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Yusufu, D., Wang, C., & Mills, A. (2018). Evaluation of an 'After Opening Freshness (AOF)' label for Packaged Ham. *Food Packaging and Shelf Life*, *17*, 107-113. https://doi.org/10.1016/j.fpsl.2018.06.002

Published in:
Food Packaging and Shelf Life

Document Version:
Peer reviewed version

Evaluation of an 'After Opening Freshness (AOF)' *label* for Packaged Ham

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Abstract

A new type of commercial time-temperature indicator, TTI, namely the 'After Opening Freshness *Label*', i.e. AOF *label*, is evaluated. The *label* comprises a plastic film colorimetric CO_2 *indicator* layer encapsulated in a polymer sheath, the permeability of which controls the rate of diffusion of the CO_2 in to and out of the indicator film. The CO_2sensitive *indicator* film inside the *label* is relatively fast in responding (recovering its original colour in 26 min at 25^{o}C) when the ambient atmosphere is changed from that of the MAPed package (containing 25% CO_2) to air, but when encapsulated in the polymer sheath used in the AOF *label*, which uses polyethylene terephthalate, PET, as a gas diffusion barrier, under the same conditions its recovery time is ca. 30 h (at 25^{o}C). Key to its commercial function –as a consume within indicator - at 5 ^{o}C, the *label*'s recovery time is ca. 96 h (i.e. 4 days). While UV/Vis spectrophotometry is used to characterise the optically transparent CO_2 *indicator*, photography, coupled with digital image colour analysis is used to characterise the AOF *label*. A study of the kinetics of colour recovery of the AOF *label* as a function of temperature revealed an activation energy, E_a, of colour recovery of ca. 43 kJ mol^{-1}, which is similar to a number of different food spoilage processes. The potential of the AOF *label* as a 'consume within' indicator to help minimise the large amount of unnecessary household food waste associated with many developed countries is discussed briefly.

Keywords: Indicator, Freshness, Ham, Packaging, MAP

1. Introduction

The Waste and Resources Action Programme, WRAP, estimate (WRAP, 2017) over10 million tonnes of food, valued at £17 bn, is wasted per annum and of which 60% could have been avoided. Given that 70% of the latter is household food waste, it follows that any technology that informs the consumer what food in the fridge is still fresh, and so safe to eat, would be a welcome, useful tool to help reduce this waste. One technology that has been used for this purpose is the time-temperature indicator, i.e. TTI. A TTI is a smart *label* that shows the accumulated time-temperature history of a product. TTIs are usually employed to improve food distribution, reduce food waste and improve shelf-labelling by highlighting any significant deviations from the recommended refrigeration temperature (Taoukis, 2001). The shelf-life label used by most packagers assumes correct refrigeration. An excellent recent review on TTIs is that of Wang and co-workers (Wang, Liu, Yang, Zhang, Xiang and Tang, 2015).

A notable commercial example is the FreshCheck® Freshness 'You Can See™' indicator (FreshCheck® indicator, 2014) sold by the TempTime Corporation, based on the polymerisation reaction of colourless diacetylenic monomers. These compounds polymerise thermally to give very dark, conjugated polymers. The kinetics of the polymerisation depends upon the type of substitution and so provides a route by which TTIs with different temperature sensitivities can be produced. In a typical indicator the polymerisation takes place in the centre of a bulls-eye pattern, with the outer part of the bulls-eye acting as reference colour ring. Fresh Check® indicators have been used in the past by the Monoprix supermarket chain in France on selected refrigerated products as well as other chain stores (Fresh-Check Indicator *Label*s Assure eatZi's Customers Freshness, 2018; Mills, 2009; Wang, Liu, Yang, Zhang, Xiang and Tang, 2015).

The Cryolog Company has developed an irreversible, novel, temperature-activated, printable TTI *label*, that utilises food-grade micro-organisms to simulate the real deterioration of food products, called the TOPCRYO™ *label* (TOPCRYO™ technology, 2018). The growth of these micro-organism parallel that of the micro-organisms found naturally in the packaged food and produces a pH change in the indicator which is revealed using a pH-sensitive dye. Thus, the initially green active *label* turns pink if the product has been incorrectly refrigerated and so is no longer fresh, due to above chill temperature storage.

As with FreshCheck™, the TOPCRYO™ TTI is a full history, temperature-only activated indicators, requiring deep-freeze storage of the label prior to its application. This obviously limits their use to initially frozen foods and there is, therefore, a clear need for a TTI that is activated by some other, simple mechanism, other than thawing.

Finally, it is worth mentioning the OnVu™ label, which is based on a solid-state photochromic reaction. Initially colourless, upon activation with UV light the photochromic pigment turns dark blue, and with time returns back to its colourless form at a rate that is temperature dependent (Kreyenschmidt, Christiansen, Hubner, Raab & Petersen, 2010).

Insignia Technologies Ltd. (Insignia Technologies Ltd., 2017) has recently introduced a new type of TTI, which they refer to as an 'After Opening Freshness *Label*', or – as we shall refer to throughout as an 'AOF' *label*, which is initially beige coloured when contained in an *unopened*, modified atmosphere, CO_2-containing, package, and only starts to change colour (to purple) once the food package is *opened* and the CO_2 is released. The key colour-changing process is therefore due to the desorption of the CO_2 from the label into the ambient air. Once 'activated' in this way, i.e. once the food package is opened, it takes ca. 4 days to change colour in air provided the package plus label are maintained at 5^{o}C, but is faster at elevated temperatures, as we shall see. Note, although it is referred to as an 'after opening freshness' indicator by Insignia Technologies Ltd., the AOF *label* does not measure food freshness directly. Instead, it is a different type of TTI in that it shows the accumulated time-temperature history of a product, once the MAPed package is opened. This indicator was recently made available at selected stores as part of a trial with packages of cooked British ham slices by Sainsbury's, as illustrated in figure 1(a). Photographs of this AOF *label in situ* after opening as a function of time at 5^{o}C are illustrated in figure 1(b) and show the gradual transition from an initial beige colour (at time of opening, t = 0) to light purple at t = 4 days. The last image of the label shows that the indicator actually continues to darken in colour after4 days , until it reaches a deep purple after 7 days, however a colour-matching scale on the indicator helps identify the 4 day (at 5^{o}C) point.

The AOF *label* shows how long the package has been opened when correctly refrigerated and in so doing indirectly provides advice regarding the freshness of the product, ham in this case, with the intention that this 'consume within' advice will stop the consumer throwing out the food unnecessarily while it is safe to eat, by reassuring them of its freshness. As with most packaged foods, the packager sets a time, after opening, for it to be consumed within, in which the properly refrigerated product will be 'fresh' and 'safe to eat'; how they arrive at that time (typically 2 days for packaged meat) and what the usual spoilage mechanisms are outside the scope of this paper, but have been addressed by the work of others (e.g. Huis in't Veld, 1996; Borch, Kant-Muermans & Blixt, 1996).

Reassurance of food freshness and safety are required particularly by the many that forget when their refrigerated food packages were opened and so are unable to follow the 'consume within' advice that is usually printed on such packages, such as 'consume within 2 days' for the Sainsbury's ham, for example. The discrepancy in 'consume within' times between the AOF *label* (4 days at 5°C) and the printed advice (2 days) arises because the latter errs on the side of caution, since research shows that many (over 70% in the UK, for example, and similar figures for the USA and Europe; James, Evans & James, 2008) household fridge temperatures exceed 5°C. In contrast, MAP packaged ham refrigerated at 5°C or less, is safe to eat up to 3-5 days after opening (Foodsafety.gov, 2018).

In this paper the indicator used in the Insignia Technologies AOF *label* is characterised and evaluated using UV/Vis spectroscopy and digital image under different conditions of temperature and CO_2. The results provide a better understanding of the features and possible limitations of this new TTI.

2. Materials and methods

2.1 Materials

Packets of Sainsbury's 7 cooked British ham slices, with their Insignia Technology AOF *label*s, were purchased from a local Sainsbury's store between June 2017 and January 2018. In all cases the AOF *label*s were stuck inside to the clear plastic film lidding (50 μm thick) of the ham package. In this paper, all tests of the AOF *label* were conducted with the label still stuck onto the lidding. The structure of the AOF *label* was probed using FT-IR and Scanning Electron Microscopy (SEM) and the latter results are illustrated in figure 2(a). SEM, combined with optical and FT-IR microscopy, showed that the AOF *label* comprised: a relatively thick (70 μm), purple-coloured low density polyethylene (LDPE) plastic film CO_2-sensitive *indicator* layer sandwiched between a thin (30 μm) white PET layer – on its 'food' side and a thick polypropylene layer (50 μm) on its 'lidding' side. Adhesive binds all the layers together, as well as the *label* to the lidding (50 μm) which appears (from FTIR) to be made of polyethylene terephthalate, PET, with a coating of EVA; the thicknesses of the EVA and adhesive layers could not be readily determined by SEM. A schematic illustration of the *label* attached to the lidding is given in figure 2(b).

In part of this study the AOF *label* was peeled apart so as to enable the purple-coloured plastic film CO_2-sensitive *indicator* to be characterised in its uncovered, i.e. **naked**, form. In all such work, the **naked** AOF plastic film *indicator* is referred to as the AOF *indicator*, in order to distinguish it from the combined system, illustrated in figure 2(b), the AOF *label*. All gases, e.g. CO_2, 25% CO_2 in air and air were purchased from BOC.

2.2 Methods

Calibration of the AOF *indicator* and *label* was achieved using different mixes of CO_2 with Ar. In this work, the appropriate gases were blended together using a Cole-Parmer – rotameter based – gas blender. An Anéolia Legend O_2/CO_2 gas analyser was used to verify the level of CO_2, i.e. the %CO_2, in final gas mixture. All UV/ Vis absorbance measurements were made using an Agilent Technologies CARY 60 UV-vis spectrophotometer. All FT-IR spectra were recorded using a Perkin Elmer model Spectrum 1 FT-IR spectrometer. SEM measurements were carried out using a FEI Quanta™ 250 SEM with a spot size of 4 mm, working distance of 10 mm and an accelerating voltage of 20 kV. Prior to SEM analysis, samples were sputter coated with a 10 nm layer of gold using a Quora Q150R S rotary pumped sputter coater. All digital photographs were taken using a Cannon 600D digital camera.

3. Theory of CO_2-based indicators; how the AOF *label* works

The AOF *label* contains a purple-coloured plastic *indicator* film that changes colour (ultimately bright yellow in 100% CO_2) when exposed to carbon dioxide. The packaged ham, illustrated in figure 1, has a modified atmosphere comprising ca. 25% CO_2: 75% N_2, so as to extend the shelf-life of the food. As a result, when in the sealed package of ham, the AOF *label* is beige coloured, but not bright yellow, which requires a much higher level of CO_2. When the package is opened, the CO_2-rich atmosphere is replaced rapidly by air, which only has 0.04% CO_2, and so the AOF *label* slowly recovers its original (purple) colour over a time period that depends upon temperature. This slow recovery is due to the diffusion of the CO_2 in the *indicator* film, slowly diffusing out through the white PET overlayer, i.e. (iv) in figure 2(b), into the ambient air. As a consequence, the AOF *label*, illustrated in figure 1, changes from beige to light purple over a period of 4 days after opening when refrigerated at 5^{o}C, as illustrated in figure 1.

The purple-coloured plastic film CO_2-sensitive *indicator* film that forms part of the AOF *label*, see figure 2(b), is an example of one of a number of smart plastic films developed originally by this group (Mills, Skinner & Grosshans, 2010; Mills & Yusufu, 2016a,b). It comprises a CO_2-sensitive pigment dispersed uniformly throughout an extruded polymer which, in this case, is low density polyethylene, LDPE. The pigment comprises fine particles (BET surface area = 130 ± 25 m^2/g), of hydrophilic silica coated with a pH sensitive dye, in this case phenol red, PR; the identity of the latter was determined using UV/Vis absorption spectroscopy. In the dye coating the silica particles the PR is in its highly coloured (purple) deprotonated form, PR^-, and ion-paired with a quaternary ammonium, Q^+, cation. The resulting complex, $Q^+PR^-.xH_2O$, reacts with CO_2 *via* the following colour-changing equilibrium reaction:

$$Q^+PR^-.xH_2O + CO_2 \rightleftharpoons Q^+HCO_3.HPR.(x\text{-}1)H_2O \qquad (1)$$

purple yellow

From eqn(1) it follows that:

$$R = [HPR]/[PR^-] = \alpha \times \%CO_2 \qquad (2)$$

where [HPR] and $[PR^-]$ are the concentrations of $Q^+HCO_3.HPR.(x\text{-}1)H_2O$ and $Q^+PR^-.xH_2O$, respectively, α is a proportionality constant (units: $\%^{-1}$), which provides a measure of the sensitivity of the CO_2-sensitive optical sensor under test, and R is a measure of the transformation of the dye from the deprotonated to protonated form due to the presence of CO_2. Experimentally, the value of R can be calculated from the measured absorbance of the indicator film at a known value of $\%CO_2$, *Abs*, at the wavelength of maximum absorbance for, say PR^-, i.e. $\lambda_{max}(PR^-)$ = 592 nm, since, from reaction (1) and eqn (2) it follows:

$$R = (Abs_0 - Abs)/(\mathrm{Abs} - Abs_\infty) = [HPR]/[PR^-] \qquad (3)$$

Where, Abs_0 is the value of absorbance due to the PR dye at $\lambda_{max}(PR^-)$ when $\%CO_2 = 0$ (i.e. when all the dye is in its deprotonated form) and Abs_∞ is the absorbance of the film when all the dye is in its protonated form, HPR, i.e. when $\%CO_2 = \infty$; the latter absorbance is assumed here to be that measured when the $\%CO_2$ = 100 %. The characterisation of other CO_2-sensitive plastic films, based on this principle, using, for example, the pH sensitive dyes: meta-cresol purple, thymol blue and hydroxpyrene trisufonic acid (HPTS), has been reported previously by this group (Mills, Skinner & Grosshans, 2010; Mills & Yusufu, 2016a,b). Other work shows that for such sensors a variation in relatively humidity, RH, from 40-100% at room temperature, has little effect on the response features of such indicators although a shift from 0 to 40% usually lowers the sensitivity of the indicator by a factor of ca. 3 (Mills & Yusufu, 2016a) and the PR indicator film reported here is assumed to behave in a similar fashion.

The patent associated with this technology is currently licensed to Insignia Technologies Ltd (Mills, Grosshans and Skinner, G. 2014).

4. Results and discussion

4.1 Characterisation of the AOF indicator

The 'naked' AOF *indicator* was fixed in a gas cell (see Supplementary information, figure S1 for a schematic illustration of the gas cell and set up), and then exposed to different levels of CO_2 at room temperature (25 °C) for 15 mins and its UV/Visible spectrum measured and digital photograph take at each level. The results of this work are illustrated in figure 3(a), including an insert plot of R, calculated using eqn (3), vs $\%CO_2$, which revealed a good straight line of gradient (which is a measure of the sensitivity of the indicator) α = 0.62 ± 0.02 $\%^{-1}$. This same procedure was carried out at number of different temperatures so as to determine the temperature sensitivity of α. An Arrhenius plot of the data, i.e. $\ln(\alpha)$ vs 1/T, illustrated in figure 3(b) yielded a good straight line, from the gradient of which an activation energy, E_a, of 45 ± 1 kJ mol^{-1} was calculated for reaction (1). This value is near to that reported elsewhere for a similar type of plastic film CO_2 indicator, using the sodium salt of the fluorescent dye, 8-hydroxypyrene-1,3,6-trisulphonic acid, i.e. E_a = 38 ± 2 kJ mol^{-1} (Mills & Yusufu, 2016b). The results of this work reveal that the CO_2 indicator films become increasingly sensitive towards CO_2 the lower the ambient temperature, i.e. α increases with decreasing T, which is not surprising given the negative entropy associated with reaction (1) and reactions of this type.

As suggested by eqn (3), all CO_2 indicators based on reaction (1) show a hyperbolic, rather than linear, response towards CO_2, and as a result exhibit response and recovery profiles that are asymmetric (Mills & Chang, 1992), as illustrated in figure 4, for the AOF *indicator*, when exposed to alternating cycles of argon (0% CO_2) and 25% CO_2.

From these profiles it is possible to calculate the average 90% response, $t_{90\downarrow}$, and recovery times, $t_{90\uparrow}$, of 1 and 26 min, respectively, which are also similar to those observed for the HPTS and thymol blue containing CO_2-sensitive plastic films, which were typically 2-3 min and 32-38 min, respectively (Mills & Yusufu, 2016ab). In such CO_2 indicators, the response and recovery times depend directly upon the rate of permeation of the CO_2 into and out of the indicator film, respectively, with a proportionality constant that is inversely proportional to the square of film thickness (Mills & Chang, 1992). The very long recovery of the AOF *label* (> 4 days at 5 ^{o}C, see figure 1), compared to the *indicator* (26 min at 25 ^{o}C), is due to the additional barrier to CO_2 permeation, namely the 30 μm layer of white PET. Permeability data for CO_2 in different polymers is given in the supplementary Information section, Table S1. Other experiments conducted using the *label* with additional barrier films on the lidding, or on the white PET side of the *label*, show, not surprisingly, that the combination of a gas diffusion barrier of 50 μm PET/EVA and 50 μm of PP, on the 'lidding' side, provides an even greater barrier to CO_2 permeation than the thin (30 μm) white PET layer on the food side, thus the rate of recovery of the original colour of the AOF *label* is primarily due to diffusion of the CO_2 from the indicator film through the white PET layer, as noted earlier. PET is known to have a relatively low permeability towards CO_2 (Ashley, 1985 and Table S1) and, indeed, that is why it is often used to package carbonated drinks. The AOF plastic film *indicator*, with its 90% response and recovery times of 1 and 26 min at 25^{o}C, respectively, utilises LDPE as the polymeric encapsulation medium, which has a permeability that is > 200 x's that of PET (Ashley, 1985 and Table S1), so that it is little wonder that the recovery time of the AOF *label* is much greater, i.e. > 4 days at 5^{o}C, than that of the (naked) CO_2 *indicator*.

4.2 UV/Visible spectroscopy and digital colour image analysis

When it comes to comparing the performance of the AOF *indicator* to the AOF *label,* there appears to be a potential problem in that the latter does not allow the transmission of light and so cannot be probed using UV/Vis absorption spectroscopy. However, an increasingly popular, simple way to monitor quantitatively the colour change exhibited by opaque samples is through photography and digital image colour analysis (Knutson et al., 2015; Williams et al., 2007). In its simplest form, as used here, photographs are taken of the indicator under test and its image analysed for the red, green and blue components, i.e. *RGB(*red*)*, *RGB(*green*)* and *RGB(*blue*)*, respectively, which will have values between 0 and 255, and which, when taken together, defined the observed colour of the indicator in the photograph. In the Insignia AOF *indicator* and *label*, the colour change is from purple to yellow and the colour component that changes most strikingly is red. Thus, when analysing photographic images of the AOF *indicator*, or *label*, here we use an apparent absorbance, *Abs(red)*, (Knutson et al., 2015; Williams et al., 2007) based on the average red component of the digital image, *RGB(R)*, of the AOF label, as a substitute for absorbance in eqn (3), in order to calculate a value for *R*, where

$$Abs(red) = \log(255/RGB(\mathrm{red})) \tag{4}$$

In order to validate this method of analysis its ability to generate a value for α for the AOF *indicator* was tested and compared to that value, determined using UV/Vis spectrophotometry for the same *indicator*, reported earlier in this work. Thus, figure 3(a) illustrates the digital photographs taken on the AOF *indicator* taken at the same time as the absorbance measurements illustrated in figure 3(a) for different levels of $\%CO_2$. Digital image colour analysis of these images of the indicator yielded a range of *Abs(red)* values, calculated using eqn (4), as a function of $\%CO_2$, which were then used to generate a straight line plot of *R* vs $\%CO_2$, via ean (3), which had almost the same gradient, i.e. same value of α (0.59 $\%^{-1}$) as that determined by UV/Vis spectrophotometry for the same *indicator* (see insert plot in figure 3(a)), i.e. α = 0.62 $\%^{-1}$. As found for other indicator systems, this work shows that simple colour-based indicators, such as the PR *indicator* film studied here, can be analysed quantitatively using the much simpler, less expensive method of digital photography coupled with colour analysis, rather than the more expensive and less amenable (for opaque samples at least) method of UV/Vis spectrophotometry. As a result, in the subsequent study of the AOF *label*, described in section 4.3, all colour measurements used the digital colour image analysis method outlined above, rather than UV/Vis spectrophotometry – which could not be applied due to the opaque nature of the label.

4.3 Characterisation of the AOF label

The sensitivity of the AOF *label towards* CO_2 should be similar, if not identical, to that of the AOF *indicator*, since the *label* is simply a polymer film encapsulated *indicator*. In order to confirm this prediction, a number of identical AOF *labels* were placed in sealed jars, each previously flushed with different CO_2/argon gas mixtures, left to equilibrate for at least 48 h, and then photographed at room temperature (25 °C) and then at 5 °C. Digital image colour analysis of the photographs allowed the calculation of values of *Abs(red)*, which were used, as a substitute for 'spectrophotometric' Abs, in eqn (3), in order to generate the plots of *R* vs %CO_2 for the AOF *label* at 25 and 5 °C, which are illustrated in figure 5. The straight lines plots in Figure 5, reveal α = 0.58 %$^{-1}$ and 2.1 %$^{-1}$ values for the AOF *label* at 25 and 5 °C. Note, as expected, the former (for the AOF *label*) value of α is almost identical to that of the AOF *indicator*, α = 0.59 %$^{-1}$. These results confirm that the CO_2 *sensitivity* of the AOF *indicator* is not markedly affected by the addition of the two polymer films, i.e. layers (ii) and (iv) in figure 1, both of which act as barriers to the permeation of CO_2 to and from the indicator film, (iii) in figure 2 (b), into the ambient air.

As noted earlier, key to the function of the AOF *label* is, after the food package is opened, the diffusion of CO_2 from the *label* to the ambient air. In order to probe this feature more thoroughly, this recovery - of the original colour - process for a typical AOF *label* was studied as a function temperature, over the range 1 to 25 °C. In all cases the *labels* were initially beige coloured, as they were stored in an atmosphere containing 25% CO_2 (75% N_2) for at least 48 h before use. After 'opening' - and rapid substitution of the CO_2 atmosphere for air - these *labels* were monitored photographically until their original (CO_2 free) purple colour was well developed, and well beyond the pale purple colour used by Insignia technologies to signify the food product (ham in this case) is 'past best', see figure 1. The plots of some of the different data sets generated as a result of this work, in the form of *Abs(red)* vs (recovery) time, are illustrated in figure 6. The broken horizontal red line signifies the point time, t_{pb}, in the recovery when the indicator has reached the pale purple colour associated with the food product being 'past best', as illustrated in figure 1. Thus, it can be seen that t_{pb} for the AOF *label* is ca. 4 days at 5 °C, as reported by Insignia Technologies Ltd. (Insignia Technologies Ltd., 2017) and that t_{pb} decreases with increasing temperature.

The variation of the 'past best' times, t_{pb}, can then be used to determine an approximate activation energy for recovery of the initial purple colour of the *label*, E_A(recovery), *via* a plot of ln(1/t_{pb}) vs 1/T, from which a value of the activation energy for recovery, E_a', of 43 ± 5 kJ mol^{-1} was determined. This value is not too surprising since E_a for small molecule gases (such as CO_2; O_2 and N_2) diffusion in polymers in general is typically 50 kJ mol^{-1} (Yam, 2009) and, although E_a can vary from 28-65 kJ mol^{-1} for CO_2 diffusion when considering a wide range of polymers, for polyethylene it is 38.5 kJ mol^{-1} (Pauly, 1999), which compares well with the value of 43 ± 5 kJ mol^{-1}reported above.

Pauly S.: Permeability and Diffusion Data. In: Polymer Handbook, 4th Edition, Brandrup, J., Immergut, E.H. and Grulke, E.A. (eds), Wiley & Sons, New York, 1999, volume 2, Chpt. VI, 543-562.

Table 1 lists the activation energy of some popular commercial TTIs from which it can be seen that the value of E_a' for the AOF *label* (43 ± 5 kJ mol^{-1}) is very similar to that reported for the MonitorMark™ TTI, which is based on the diffusion of a coloured liquid along a wick (30-50 kJ mol^{-1}; Pocas, 2008). Other reported TTI activation energies include: 84-100 kJ mol^{-1} for Fresh-Check™ (Pocas, 2008) and 97-106 kJ mol^{-1} for OnVu™ (Kreyenschmidt, Christiansen, Hubner, Raab & Petersen, 2010).

Ideally, any TTI *label* should have an activation energy similar to the major spoilage mechanism associated with the food. However, the latter are many (Maroulis & Saravacos, 2003; Maroulis & Saravacos, 2011) and varied so that their associated E_a values span a wide range which cannot be covered by just one TTI. Thus, for example, E_a for enzymic spoilage is usually low, (4 – 60) kJ mol^{-1} whereas protein denaturation is very high (300 – 500) kJ mol^{-1}. Interestingly, common microbial spoilage lies in between these extremes (60-120) kJ mol^{-1} (Labuza, Fu & Taoukis, 1992).

It follows that the AOF *label* would be best suited when used with foods for which the major spoilage process has an E_a value that is < 50 kJ mol^{-1}, which includes enzymic spoilage, chlorophyll and ascorbic acid degradation, non-enzymic browning and lipid oxidation (Maroulis & Saravacos, 2003; Maroulis & Saravacos, 2011). Unfortunately, in the case of packaged ham, in which microbial spoilage is often a major process after opening, the AOF label is not ideally suited to respond (to temperature changes) in a manner that reflect that of the likely spoilage mechanism associated with ham and many food stuffs. However, that isn't its primary function, which is to signal when the recommended 2 day period is up, when the food is stored under the recommended refrigeration conditions.

Conclusions

The 'After Opening Freshness *Label*', i.e. AOF *label*, currently being trialled by Sainsbury's comprises a plastic film colorimetric CO_2 *indicator* layer encapsulated in a polymer sheath that limits the rate of diffusion of the CO_2 into and out of the indicator film. The system is designed to change from a beige colour, when in the presence of ca. 25% CO_2, in a MAPed package of ham, to purple, 4 days after opening the package, when held at 5 ^oC. When used in this way it provides an indirect indication if the food is still 'fresh' and so safe to eat by measuring the CO_2 loss from the sensor which is correlated to 'freshness' and 'safety'. The basic principle of this novel commercial consume within indicator has be outlined earlier by this group using an O_2 indicator (Mills et al., 2012). The indicator itself utilises the pH sensitive dye phenol red and is fast responding (recovering its original colour in 26 min at 25^oC), but this response time is greatly increased when encapsulated in the polymer sheath used in the AOF *label*, where its recovery time is ca. 30 h (at 25^oC) – which is tripled to 96 h (i.e. 4 days) at 5^oC. The activation energy for colour recovery is ca. 43 kJ mol^{-1}, which is similar to a number of different food spoilage processes, although not the very temperature sensitive ones, such as protein denaturation and bacterial spore destruction for which E_a is typically > 200 kJ mol^{-1}. Overall, the AOF *label* is a promising new technology which, if embraced by the general public, could help minimise the large amount of unnecessary household food waste associated with many developed nations. In order to use it as an AOF *label* for many other very different foods, further possible work includes: a study of how the film response time varies with the %CO_2 in the headspace and humidity and attempts to reformulate the indicators so that it exhibits and activation energy which is nearer to that for microbial spoilage, (60-120) kJ mol^{-1} (Labuza, Fu & Taoukis, 1992).

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