Additives in Polymer Packaging for Sensing Food Spoilage

Swapnil D. Patkulkar
T.Y.B.Tech.
Polymer Engineering and Technology Department

Pratiksha G. Nihul
T.Y.B.Tech.
Polymer Engineering and Technology Department

Abstract

Food spoilage due to microorganisms is a major cause of concern to both food manufacturing and packaging industries. Shelf-life of the product cannot be accurately determined as spoilage depends on the conditions during transport and storage, which vary. Monitoring the food quality on an ongoing basis will require repeated penetration of the packaging in order to perform testing, followed by repackaging, which adds to cost of product. Hence the need of a sensor that can give us a continuous indication about the freshness of the food item without penetrating the packaging is felt. The solution can be incorporation of sensor into the packaging as an additive so that the packaging itself will help us continuously monitor the quality of food as it is in continuous contact with it. Some sensors of natural origin such as betalains, turmeric, as well as some other pH indicators give an observable colour change in presence of amines or other food degradation products. Also, Molecularly Imprinted Polymers (MIPs) can be incorporated into the polymer packaging to specifically react with biogenic amines produced by food spoiling microorganisms to give a change in fluorescence emission, which can be observed using a scanner. All this will help the common man in checking the quality of the food without opening the packaging.

Keywords: Molecularly Imprinted Polymers, pH indicators.

1. Introduction

Food is a basic need for survival. Man has known for centuries how to cultivate food. Earlier days, food was not cultivated in order to store it for a long time; it used to be consumed as soon as possible. Man then learned to store food and also to pack and export it. Earlier packaging generally used to be primitive, but slowly and progressively, variety of packaging and storing techniques emerged. In the modern era, polymers (plastics) are effectively used for this purpose with improved shelf-life. The polymers used include Polypropylene (Snack food bags & Confectionery bags), Polyethylene (Low Density PE (LDPE) - rice & for bag manufacture (bread), High Density PE (HDPE) - for making containers, e.g., crates, bottles (for milk), bags, forks, etc.), Polyvinylchloride (shrink wrapping of cheese & meat), Polystyrene (disposable plates & cups), High Impact PS (yogurt & ice cream tubs), Acrylonitrile Butadiene Styrene (ABS - Margarine tubs), etc.[6]

2. The Need for Introduction of a Sensor

Food's shelf-life can be enhanced by packaging suitably; however, chances of it getting spoiled cannot be altogether neglected. Conditions during transport and interim storage cannot be fully predicted, monitored and controlled continuously. Due to this, packed food quality invariably changes at varied and unpredictable pace. This helps in breeding of certain disease causing microorganisms called pathogens. Hence food has to be tested at regular intervals. For this, one has to have direct access to the food product, which means piercing or even breaking the packaging. After testing, the food needs to be repacked. This involves labour, time, resources and hence money. The solution to this can be incorporation of a sensor into the packaging as an additive so that the packaging itself will help us continuously monitor the quality of food as it is in continuous contact with it.

3. Existing Sensors

Additives used for this purpose include colour changing pH indicators, time-temperature Indicators, etc. Degradation of many food products changes pH because of generation of specific types of compounds. Food degradation is a function of time and/or temperature. When food such as meat, fish, etc. degrades, certain amines are produced, while in milk and some of its by-products acids are produced (lactose getting converted to lactic acid). Certain sensors, like betalains, flavonoids, turmeric, methylene blue, etc., can be used to indicate generation of these food spoiling by-products by reflecting an observable change in colour.

3.1 Working

Pathogen is an agent, especially a living microorganism such as a bacterium or fungus, which causes disease[13]. Sensor compounds, in the presence of pathogens, undergo colour change & this colour change is employed as an indicator of food quality. The pH indicators are pre-exposed to an opposite pH initially[3]. For the presence of an amine (basic), turmeric can be an effective indicator. It is pre-exposed to an acidic pH where it is yellow. When the food degrades, amines are produced, basicity is imparted on the indicator and it turns red[12].

3.2 Selection of Indicators

The indicators which are to be used must be easily activated and must exhibit an easily measurable, reproducible time-temperature dependent change. This change must be irreversible and should be easily correlated to the extent of food deterioration[10]. The indicators which can be used for this purpose include betalains (obtained from beet), flavonoids (obtained from cabbage), turmeric, etc. For e.g., considering the case of Flavonoids; Anthocyanins, which are one of the major flavonoid classes, are responsible for various shades

of red and blue in many fruits. At pH 1, they are orange red. With increase in pH colour gradually fades as colourless pseudobases are formed. In mild alkaline conditions, they are blue. This is a reproducible change[7].

3.3 Ways of Making Sensor Strips

Indicators are associated with or applied to packaging material for e.g. in the form of label or as a part of a cap (e.g. in case of milk), or as a part of packaging material itself (e.g. chemically integrated within a polymer wrap or container). Consumer may judge the quality of food by comparing the colour of indicator to a reference chart supplied with the food ideally located adjacent to the indicator which illustrates the colour shadings & the corresponding food quality level.

A variety of other readouts is possible, for e.g., words or symbols, may be printed using a colour changing indicator as ink on a clear or a white background or on a coloured background where the coloured background is non indicating (i.e. a fixed colour) (see Fig.1).

If the colour matches the initial colour of the indicator, then letters or symbols will appear as the food deteriorates. The indicator comprises, a matrix having at least one surface for establishing fluid communication with the food to be monitored &, immobilized within

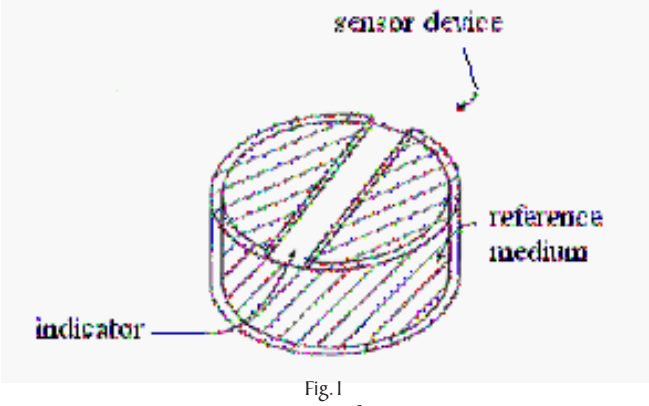

Fig.1
Source- Ref. 3

the matrix, an amine responsive compound that itself comprises or consists of betalains (or derivatives), flavonoids (or derivatives) or a combination of these[3].

4. A new approach - Molecularly Imprinted Polymers as Sensors

There can be one more method to check food quality. It can be the use of MIPs. A Molecular Imprinted Polymer, or MIP, is a polymer that was formed in the presence of a molecule that is extracted afterwards, thus leaving complementary cavities behind. These polymers show a certain chemical affinity for the original molecule[11]. Dendritic polymers are a very good choice for making MIPs as they possess molecular homogeneity, monodispersity and large solubility. MIPs can be prepared from different functional monomers (e.g. methacrylic acid (MAA) and acrylamide) and a cross-linking copolymer (e.g. ethyleneglycol dimethacrylate (EDMA)) in porogenic solvents such as chloroform, toluene, tetrahydrofuran and acetonitrile. MIPs prepared with trifunctional crosslinkers, like pentaerythritol triacrylate and trimethlolpropane trimethacrylate are superior to those prepared with difunctional ones, in that higher load capacities and better resolution can be obtained. One of the many attractive features of the molecular imprinting method is that it can be applied to a diverse range of analytes. MIPs suffer from a limitation of slow mass transfer. The large solubility of dendritic polymers can help overcome this problem[9].

4.1 Properties and Applications of MIP

Because of highly cross-linked nature, MIPs are intrinsically stable & robust, facilitating their applications in extreme conditions such as in presence of acids, bases or metal ions, in organic solvents or at high temperatures & pressures. They are cheap to produce & can be stored in dry state at room temperature for a long time. Molecularly Imprinted Polymers (MIPs) are suited as antibody like materials due to their long-term stability, chemical inertness and insolubility in water and most organic solvents[2].

MIPs have found their applications in many areas, like in the chemical and biological sensing, as a sorbent for molecularly imprinted solid-phase extraction (MISPE) in column chromatography, in Thin Layer Chromatography (TLC), structure elucidation, etc. Apart from analysis, MIPs can also be used as catalysts in synthesis. For example, MIPs using the product as template can continuously remove it from the bulk solution by complexation. This results in an equilibrium shift towards product formation[14-16].

4.2 Preparation

MIPs are prepared by normal polymerization techniques. The food pathogen which will be produced after the food degrades is known- in case of water or meat, it is Salmonella or Escherichia Coli and that for cheese is Listeria[8]. It is this molecule which the MIP has to be sensitive towards. Hence it is used as the template molecule during the preparation of MIP. The classical approach to preparation of MIPs involves the copolymerization of functional and cross-linking monomers in presence of the template. The polymerization is often carried out in a solvent as it imparts a porous structure to the MIP. The porous structure facilitates extraction of the imprint molecule and subsequent ingress of the pathogen to the imprinted sites. Prior to polymerization, either a complex between the imprint molecule and the functional monomer based on weak intermolecular interactions is made or covalent bonds are formed between them producing a polymerizable derivative of the imprint molecule. Template removal in the former case can be brought about by washing the MIP with the solvent, while in the later case the bonds have to be broken. The covalent approach ideally yields a larger and more homogeneous population of binding sites than the non-covalent approach for a given amount of imprint molecules. However, the non-covalent approach is more flexible with respect to the choice of functional monomers and possible target molecules. Either of the approaches is made use of depending upon final requirement from the MIP[5] (see Fig.2).

4.3 Working

When food degrades, the pathogen is produced. This pathogen selectively binds to the imprinted site on the MIP. The MIPs

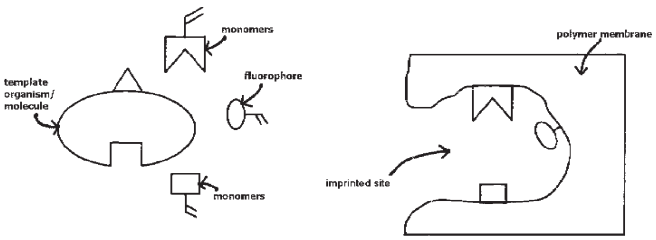

Fig. 2 :- Preparation of MIP
Source - Ref. 2

contain copolymerized fluorophores whose fluorescence emission is suppressed (quenched) when pathogens are bound, but is unaffected in absence of strong binding. As food degradation continues, more and more pathogens are produced which selectively bind to and suppress the fluorescence emissions from other imprinted sites. Hence there is a reduction in the overall fluorescence emission by the sensor strip. This reduction in emission can be measured using a fluorescence scanner[2] (see Fig.3).

4.4 Sensing

Extent of food deterioration is monitored by scanning the sensor strip with an automated external fluorescence scanner that detects the

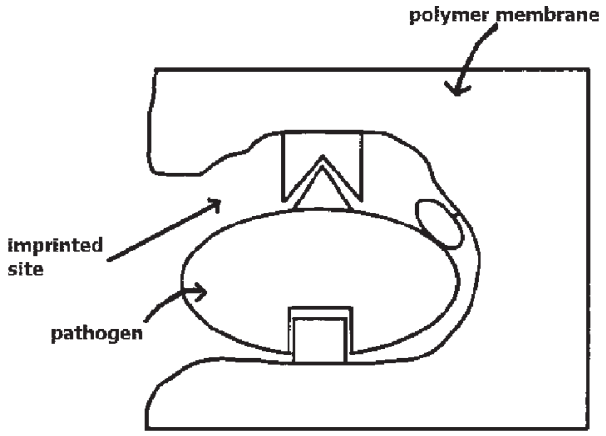

Fig. 3 :-Working of MIP
Source – Ref. 2

patterns & magnitude of fluorescence quenching. The fluorescence scanner emits an excitation beam as it scans the sensor strip on the package. When the fluorescence emission falls below a specific value, the food is declared "unfit for consumption". This process can be done on a large scale by rapidly passing the sensor strip-containing packages on a conveyer belt under an automated fluorescence scanner, or using a handheld version of the scanner on the packages or food samples[2].

5. Incorporation of the Sensor Strip in the Packaging

5.1 pH indicator Sensor Strip

A device for detecting presence of bacteria in a perishable food product comprises a gas–permeable sensor housing that is positioned in the interior of food packaging including a pH indicator within the housing. Here the sensor is sealed within a food packaging element, with a food product supported on a tray. Such unitary sensor is positioned within an interior of a sealing film (polymer packaging). A plurality of such sensors could be used in some cases, and that the packaging element could also comprise, for example, a consumer-type sealable bag or container. An initial state of the sensor is represented by dotted shading; the sensor initially senses a metabolite concentration of the air trapped within the packaging (see Fig.4).

With elapsed time and possible changes in storage temperature, bacterial colonies (pathogens) begin to form on and in the food product. They emit a gaseous metabolite that diffuses into the

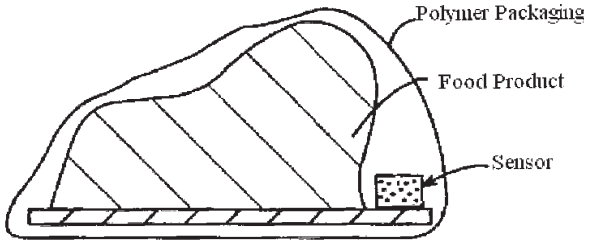

Fig.4
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sensor (here sensor incorporated within the polymer packaging) (see Fig.5).

This sensor undergoes a chemical change indicative of the concentration of the metabolite[3].

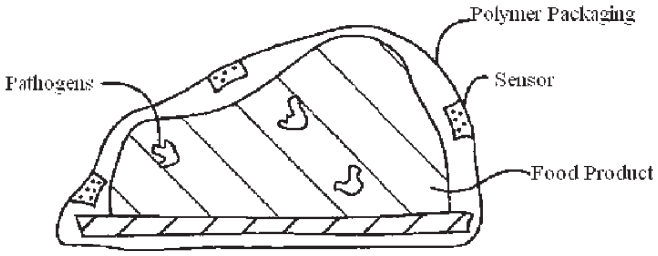

Fig.5
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5.2 MIP sensor strip

MIP strip is made using the pathogen, which is to be detected, as the template. The pathogen (template molecule) is completely removed from the strip. This strip now is ready for use and is pasted on the inside of the packaging. That portion of the packaging is made transparent in order to make sensing easier without opening the packet. The strip remains in continuous contact with the food and can be checked for quality whenever needed.

6. Advantages

1. Have high molecular sensitivity
2. Does not require expensive biological components (antibodies, other proteins, or nucleic acids) for detection as against currently available food pathogen sensors
3. The signal detection system can be used for high-volume screening of packaged foods
4. Can be mass-produced cheaply & incorporated in packaged foods as easily as barcodes
5. Much more resistant to environmental, biological and chemical

degradation than detectors based on biological components
6. Have a high tolerance to mechanical & thermal stress
7. Have excellent storage stabilities[2].

7. Disadvantages of Biological Sensors

1. Extensive & time-consuming laboratory workups by highly trained personnel are required.
2. Very few pathogens can be reliably measured commercially.
3. Available detectors contain biomolecule-derived elements, which suffer from the expense of isolation and production of biomolecules and their susceptibility to destruction by dehydration, bacterial action, moderately high temperatures, and other environmental conditions.
4. More expensive technique as compared to MIPs[2].

8. Conclusion

The losses incurred in quality check of the food product due to repeated opening and repacking can be avoided by using the above techniques. By making use of pH indicators and MIP as additives in food packaging, people can be made aware of its contamination beforehand. Colour change can also be incorporated in MIPs but fluorescence detection is orders of magnitude more sensitive. But still there are problems related to MIP incorporation in the packaging and also pathogen sensing. MIPs suffer from the drawback of incomplete template removal, broad guest affinities and slow mass transfer, of which a solution could be found to only the last one. Nevertheless, more systematic research work may tackle these problems as well, which unfortunately is not being done in India to that scale. Hence these techniques are not used here as of today. However, the use of MIPs instead of biomolecules greatly reduces production costs of the final food pathogen detection system while at the same time increases the system's stability in the face of environmental challenges.

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