Talanta 161 (2016) 105–113

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Inkjet-printed CO_2 colorimetric indicators

Yanan Zhang, Loong-Tak Lim*

Department of Food Science, University of Guelph, ON, Canada N1G2W1

ARTICLE INFO

Article history:
Received 29 May 2016
Received in revised form
31 July 2016
Accepted 3 August 2016

Keywords:
Inkjet-printed
Colorimetric indicators
Carbon dioxide
Multiplexing
Intelligent packaging

ABSTRACT

Colorimetric CO_2 indicators were prepared by printing pH dyes (M-cresol purple or phenol red, tetrabutylammonium hydroxide, ethylcellulose, 1:2 ethanol:1-butanol solvent), using a commercially available thermal inkjet printer, on either cellulose paper or plastic transparency film. Indicators inks printed on the papers had higher sensitivity to CO_2, greater color change, and more producible than those printed on plastic film. Varying the print intensities of the two pH dyes resulted in multiplexed indicators with tunable sensitivity and expanded detection concentration range towards CO_2. The ink-jet printing method is simple and highly flexible for the development of indicator to detect CO_2 – a gas indicative of product quality in many food products. Further optimization can potentially lead to application of the indicators in intelligent food packaging systems.

1. Introduction

Many consumers rely on “Best Before” date to evaluate the freshness of packaged products. However, because the printed information does not account for the potential thermal abuses or microbial contamination/proliferation that occur during distribution/storage, it can only be used as a guideline for freshness evaluation. In the worst-case scenario, false assurance from the “Best Before” date can lead to serious foodborne illnesses [1]. On the other hand, the “Best Before” can also result in food wastage because consumers misinterpreted it as an “expiry” date. Significant amount of foods are being discarded in North America and elsewhere in the world because they passed the “Best Before” date, although the products are still fit for consumption [2,3].

To address these issues, various intelligent packaging systems are being developed. Unlike “Best Before” date approach, intelligent packaging systems are capable of providing information on the actual product freshness, through interacting with compounds associated with product spoilage. For example, colorimetric indicators (e.g., label, prints, patch) are capable of exhibiting visible color changes upon interacting with the target compounds present in the package headspace, such as CO_2, O_2, ammonia gas, and aldehydes [4–6]. Among these gases, CO_2 is a promising indicator analyte for many packaged food products since it is related to microbial activities, respiration in live tissues, degassing phenomena in roasted products, mass transfer in modified atmosphere packaging (MAP), and so on [7–9]. The incorporation of CO_2 indicator in packages for these foods may be beneficial to monitor product freshness.

Several colorimetric indicators have been developed for the detection of CO_2. For example, researchers have exploited the pH-dependent solubility of proteins in solutions in developing CO_2 indicators. At pH far away from the isoelectric point, the proteins remain soluble and the indicator solution appears transparent. However, when the pH approaches the isoelectric point (i.e., the net charge of a protein is zero), the protein would precipitate out from the solution and appear opaque or turbid [10–13]. Considering that the isoelectric points of proteins occur in a narrow range and that these indicators provide only transparency changes, the sensitivity of the protein solution may be limited. An alternate approach would be to use pH-sensitive dyes capable of providing color response over a wide pH range. However, the main limitation of pH dye indicators is that water is needed to facilitate the proton transfer to induce color change. Thus, the sensitivity of dye-based CO_2 indicators is humidity-dependent, and they tend to be useful for intermediate to high moisture food products. To overcome this limitation, some researchers have utilized a non-volatile phase transfer agent (PTA) to facilitate the dispersion of hydrophilic pH dye in a hydrophobic polymer to prevent dye leaching. The PTA also provides a trace amount of water to solvate the hydrophilic dye, allowing the hydration of CO_2 to facilitate the proton transfer [6,14–17]. Tetraoctylammonium hydroxide and tetrabutylammonium hydroxide (TBAH) have been used as PTAs in CO_2 indicators containing pH dyes (e.g., m-cresol purple and cresol red) encapsulated within hydrophobic matrices (e.g., ethylcellulose, polyethylene, and poly(vinyl butyral)), achieving a detection limit of as low as 1.25% CO_2 [6,18,19].

Inkjet printing is an efficient, flexible, and cost-effective

* Corresponding author.
E-mail address: llim@uoguelph.ca (L.-T. Lim).

http://dx.doi.org/10.1016/j.talanta.2016.08.014
0039-9140/

downstream processing technology used in the food packaging industry. Inkjet printing can be based on thermal or piezoelectric technologies [20]. In thermal inkjet printing, also known as bubble-jet printing, ink droplets are ejected from print nozzle due to the pressure generated from vapour bubble expansion, while piezoelectric inkjet printing is achieved via physical deformation of piezoelectric materials within a nozzle in response to an applied pulse electric field. Thermal inkjet printing tends to produce smaller droplet size and higher nozzle density than the piezoelectric counterpart. The solution properties of the ink, such as viscosity, surface tension, and solvent volatility, are important for manipulating the droplet formation, controlling the tendency of nozzle clogging, and determining the ink-substrate compatibility [21]. Typical substrates for printing are papers and polymer films, selected based on the end-use requirements and conditions [22–24].

The purpose of this study is to develop a colorimetric indicator sensitive to CO_2 under dry condition, with the following specific objectives: (1) to develop a pH dye-based CO_2 colorimetric indicator using thermal inkjet printing technology; (2) to investigate the effects of printing parameters and substrates on indicator performance; and (3) to characterize multiplexing indicators containing two sensing inks.

2. Materials and methods

2.1. Material

Unless otherwise indicated, chemicals used were purchased from Fisher Scientific (Ottawa, ON, Canada) and were used without further purification. All gases were purchased from Linde Canada Limited (Mississauga, ON, Canada).

2.2. Preparation of sensing ink

Ethylcellulose (EC; Ethocel Std. 4, The Dow Chemical Company, Calgary, AB, Canada) solutions were prepared at various concentrations (0.25–6%) in different solvents (0:1, 1:2, 1:1, 2:1, 1:0 ethanol:1-butanol), followed by the addition of pH dye (bromophenol blue, chlorophenol red, methyl red, M-cresol purple (MCP) or phenol red (PR)) and tetrabutylammonium hydroxide (TBAH, 1.0 M). The solutions were stirred with the aid of a magnetic stirrer until the pH dyes fully dissolved to form the final ink formulations. The inks were stored in the dark until use. Preliminary studies showed that MCP- and PR-based indicators exhibited the most sensitive color responses. Therefore, these two dyes were chosen for further investigation, in single-ink and two-ink (9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 PR:MCP) formulations.

2.3. Thermal inkjet printing

Indicators were printed using a thermal inkjet printer (HP DeskJet F4435, Hewlett-Packard Inc., Mississauga, ON, Canada). Before printing, ink cartridges (HP 60 tri-color and black inkjet cartridges, CC643WC, Staples, Guelph, ON, Canada) were cut open, the sponge inside was removed, and the ink reservoir was cleaned thoroughly with ethanol and then 1-butanol. An aliquot of 2 mL of the formulated ink, pre-filtered through a 0.2 μm nylon membrane (Fisher Scientific, NJ, USA), was syringed into the cartridge. The commercial printer used in this study adopted the CMYK color model with four different inks, namely cyan (C), magenta (M), yellow (Y) and key (K, i.e., black). Cyan, magenta and yellow inks were contained in separate reservoir compartments within one cartridge, while the black ink was contained in a separate cartridge. PR-based sensing inks were loaded into the magenta compartment while MCP-based sensing inks were loading into the cyan compartment in the tri-color cartridge. Photoshop software was used to design printing templates with different C:M ratios (9:1, 1:9, 8:2, 2:8, 7:3, 3:7, 6:4, 4:6, 5:5). The printer was set to print at 600 dpi resolution on either pure cellulose chromatography papers (0.19 mm thickness, No. 05-714-1, Fisher Scientific, NJ, USA) or poly(vinyl chloride) transparency film (0.098 mm thickness, M280/01, Klöckner Pentaplast, Oshawa, ON, Canada). Printing was done in 2, 5, 10 or 15 passes to evaluate the effect of ink quanity deposited on the substrates. After printing, the indicators were store in a glass container and continuously purged with nitrogen in the dark for at least 2 days to remove the solvent.

2.4. Characterization and color measurements of indicators

Color response of the indicators was measured in situ by exposing them to different concentrations of CO_2 in nitrogen (3:97, 5:95, 15:85, 25:75, 60:40 and 100:0v/v CO_2:N_2) at 25ºC. To this end, the printed indicators (1cm × 1cm) were placed within cuvettes and held down by a holder, pushing the indicator specimens against the cuvette sidewall facing a flatbed scanner (HP Scanjet 4890 Photo scanner, Hewlett-Packard Co., Mississauga, ON, Canada), as illustrated in Fig. 1. Digital images of the indicators before and after the exposure to CO_2 were collected on the scanner at 600 dpi resolution. A stopwatch (A09Q67, Traceable Products, Texas, USA) was used to determine the gas exposure time. The color recovery of the indicators was monitored by flushing N_2 through the cuvette for 3min. A proportional gas mixer (Model 299-016-3; Tescom Corp., MPLS, MN) was used to prepare CO_2 and N_2 gas mixtures. A gas analyzer (Gaspace Advance Headspace Analyzer; Illinois Instruments Inc., IL, US) was used to determine the CO_2 concentration in the gas mixtures.

To quantify the color change, the images were analyzed with Adobe Photoshop CS6 software (Adobe Systems, Inc., Mountain View, Calif.) using the histogram analysis module function. To eliminate the edge effect of the printed inks, only the central portion of the indicator, representing about 2/3 of the surface coverage, was analyzed. The colors of the area being analyzed were averaged and converted into RGB color scale. All the analyses were conducted in triplicate. Euclidean distance (ΔE) values were calculated to evaluate the overall change in color before and after exposing the indicator specimens to CO_2:

$$\Delta E = \sqrt{(R_0 - R_1)^2 + (G_0 - G_1)^2 + (B_0 - B_1)^2} \quad (1)$$

where the subscripts "0" and "1" represent the R, G, B values of the indicators "before" and "after" the exposure to CO_2, respectively.

2.5. Scanning electron microscopy analysis

The surface morphologies of the paper and transparency film substrates, before and after printing, were analyzed using a scanning electron microscope (SEM; S-570 Hitachi High Technologies Corp., Tokyo, Japan) at 10 kV accelerating voltage. Samples were coated with gold (20 nm) with a sputter coater (Model K550; Emitech, Ashford, Kent, England) prior to SEM analysis.

2.6. Characterization of ink properties

Dynamic surface tension values of the ink solutions (PR, MCP, and PR-MCP mixed formulations) were determined at 22+/-2ºC with a bubble pressure tensiometer (SITA Pro Line F10; SITA Messtechnik, Dresden, Germany) using bubbling frequencies ranging from 1 to 10 Hz. Viscosity values of the ink solutions were characterized using a rheometer (AR2000; TA instruments, New Castle, DE). A 2.09º cone (4 cm dia) and plate geometry was