14

DOI:10.17270/J.LOG.2015.1.1

http://www.logforum.net p-ISSN 1895-2038 e-ISSN 1734-459X

INTELLIGENT FOOD PACKAGING - RESEARCH AND DEVELOPMENT

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ABSTRACT. Packaging also fosters effective marketing of the food through distribution and sale channels. It is of the utmost importance to optimize the protection of the food, a great quality and appearance - better than typical packaged foods. In recent years, intelligent packaging became very popular. Intelligent packaging is becoming more and more widely used for food products. Application of this type of solution contributes to improvement of the quality consumer life undoubtedly. Intelligent packaging refers to a package that can sense environmental changes, and in turn, informs the users about the changes. These packaging systems contain devices that are capable of sensing and providing information about the functions and properties of the packaged foods. Also, this paper will review intelligent packaging technologies and describe different types of indicators (time-temperature indicators, freshness indicators).

Key words: intelligent packaging, time-temperature indicator, freshness indicator.

INTRODUCTION

Packaging food technologies are developing as a response to consumer demands or industrial production trends towards mildly preserved, fresh, tasty and convenient food products with prolonged shelf-life and controlled quality. In addition, changes in retailing practices, or consumers lifestyle, present major challenges to the food packaging industry and act as driving forces for the development of new and improved packaging concepts that extend shelf-life while maintaining and monitoring food safety and quality [Dainelli et al. 2008]. Introduction of active and intelligent packaging can extend the shelf life of food or to improve its organoleptic properties and thus prevent food losses. According to the FDA report of 2011, every year is thrown away about 1.3 billion tons of food. Every year only in Europe, 89 million tons of wasted food, and the average European household rubbish thrown on 20-30% of food purchased. New packaging solutions allow to improve the economic aspect. Each year is grows interest in active and intelligent packaging. This is evidenced by the fact that the global market for food and beverages of active and intelligent coupled with controlled/modified atmosphere packaging (CAP/MAP) increased from $15.5 billion in 2005 to $16.9 billion by the end of 2008 and it should reach $23.6 billion by 2013 with a compound annual growth rate of 6.9%.

The interest in intelligent packaging is also reflected in the increasing number of patents granted within the field of TTIs as well as freshness and gas indicators that have been

Citation: Dobrucka R., Cierpiszewski R., Korzeniowski A., 2015, Intelligent food packaging - research and development. LogForum 11 (1), 7-14. DOI:10.17270/J.LOG.2015.1.1
URL: http://www.logforum.net/vol11/issue1/no1
Accepted: 23.11.2014, on-line: 29.12.2014.

granted in the recent years. It is related not only to the change in consumers' lifestyle, but also to the opportunity to use the produced food in a better way. The use of intelligent packaging, i.e. freshness indicators, would help optimise the time limit of product storage. Research shows that although the majority of respondents perceive perishable food products as safe, about 90% of them are sure that freshness indicators would help them monitor the quality of food products kept at home. The respondents would accept the increase of product price related to equipping the packaging with the indicator. The acceptable increase would be USD 0.14 for fresh meat and USD 0.25 for salads [Fortin et al. 2009].

The aim of this paper is the overview of active and intelligent packaging materials, developed in relation with the search for environment friendly packaging solutions, which at the same time fulfil the requirements of clients.

INTELIGENT 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]. 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].

Another division may be made in relation to the use of measurement instruments: indicators that can be read without using measurement instruments and indicators that require such instruments. From the perspective of an individual customer, who usually uses products in unit packaging where the indicator is to show the quality of the bought product, the necessity to use measurement instruments is unacceptable. Smart packaging can be divided into three groups:

1. indicators of product exposure to high temperature and duration of activity,
2. indicators of freshness,
3. indicators of the presence of gas and indicators of integrity.

Besides, each indicator used in packaging should be characterised by the following features [Mills 2005]:

- low price,
- ability to read without having to use the apparatus,
- non-toxic,
- stability,
- sensitivity,
- reaction should be irreversible,
- easily introduced into the package.

TIME-TEMPERATURE INDICATORS (TTIS)

Time-temperature indicators or integrators (TTIs) are defined as simple, cost-effective and user-friendly devices to monitor, record, and cumulatively indicate the overall influence of temperature history on the food product quality from the point of manufacture up to the consumer [Taoukis & Labuza 1989; Giannakourou et al. 2005]. Temperature indicators show whether products have been heated above or cooled below a reference (critical) temperature, warning consumers about the potential survival of pathogenic micro-organisms and protein denaturation during, for example, freezing or defrosting processes. Furthermore, TTIs have also been applied to assess the pasteurization and sterilization process [Mehauden et al. 2007, Tucker et al. 2007, 2009].

The visible response thus gives a cumulative indication of the storage temperature to which the TTI has been exposed. TTIs may be classified as either partial history or full history indicators, depending on their response mechanism. Partial history indicators do not respond unless a temperature threshold has been exceeded and indicate that a product has been exposed to a temperature sufficient to cause a change in product quality or safety. Full history TTIs give a continuous temperature-dependent response throughout a products history and constitute the main focus of interest for research and commercial exploitation [Kerry et al 2006]. Besides, time table indicators display a continuous temperature-dependent response of the food product. The response is made to chemical, enzymatic or microbiological changes that should be visible and irreversible, and is temperature dependent [Rodrigues & Han 2003]. Wu et al. [2013] prepared TTI indicator on the basis of the chemical reaction between urease and carbamide was developed. The discoloration kinetics of urease-based TTI was explored. The mathematics formula that revealed the relationships of the change of TTI color with time and temperature has been established. The activation energy of urease-based TTI was 23.05 ± 1.15 kJ/mol (±95% confidence interval). This type of TTI indicator has the potential to apply to some time-temperature dependence foods with similar Ea values. The most popular commercial TTIs are apparently TEMPTIME (formerly LifeLine™) 3M Monitor Mark®, and Vitsab®. TEMPTIME Fresh-Scan test operates on the basis of polymerisation process. During polymerisation, the absorption of radiation is shifted in such a way that it becomes visible. Before it is used, the indicator must be stored in low temperature in order to avoid premature reaction. A suitable solution for customers is provided by the indicator TEMPTIME Fresh-Check® on self-adhesive labels. The indicator is of round shape and it is encircled with a ring of the reference colour. As the product ages, the shade of the circle surface becomes deeper. In 3M Monitor Mark, if the set parameters are exceeded, it is signalled by the change of colour of a rectangular window on the label and a moving colour. The pace of colour movement depends on temperature. The colour changes within less than 24 hours upon exceeding the set temperature by 1^{o}C.

VISTAB is an indicator that provides comprehensive information about all deviations from the optimal temperature during the whole distribution cycle. The indicator consists of an external rectangular body and a transparent container located inside it. The container is divided into two parts. One of them contains lipase and pH indicator, while the other - suitable fatty substance. After the activation of the indicator, which is effectuated by the destruction of the barrier between the two containers, the process of enzymatic hydrolysis of fats starts. It results in the change of pH and, at the final stage, change of the solution colour. OnVu ™ indicator is another proposal introduced in cooperation with BASF. At present, it is offered in the form of a label, but it can also be printed directly on packaging. After activation with UV radiation, the ink becomes intensely blue. During exposition to temperature, this part of the drawing is becoming more and more bright. The product is suitable for use as long as there is a marked contrast between the ink and the surface of the model.

FRESHNESS INDICATORS

The indicators of freshness are used in order to signal when the condition of the product becomes unacceptable during storage, transport, retail sale and in the consumer's house [Smolander 2003]. The signalisation operates on the basis of the change of the look of the indicator, which occurs as a result of the change of the composition of packaging atmosphere, which is a consequence of chemical and microbiological changes of the packed product. As a result of these changes, various chemical compounds, such as carbon dioxide, volatile amines, acetic acid, are emitted to the atmosphere of packaging [Smolander 2003, Kuswandi et al. 2013]. These metabolites react with the substances contained in the indicator, usually causing the change of the metabolite colour. The metabolite used most frequently for the structure of indicators is carbon dioxide. The indicator consists in a solution with a dye that changes its colour due to pH alternations, and a membrane which passes carbon dioxide which separates it from solution environment. Carbon dioxide from the atmosphere of packaging permeates through the membrane and dissolves in the solution, which leads to the change of pH. The balance is achieved very quickly, and the colour of the solution changes when the relevant concentration of hydrogen ions is exceeded. The colour change can be measured and compared with the model. The solutions based on this mechanism were suggested in numerous patents and publications.

One of the examples of application is the suggestion presented in the work of Nopwinyuwonga [Nopwinyuwong et al. 2013]. The work presents the relation between the amount of volatile compounds emerging during the storage of Thai desserts and the number of microorganisms developing within them. The products of metabolism are compounds of low molecular mass such as organic acids, ethanol, carbon dioxide, and sometimes also aldehydes or ketones. Carbon dioxide emerging as a result of decomposition was used in order to change the colour of the indicator. Freshness indicators based on the measurement of carbon dioxide are used also in order to assess the freshness of kimchi, a popular Korean dish. It consists of fermented vegetables, mainly napa cabbage, a large amount of garlic, onion and seafood. Unfortunately, the commercially available packed products still undergo fermentation; therefore, they cannot be tested without destroying the packaging. For this reason, there has been suggested a solution using carbon dioxide sensor. Another suggested way to control the composition of product packaging atmosphere is the use of the suspension of chitosan and 2-amino-2-methyl-1-propanol in distilled water. The suspension is packed in packets and placed in the packaging. Studies show that when the dish was stored, pH of the solution dropped to 5.8. At the end of the storage period, the transparency of the liquid changed considerably. When pH drops, the non-transparent white solution of chitostan gradually transforms into a solution which is visibly transparent. According to the authors, the indicator can easily be used in order to determine which product packaging is not fermented and to detect the beginning of optimal fermentation [Jung et al. 2013].

Another proposal is a colourful indicator based on bromophenol blue. It was suggested in order to assess the freshness of guava fruit (Psidium guajava L.). It operates similarly to the solutions described earlier. When the fruit ripens, the colour of the indicator changes from blue to green. Green colour means that the fruit is too ripen. The authors claim that the cost of the indicator should be relatively low (about USD 0.15) in industrial production and mass use.

A more interesting solution is the use of quaternary ammonium salts in order to solubilise pH factor in a hydrophobic polymer, e.g. ethyl cellulose. This sensor does not contain the classic water buffer, and its role is performed by tetraoctylammonium hydroxide (TOA-OH). The indicator also includes a polymer which permeates gases. The process of detecting carbon dioxide consists of several stages. In the first place, there should emerge an ion pair between protonated indicator (DH) and quaternary ammonium base (QOH). As a consequence, there emerges a hydrate with an intense colour ($D^{+}Q^{-}\cdot H2O$). The hydrate is then dissolved in polymer. The indicator obtained this way can react with CO2 in the atmosphere [Mills et al. 1992].

OXYGEN AND CARBON DIOXIDE INDICATORS

Oxygen and carbon dioxide indicators can also be used to monitor food quality. They can be used as a leakage indicator or to verify the efficiency of, for example, an oxygen scavenger. 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]. Conventional oxygen indicators are known to use methylene blue (methyl thionine chloride) MB, a dye that reversibly changes its color upon oxidation and reduction [Sumitani et al. 2004]. 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 TiO_2, 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. Indicator is not active until it is exposed with UV light.

There are indicators based on fluorescence. The reaction is based on the phosphor layout has been extinguished when in contact with molecular oxygen. Luminescent compounds are placed in the gas permeable and impermeable to ions materials such as silicone rubber or an organic polymer, such as poly(vinyl chloride), to create thin film, oxygen indicators [Mills & Thomas 1997]. One of most popular is tris (4,7-diphenyl-1,10-phenanthroline) ruthenium (II) perchlorate, i.e. $[Ru(dpp)_3](ClO_4)_2$, where dpp is the complexing ligand, 4,7-diphenyl-1,10-phenanthroline. The most commonly-employed leak indicator used in food packaging is a colorimetric redox dye-based indicator [Mills 2005].

Changes in the concentration of organic acids such as n-butyrate, L-lactic acid, D lactate and acetic acid during storage offer potential as indicator metabolites for a number of meat products [Shu et al. 1993]. Colour based pH indicators offer potential for use as indicators of these microbial metabolites. Another example of microbial indicators is system based on immunochemical reactions that occur in the barcode [Goldsmith 1994], and the barcode will become unreadable when a particular microorganism is present [Rodrigues & Han 2003].

Ethanol, like lactic acid and acetic acid, is an important indicator of fermentative metabolism of lactic acid bacteria. Randell et al. [1995] reported an increase in the ethanol concentration of anaerobically MA packaged marinated chicken as a function of storage time. The Lawrence Berkeley National Laboratory has developed a sensing material for the detection of Escherichia coli 0157 enterotoxin [Cheng & Stevens 1998]. The material is composed of cross-polymerized polydiacetylene molecules that can be incorporated into the packaging film. As the toxin binds to the molecules, the color of the film changes permanently from blue to red [Smolander 2000].

According to Mills, an ideal oxygen indicator for the food packaging industry should also exhibit an irreversible response towards oxygen. Indicator should illustrate why this latter feature is so desirable it is worthwhile considering the response of a reversible oxygen indicator in a MAPed food package that, in a not too unlikely scenario, sometime later develops a small leak. Obviously, the indicator will show no oxygen is present in the package until the leak develops, at which time it will indicate the presence of oxygen. However, if the leak is small, it is very possible that the subsequent rapid increase in microbial growth will be such that within a short time the oxygen in the atmosphere in the package will be converted to carbon dioxide and the rate of bacterial metabolism will be matched by the rate of oxygen ingress. Besides, an ideal oxygen indicator should be easily incorporated into the food package and so is best applied as an ink, which must be printable on paper and plastic. In the food industry such an ink falls under the umbrella heading of intelligent packaging. Besides, this is technology able to monitor and/or give information about the history and/or quality of the packed food [Mills 2005].

CONCLUSIONS

Changes in consumer preferences have led to innovations and developments in new packaging technologies. Research and development in the field of active and intelligent packaging materials is very dynamic and develops in relation with the search for environment friendly packaging solutions. Active and intelligent packaging is becoming more and more widely used for food products. Application of this type of solution contributes to improve the quality of consumer life, undoubtedly the consumer. Besides, innovation systems will improve the product quality, enhance the safety and security of foods, and consequently decrease the number of retailer and consumer complaints.

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INTELIGENTNE OPAKOWANIA - BADANIA I ROZWÓJ

STRESZCZENIE. Opakowania umożliwiają efektywny marketing żywności przy zastosowaniu różnych kanałów sprzedaży i dystrybucji. Najważniejszym zadaniem jest optymalizacja ochrony żywności, jej jakości i wyglądu. W przeciągu ostatnich lat, wzrasta popularność opakowań inteligentnych, które zaczynają być stosowane dla coraz to większej liczby produktów żywnościowych. Zastosowania ich przyczyniają się do poprawy życia konsumenta. Określenie "opakowania inteligentne" stosuje się do opakowań wyczuwających zmiany w otoczeniu oraz będących w stanie informować o tych zmianach. Systemy opakowaniowe zawierają w sobie urządzenia wykrywające i dostarczające informacji dotyczących stanu zapakowanej żywności. Praca ta dokonuje przeglądu technologii opakowań inteligentnych oraz opisuje różnego rodzaju wskaźniki (temperatury, czasu i świeżości).

Słowa kluczowe: opakowanie inteligentne, wskaźnik temperatury, wskaźnik świeżości.

INTELLIGENTE VERPACKUNGEN - FORSCHUNG UND ENTWICKLUNG

ZUSAMMENFASSUNG. Verpackungen ermöglichen ein effizientes Marketing von Nahrungsmitteln mit der Anwendung verschiedener Verteilungs- und Verkaufskanäle. Die wichtigste Aufgabe dabei stellt die Optimalisierung des Schutzes von Nahrungsmitteln, deren Qualität und Aussehen dar. In den letzten Jahren wächst ständig die Popularität von intelligenten Verpackungen, die bei immer höherer Anzahl von Nahrungsmitteln Anwendung finden. Deren Anwendung trägt zur Verbesserung des Kunden-Lebens bei. Die Bezeichnung "intelligente Verpackungen" nimmt man in Anspruch für die Verpackungen, die auf die Veränderungen der Umwelt zu reagieren und über die sich vollziehenden Veränderungen zu informieren imstande sind. Systeme für die intelligenten Verpackungen haben Einrichtungen zur Ermittlung und Mitteilung von relevanten Informationen über den Zustand der verpackten Nahrungsmittel inne. Die vorliegende Arbeit nimmt einen Überblick über die Technologien für intelligente Verpackungen vor und beschreibt verschiedenartige Anzeigegeräte für die Temperatur-, Zeit- und Frischwerte.

Codewörter: intelligente Verpackungen, Temperatur-Anzeiger, Frischzustand-Anzeiger

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