Food Packaging and Shelf Life 17 (2018) 129–133

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

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

Effects of diffusion controlled release of tocopherol on lipid oxidation

Luni Shen[a], Xi Chen[a], Dong Sun Lee[b], Xuntao Zhu[c], Mo Chen[d], Kit L. Yam[a,*]

[a] Department of Food Science, Rutgers, the State University of New Jersey, 65 Dudley Rd, New Brunswick, NJ 08901, USA
[b] Department of Food Science and Biotechnology, Kyungnam University, 449 Woryeong-dong, Masanhapo-gu, Changwon, 631-701, Republic of Korea
[c] Department of Food Science, Nutrition and Management, Delaware Valley University, 700 E. Butler Ave., Doylestown, PA 18901, USA
[d] College of Engineering, QuFu Normal University, Rizhao, Shangdong 276800, China

ARTICLE INFO

Keywords:
Diffusion controlled release
Tocopherol
Lipid oxidation
Controlled release packaging

ABSTRACT

Our previous study showed that constant rate release of antioxidant was more effective than instant addition of antioxidant to inhibit oxidation of linoleic acid. However, the release rate of antioxidant from a packaging film is not constant—instead it varies with time, typically governed by diffusion of antioxidant in the film. This work investigated the effects of diffusion controlled release of tocopherol on inhibiting oxidation of linoleic acid. The results show that diffusion controlled release is more effective than constant rate release and instant addition, probably because the rate of diffusion controlled release of tocopherol more closely matches the rate of formulation of free radicals by linoleic acid. This finding provides useful insights for the design of controlled release packaging, an emerging technology by which antioxidants or other active compounds are released from the package in a controlled manner to extend shelf life of food.

1. Introduction

Lipid oxidation is a major deterioration mode of fatty food that can lead to significant loss of flavor, color, texture, and nutrients. There are three stages of lipid oxidation: induction, propagation, and termination (Schaich, 2009). The first stage during which no rancidity can be detected, known as the induction period, is commonly used as an indicator of shelf life since it is followed by a propagation phase during which off-odors and off-flavors occur rapidly (Labuza & Dugan, 1971). A longer induction period indicates a longer shelf life. To inhibit lipid oxidation and extend shelf life, antioxidants are often added to fatty food products.

Two methods can be used to add an antioxidant to a food. The first method is to add the antioxidant as an ingredient directly into the food formulation. This method is called instant addition, since the addition of antioxidant is completed either instantly or within a very short time as shown by the solid line in Fig. 1. Unfortunately, this traditional method often leads to the undesired situation that more antioxidant molecules are available than free radicals produced during the early stage of oxidation, leaving the excessive and prematurely added antioxidant molecules to degrade through the formation of dimers or other products, thereby reducing the antioxidant level to quench free radicals at later times (Yamauchi, Kato, & Ueno, 1995).

The second method, which has attracted much interest by researchers in recent years, is to first incorporate an antioxidant into a food package (e.g., in the form of a film or a sachet) and then allow the antioxidant to be released to the food to inhibit oxidation (Busolo & Lagaron, 2015; De Freitas et al., 2018; Gómez-Estaca, López-de-Dicastillo, Hernández-Muñoz, Catalá, & Gavara, 2014; Marcos et al., 2014). Unlike instant addition, the antioxidant is not added to the food at once, but it is added to the food in a time-release manner. A special form of time-release is controlled release which has a release profile (defined here as the rate of release of antioxidant as function of time) that is deliberately controlled.

Controlled release packaging is an emerging technology by which active compounds such as antioxidants and antimicrobials are encapsulated into the package such that these active compounds can later be released to the food in a controlled manner to improve quality and safety (LaCoste, Schaich, Zumbrunnen, & Yam, 2005; Yam & Zhu, 2012). There are many possible controlled release profiles; for example, the constant rate release profile and the diffusion controlled release profile are shown by the dashed line and the dashed curve in Fig. 1, respectively, and the area under the line or curve is the total amount of antioxidant that has been added or released at a given time. From a practical viewpoint, a wide range of release profiles is needed to meet the requirements of different foods.

Our previous study compared the methods constant rate release and instant addition of tocopherol to inhibit oxidation of linoleic acid (Zhu, Schaich, Chen, Chung, & Yam, 2012). The results showed that constant rate release was more effective than instant addition, in one case

* Corresponding author.
E-mail address: yam@aesop.rutgers.edu (K.L. Yam).

https://doi.org/10.1016/j.fpsl.2018.06.010
Received 18 August 2017; Received in revised form 22 June 2018; Accepted 25 June 2018

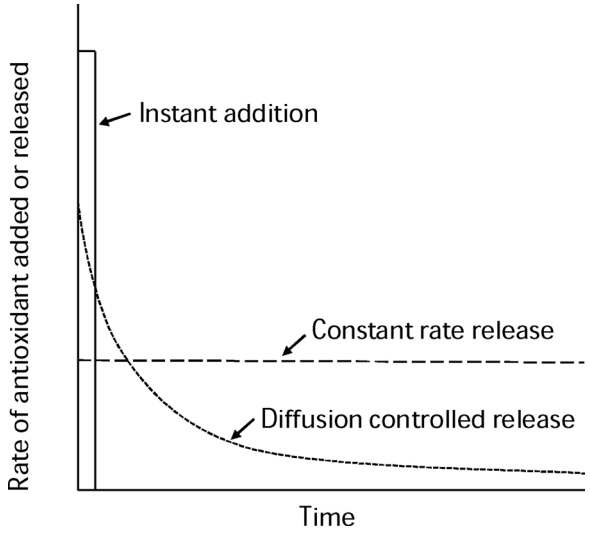

Fig. 1. Different profiles of adding or releasing tocopherol.

requiring only 15% of the amount of tocopherol used by instant addition to achieve the same inhibition effect. A possible explanation of this superior result is that tocopherol was added to linoleic acid gradually by the method of constant rate release, thereby reducing the extent of degradation due to prematurely available tocopherol. It is important to mention that a certain minimum rate is required for constant rate release, depending on the food system. Below this minimum rate, lipid oxidation occurs quickly and subsequent release of antioxidant cannot reverse the situation.

Although the study on constant rate provides insights on how release profiles can affect the effectiveness of antioxidant, the release rate of antioxidant from the package is not constant but changes with time. In most cases, the release of antioxidant and other active compounds from a packaging film to the food follows three steps: diffusion of antioxidant from the inside to the surface of the film, desorption of antioxidant from the film surface, and dispersion of antioxidant onto the food. Among them, diffusion is usually the slowest step or the rate-determining step. As shown by the dashed curve in Fig. 1, the diffusion controlled release profile is characterized by fast release rate in the beginning with progressively slower release rates in later times. This release profile is most relevant for the development of controlled release packaging

The method of diffusion controlled release of antimicrobials has been found to be highly effective, with its fast initial release rate to kill or injure bacteria and its subsequent slower release rates to kill or suppress growth of the injured bacteria (Balasubramanian, Lee, Chikindas, & Yam, 2011; Wang & Yam, 2018). However, there is a scarcity of knowledge about how diffusion controlled release affects the effectiveness of antioxidants. To fill this knowledge gap, the objective of this work was (1) to investigate the effects two variables (diffusivity and loading) t diffusion controlled release of tocopherol on inhibiting oxidation in linoleic acid, and (2) to compare the effectiveness of diffusion controlled release versus constant rate release and instant addition of tocopherol on inhibiting oxidation in linoleic acid. An electronic controlled syringe system was used to simulate the diffusion controlled release from packaging films (Yam & Zhu, 2012).

2. Materials and methods

2.1. Materials

Linoleic acid (60%), cyclohexane, and methanol were purchased from Fisher Scientific Inc. (Suwanee, GA, USA). Tocopherol extracted from soybean consisting of 10% α-, 5% β-, 65% γ-, and 20% δ-homologues was donated by Cargill® (Minneapolis, MN, USA). To prevent oxidation, linoleic acid and tocopherol were flushed with argon gas and stored in a freezer before use.

2.2. Mathematical model to simulate diffusion controlled release

To simulate the diffusion-controlled release profile of tocopherol from a packaging film to linoleic acid, the following Fickian diffusion model (Lee, Yam, & Piergiovanni, 2008) was used.

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \sum_{n=1}^{\infty} \frac{8}{(2n-1)^2\pi^2} exp\left[\frac{-D(2n-1)^2\pi^2 t}{4L_p{}^2}\right] \quad (1)$$

where $M_{F,t}$ (mg) is amount of tocopherol released at time t (s), $M_{F,\infty}$ (mg) is amount of tocopherol released at infinite time (or when the amount of tocopherol released is negligible), L_P (m) is thickness of the film; D (m^2/s) is diffusivity of tocopherol in the packaging film. This model assumes single side contact between the film and linoleic acid, volume of linoleic acid much larger than volume of the film, and total migration of linoleic acid from the film to the food simulant at infinite time. The third assumption implies that $M_{p,o} = M_{F,\infty}$, where $M_{p,o}$ (mg) is initial loading of tocopherol in the film. It can be seen from Eq. (1) that the diffusion controlled release is determined by the variables of D, L_p, and $M_{p,o}$.

In our earlier study (Shen, Zhu, Lee, & Yam, 2012), the diffusivities (D) of tocopherol in an LDPE film and in an LDPE/PP film at 40 °C were measured as 1.03×10^{-13} and 3.56×10^{-15} m^2/s, respectively; the film thicknesses (L_p) of LDPE film and LDPE/PP film were measured as 1.09×10^{-4} and 9.37×10^{-5} m, respectively. These experimental values were used in this study to simulate real situations. In addition, tocopherol loadings of 1 mg and 3 mg were used for the LDPE film, and tocopherol loading of 1 mg was used for the LDPE/PP film. For a pouch with a surface area of 600 cm^2 and a thickness of 1.0×10^{-4} m, these 1 and 3 mg tocopherol loadings are equivalent to 167 and 500 ppm loadings, which are within practical range since good quality films can be obtained with tocopherol loadings up to 3000 ppm based on our experience.

The above values were substituted into Eq. (1). Microsoft Excel were used with n = 15 to calculate values to obtain diffusion controlled release profile (a plot of $M_{F,t}$ versus t).

2.3. Syringe pump system to mimic tocopherol release from packaging films

Fig. 2 shows the syringe pump system used to simulate the diffusion controlled release of tocopherol from a packaging film to linoleic acid. The system was placed inside an environmental chamber (Lab-Line Instruments Inc., Melrose Park, IL, USA) in the dark at 40 °C.

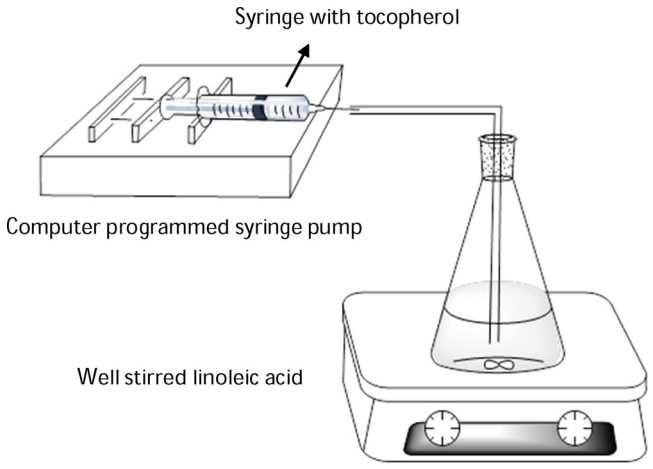

Fig. 2. Experimental setup of syringe pump system.