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System feasibility: Designing a chlorine dioxide self-generating package label to improve fresh produce safety part I: Extrusion approach☆

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ABSTRACT

There is need for in-package anti-microbial technology to control microbial growth on packaged fresh food. This research evaluated the feasibility of delivering chlorine dioxide (ClO_2) via package labels made of synthetic polymers extruded with citric acid (CA) and sprayed with sodium chlorite. Heat pressing facilitated ClO_2 generation and moisture triggered ClO_2 release. Of three synthetic polymers tested, only ethylene vinyl acetate (EVA) label withstood extrusion and storage conditions without structural changes.

EVA labels containing 15 or 7.5% CA generated 3.2–4.2 and 0.5–1.0 mg ClO_2/L air, respectively. Total inactivation of *Salmonella* cells on TSA plates (2.13 log CFU/plate) was achieved following exposure to 15% CA labels for 2 h; 7.5% CA labels gave partial inactivation (1.03 log CFU/plate) following up to 6 h of exposure.

Our findings demonstrate: 1) the practical feasibility of this synthetic package label design; 2) ClO_2 generation and release following activation; and 3) antimicrobial effectiveness against *Salmonella* growth.

Industrial relevance: Feasibility for synthesizing a package label to generate and deliver chlorine dioxide (ClO_2) as an effective antimicrobial inside individual food packages has been demonstrated. The approach extrudes polymers with citric acid, then sprays the surface with sodium chlorite. Heat pressing the label just before application initiates reaction between these two agents to generate ClO_2. Release of ClO_2 is stimulated and maintained by moisture in the film and emanating from fresh foods.

1. Introduction

The industrial practice most commonly used to minimize microbial growth on fresh produce consists of washing fresh fruits and vegetables with aqueous sanitizers, mostly chlorine (Parish et al., 2003). This practice presents some limitations with regard to microbial inactivation due to surface irregularities of fresh produce and possible physical injuries, which can create protection sites against the access of aqueous sanitizers from hydrophobicity of these regions and surface tension (Gómez-López, Ragaert, Debevere, & Devlieghere, 2008). One way to overcome these limitations is to complement the washing step with exposure to gaseous sanitizers such as chlorine dioxide (ClO_2) that have greater penetration into otherwise inaccessible regions and therefore greater effectiveness on pathogen inactivation (Annous & Burke, 2015; Han, Sherman, Linton, Nielsen, & Nelson, 2000; Prodduk, Annous, Liu, & Yam, 2014).

Chlorine dioxide received FDA approval in 2001 to reduce or eliminate microorganisms in a wide variety of food products such as fruits and vegetables (Rulis, 2001). It is a true gas (greenish yellow) at room temperature with effective biocidal activity over a wide range of pH (3–8) (Bernarde, Israel, Olivieri, & Granstrom, 1976; Keskinen & Annous, 2011). A number of commercial ClO_2 generators have been developed throughout the years to synthesize this compound for diverse applications. One simple and easy method to generate ClO_2

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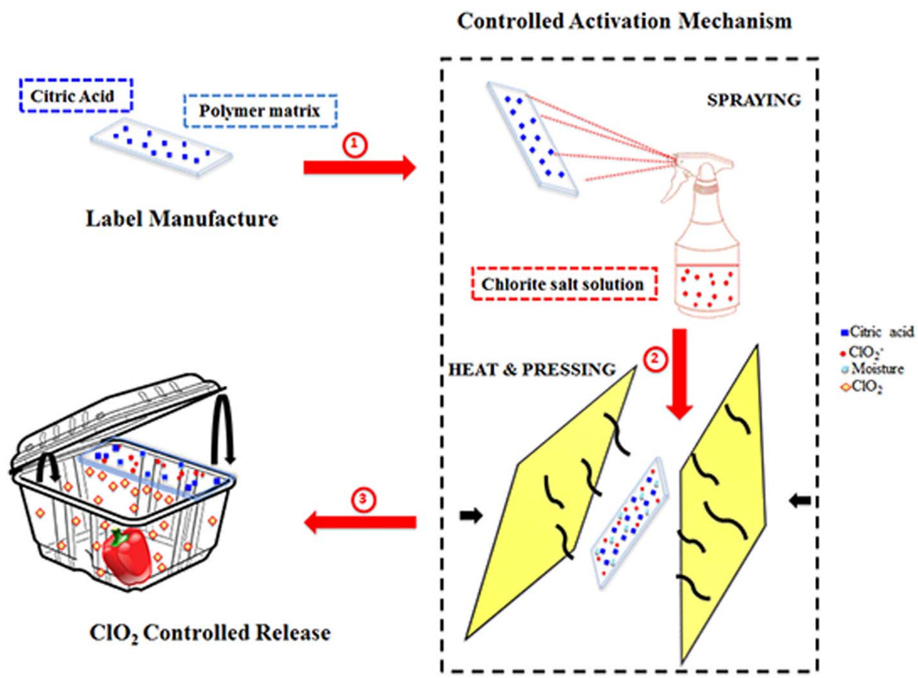

Fig. 1. Concept development of the synthetic polymer embedded with citric acid for the manufacturing of ClO_2 self-generating package labels.

is to react citric acid with sodium chlorite salt in the presence of moisture (Deshwal & Lee, 2005). The reaction can be approximated by: $4ClO_2^- + 2H^+ \rightarrow 2ClO_2 + ClO_3^- + Cl^- + H_2O$ (Deshwal & Lee, 2005).

Chlorine dioxide is a selective and strong oxidizing agent, which, unlike chlorine does not chlorinate organic compounds to produce carcinogenic trihalomethanes (THMs) (Aieta & Berg, 1986; Keskinen & Annous, 2011). Also, it does not react with ammonia to form chloramines (Keskinen and Annous, 2011; Oxenford, 1995), which makes it very attractive for use as an antimicrobial in foods. Chlorine dioxide is explosive at concentrations ≥ 10% v/v at atmospheric pressure (Keskinen & Annous, 2011). Due to its instability, this compound is usually generated on-site upon demand to eliminate safety hazards associated with its storage and transportation (Keskinen & Annous, 2011).

Current on-site ClO_2 generation systems include: 1) stand-alone generators (Annous & Burke, 2015; Prodduk et al., 2014), 2) sachets containing the mixed precursors, e.g. acid with sodium chlorite (Rubino, Netramai, Auras, & Annous, 2014; Rubino, Siddiq, Auras, Annous, & Netramai, 2011), or 3) package films impregnated with the precursors (Ray, Jin, Fan, Liu, & Yam, 2013).

Stand-alone generators, which are on/off systems, offer precise control over when and how much gas to generate but are expensive to operate due to high initial investment and continuous service requirements. They are appropriate for large-scale treatments such as gassing large rooms containing large amount of products. Since the risk of post-treatment re-contamination during packaging does exist, the use of an in-package ClO_2 source as primary and/or secondary treatment would serve as an additional hurdle for microorganism to survive within the package.

In contrast to on/off stand-alone generators, mixing ClO_2 precursors within a sachet initiates the reaction and continues ClO_2 production until all reactants are consumed. Sachets with ClO_2 precursors can be packaged with target products to provide treatments in situ. Yet, the ClO_2 precursors (acid and sodium chlorite) are usually separated by a thin membrane increasing the risk of premature reaction prior to use. In addition, chemical contamination of food from possible rupture of sachet, along with consumers' negative perceptions towards sachets of chemicals within packages make this system less effective and less appealing.

Impregnating package films with both precursors eliminates potential hazard of contaminating the packaged product with ClO_2 precursors. However, in this case, ClO_2 generation begins when the film is manufactured and both chemicals embedded within the film start reacting. This shortens the film shelf life and the antimicrobial activity decreases with storage of the film, resulting in inconsistent levels of ClO_2 produced when the film is used.

An active packaging system capable of generating and releasing ClO_2 when needed could overcome these limitations. The main objective of this work, therefore, was to evaluate the feasibility of manufacturing an innovative stable package label to generate and deliver ClO_2 within packages.

1.1. Package label concept development

The package label is synthesized by extruding a synthetic polymer with citric acid, then spraying the film surface with a concentrated sodium chlorite solution to supply the other reactant and moisture necessary for ClO_2 generation. Reaction between citric acid and sodium chlorite to generate and release ClO_2 is facilitated by heat pressing the label. This accelerates diffusion of reactants in the film and increases their kinetic energy. After activation, the label is attached to the inner side of the primary package containing the food product, such as fresh produce, and immediately sealed. Moisture from the sodium chlorite solution and/or from respiration of the packaged food product then maintains ClO_2 generation and release until all citric acid and sodium chlorite are consumed (Fig. 1).

This label is innovative is several aspects: 1) It separates the acid from the sodium chlorite salt, preventing premature ClO_2 generation and loss. 2) It is activated by spraying with a solution of sodium chlorite salt, followed by heat pressing to trigger ClO_2 generation and release over time. 3) It is attached to the inner side of the primary package, which eliminates risk of food contamination from ClO_2 precursors due to rupture, e.g. of a sachet. 4) It is manufactured using an existing commercial technology (extrusion) and can be easily integrated into fresh produce packaging where wrapping and label activation occur at the same time.