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Kinetic study on photostability of retinyl palmitate entrapped in policosanol oleogels

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ABSTRACT

Photostability of all-*trans* retinyl palmitate (RP) (100% bioactivity) was studied in policosanol oleogels (PCOs) (7–12% w/w policosanol in soybean oil) after UVA irradiation. RP was incorporated into PCOs at levels of 0.04%, 0.1% and 1% (w/w). PCOs efficiently protected RP from UVA-mediated degradation. Over 75% RP-activity remained in PCOs after 4 days of UVA irradiation, while 12% RP-activity remained in soybean oil. HPLC analysis showed that *cis*-RP was formed in liquid soybean oil after 2 days of UVA irradiation while it was absent in PCOs matrices. PCOs blocked the energy absorption from UVA and further dampened the UVA-mediated ionic photodissociation and free radical reaction due to matrix immobilization. For all samples, RP photodegradation followed a 2nd order reaction. From the reaction kinetics, it would be possible to predict the RP photodegradation rate in PCO matrices. PCOs were shown to be a promising matrix to protect RP from photodegradation.

1. Introduction

Vitamin A is a group of nutritional components, including retinol, retinal, retinoic acid, and several provitamin A carotenoids (e.g. beta-carotene), that are essential for visual functions and for the maintenance of healthy epithelia tissues (skin, immune system organs, lungs, and others) (Coates et al., 2004). Retinyl palmitate (RP) is an ester form of vitamin A and is widely used in food products, medical treatments and cosmetics products. However, RP is very sensitive to UVA irradiation, which results in its photodegradation. Loveday and Singh (2008) summarized strategies for vitamin A protection based on the entrapment or encapsulation of vitamin A, including emulsion systems (Carlotti, Rossatto, & Gallarate, 2002; Flanagan & Singh, 2006; Yaghmur et al., 2012), solid lipid nanoparticles (Carlotti et al., 2005; Jenning & Gohla, 2001; Lim, Lee, & Kim, 2004), polymer encapsulation (Çirpanli, ünlü, Çaliş, & Atilla Hincal, 2005); Duclairoir et al., 1999; Jeong et al., 2003), and addition of antioxidants (Carlotti et al., 2002; Ihara, Hashizume, Hirase, & Suzue, 1999; Yoshida, Sekine, Matsuzaki, Yanaki, & Yamaguchi, 1999).

However, the aforementioned strategies are still technologically challenging. For instance, labor demands, high cost and limited protection are some of the current drawbacks. Thus, there is still a need to explore new approaches to protect vitamin A in an easy and economical way. Oleogels are promising technology that can be appropriate for practical application and health benefits. An oleogel is defined as a gel where the liquid phase is oil (Marangoni & Garti, 2011). Gelators can crystallize or self-assemble to form a 3D network, which entraps liquid oil in a solid-like gel system. The physical features of oleogels are greatly affected by the preparation method used, such as gelator concentration, as well as cooling and shear rate (Marangoni, 2012). Oleogels can be engineered to have desirable features and thus have the potential to replace solid fat in food products (Jang, Bae, Hwang, Lee, & Lee, 2015), delivery bioactive components (Yu, Shi, Liu, & Huang, 2012), and use in pharmaceuticals as delivery vehicles (Satapathy et al., 2013).

Policosanol is a mixture of long chain fatty alcohols, mainly including docosanol (C22), tetracosanol (C24), hexacosanol (C26), octacosanol (C28), and triacontanol (C30) (Irmak, Dunford, & Milligan, 2006). Long chain fatty alcohols can self-assemble and form the three dimensional structure of an oleogel. Gandolfo, Bot, and Flöter (2004) reported that the hardness of fatty alcohols oleogels have an approximately positive relationship with the fatty alcohol concentration, and fatty alcohols yield harder oleogels than the same chain length fatty acids at the same concentration. Lupi et al. (2013) found that a PC concentration in the range between 2.5% and 3% (w/w) was high enough to form a large number of crystals that aggregate into a 3D network. In another study, Lupi et al. (2013) reported that 3% policosanol organogels can be used as drug delivery system for ferulic acid (5% w/w).

As previously mentioned, several strategies have been studied with

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the aim to protect RP from photodegradation. However, the capacity of oleogel matrices to protect photolabile components has not been explored yet. Based on reports from previous studies on oleogels, PCOs have great potential to be used as delivery system of oil soluble compounds, such as RP. We hypothesize that PCOs have great potential to prevent RP photodegradation. The crystal network formed in PCOs may entrap and stabilize RP, while blocking UVA energy absorption. The objectives of this study were to investigate the effect of policosanol concentration in PCOs on the RP-photostability and to determine the kinetics of its photodegradation upon UVA exposure. We chose to prepare PCOs at concentrations ranging between 7 and 12% (w/w) in order to ensure a desirable solid-like behavior of the gel systems. Concentrations of incorporated RP were chosen to ensure an appropriate RP amount in one serving of soybean oil (one tablespoon, 13.56 g) based on the recommended daily allowance (RDA) and the upper level (UL) of vitamin A for adults, which is 900 μg retinol activity equivalents (RAE)/day and 3000 μg/day of preformed vitamin A, respectively (Russel et al., 2001). Soybean oil was used as liquid phase since it is widely used in the United States due to its relatively low cost and significant consumer acceptance.

Microstructure, mechanical and thermal properties, as well as oil binding capacity and matrix mobility of PCO matrices were analyzed. To evaluate the efficiency of PCO matrices to protect RP from photodegradation and to study the reaction kinetics, RP-PCOs were exposed to UVA radiation (365 nm) and the remaining *trans*-RP was subsequently analyzed by normal phase high performance liquid chromatography (HPLC).

2. Materials and methods

2.1. Materials

Soybean oil was generously provided by ADM oils (Decatur, IL, USA). 98% Policosanol containing 60% octacosanol was purchased from PureBulk Inc. (Roseburg, OR, USA). 2-Propanol (HPLC grade) and RP (1,600,000 – 1,800,000 USP units per gram) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Hexane (HPLC grade) and ethyl ether were from Fisher Chemical (Fair Lawn, NJ, USA).

A UVA lamp Model ENF-280C (365 nm, 115 V, 60 Hz, 0.20 A) was used for UV irradiation treatment (Spectroline, NY, USA). The lamp provides 1.488×10^{-6} W/cm^2 measured by UV safety meter model 6D (Solar Light, Glenside, PA, USA).

2.2. Oleogel preparation

Policosanol (7, 10, 12%, w/w) was added to soybean oil. The samples were heated at 85 °C and stirred at 250 rpm for 30 min. Samples were cooled at 4 °C with a cooling rate of 3 °C/min and stored at 4 °C for one week before analysis. RP (0%, 0.04, 0.1%, and 1%, w/w) was added during the cooling stage while mixing. The range of RP concentration used was chosen based on RDI and UL requirements. For instance, one serving of PCOs with 0.04% RP can provide the RDI for vitamin A, while one serving of PCOs with 0.1% RP is the maximum dose without adverse effects as established by the UL. Samples with 1% RP in PCOs were also prepared with the aim of reaching higher concentrations with potential cosmetics applications.

2.3. Microstructure

Differential interference contrast (DIC) microscopy was used to analyze the microstructure of the PCOs. A small drop of liquid sample was placed between a preheated microscope slide and glass cover. The slides were subjected to a heating and cooling program to achieve the desired cooling rate (3 °C/min) before observation. The images were acquired with a DIC microscope (Olympus BX53, Olympus Corporation, MA, USA) using the CellSens Dimension software (Olympus Corporation, MA, USA). 3 replicates were prepared and 10 images of each slide were recorded. The images were analyzed by using software ImageJ (NIH, MD, USA) to report crystal particle area (μm^2).

2.4. Oil binding capacity

To test the oil binding capacity of PCOs, discs were prepared by pouring the hot liquid oleogel mixture into PVC disc molds (22 mm diameter and 3.2 mm thickness). The samples were cooled in the molds to 4 °C with a cooling rate of 3 °C/min and stored at that temperature for a week before analysis. Each oleogel disc was removed from the mold, placed on a round filter paper (Whatman #5, 110 mm diameter) and incubated at 20 °C. The weight of each filter paper was recorded after 0, 24, and 48 h of storage time. A filter paper without sample on it was used as control in the experiments to account for the environment effect on the filter papers. Filter papers were large enough to absorb all the oil released from samples during the experiment without saturation. At least 10 replicates were prepared and means and standard deviation are reported. Oil loss (%) was calculated by using the following equation:

$$\%\text{Oil Loss} = \frac{[wt.\ paper(x\,h) - wt.\ paper(0\,h)] - [wt.\ blank(x\,h) - wt.\ blank(0\,h)]}{Total\ mass\ of\ sample} \times 100 \quad (1)$$

2.5. Mechanical properties

The rheology behavior of the PCOs was studied with a Rheometer Haake RS 150 Rheostress (ThermosScientific, Waltham, USA). Sample discs were prepared as explained in the previous section with PVC molds (35 mm diameter, 3.2 mm thick). A 35 mm diameter serrated stainless steel plate (PP35Ti) was used for the measurements. To determine the linear viscoelastic region (LVR), an oscillatory stress sweep from 10 to 1000 Pa at 20 °C was performed with a frequency of 1 Hz and normal force of 5 N. Storage modulus (G′) and loss modulus (G″ were determined from the stress sweep curves as the average value (in Pa) of the LVR. The yield stress (σ^*) was calculated as the stress value (in Pa) when a reduction in G′ of 10% was achieved. The complex modulus G^* was calculated by using the following equation:

$$G^* = \sqrt{G'^2 + G''^2} \quad (2)$$

Mean values and standard deviation of at least 5 replicates are reported.

2.6. Thermal properties

Analysis of the thermal properties of PCOs was carried out by differential scanning calorimetry (DSC, TA Instruments, New Castle, DE, USA). Samples were heated from 0 °C to 100 °C with a ramp of 5 °C/min, then held at 100 °C for 10 min and cooled to 0 °C at 5 °C/min. TA Universal Analysis software (TA Instruments, New Castle, DE, USA) was used to obtain melting temperature (T_m), gelation temperature (T_g), melting enthalpy (ΔH_m), and gelation enthalpy (ΔH_g) from the thermograms. Means and standard deviations for at least 3 replicates are reported.

2.7. Matrix molecular mobility

Matrix mobility of PCOs were measured by ^{1}H nuclear magnetic resonance (NRM) spectrometer (Bruker Bio Spin Corporation, Billercia, MA, USA). Liquid samples were poured into flat-bottom glass NMR tube (10 mm diameter, 180 mm length) up to a height of 4 cm and cooled at 3 °C/min and afterwards stored at 4 °C for one week before testing. Each sample was prepared and analyzed in triplicate; means and standard