CONTROLLED RELEASE OF NATURAL ANTIOXIDANTS FROM POLYMER FOOD PACKAGING BY MOLECULAR ENCAPSULATION WITH CYCLODEXTRINS

John L. Koontz

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Food Science and Technology

Approved:

Joseph E. Marcy, Chairman

Sean F. O'Keefe

Susan E. Duncan

Timothy E. Long

April 4, 2008
Blacksburg, Virginia

Keywords: natural antioxidant, α-tocopherol, quercetin, cyclodextrin, inclusion complex, packaging, polymer, linear low density polyethylene, controlled release

CONTROLLED RELEASE OF NATURAL ANTIOXIDANTS FROM POLYMER FOOD PACKAGING BY MOLECULAR ENCAPSULATION WITH CYCLODEXTRINS

John L. Koontz

ABSTRACT

Synthetic antioxidants have traditionally been added directly to food products in a single initial dose to protect against oxidation of lipids and generation of free radicals. Natural antioxidants have been shown to undergo loss of activity and become prooxidants at high concentrations; therefore, a need exists to develop active packaging which can gradually deliver antioxidants in a controlled manner. The objectives of this research were to (1) form and characterize cyclodextrin inclusion complexes with the natural antioxidants, α-tocopherol and quercetin, (2) incorporate cyclodextrin inclusion complexes of natural antioxidants into linear low density polyethylene (LLDPE), and (3) measure the release kinetics of inclusion complexes of natural antioxidants from LLDPE into a model food system. Cyclodextrin inclusion complexes of α-tocopherol and quercetin were formed by the coprecipitation method and characterized in the solid state by NMR, IR spectroscopy, and thermal analyses. Solid inclusion complex products of α-tocopherol:β-cyclodextrin and quercetin:γ-cyclodextrin had molar ratios of 1.7:1 as determined by UV spectrophotometry, which were equivalent to 18.1% (w/w) α-tocopherol and 13.0% (w/w) quercetin. Free and cyclodextrin complexed antioxidant additives were compounded with a twin-screw mixer into two LLDPE resin types followed by compression molding into films. Release of α-tocopherol and quercetin from LLDPE films into coconut oil at 30 °C was quantified by HPLC during 4 weeks of storage. The total release of α-tocopherol after 4 weeks was 70% from the free form and 8% from the complexed form averaged across both LLDPE resins. The mechanism by which α-tocopherol was released was modified due to its encapsulation inside the β-cyclodextrin cavity within the LLDPE matrix as indicated by its diffusion coefficient decreasing by two orders of magnitude. Molecular encapsulation of natural antioxidants using cyclodextrins may be used as a controlled release mechanism within polymer food packaging to gradually deliver an effective antioxidant concentration to a food product, thereby, limiting oxidation, maintaining nutritional quality, and extending shelf life.

In memory of my grandparents,

John and Madeline McLaughlin

and

Layton and Marye Koontz

They were always very supportive and interested in my education. I know that they would be very proud of me and I wish I could share this accomplishment with them.

ACKNOWLEDGEMENTS

I would like to thank my major professor, Joseph Marcy, for his guidance, patience, understanding, and friendship throughout my doctoral research and studies. He was always there to remind me to take a step back and look at the big picture. I would like to thank Sean O'Keefe who was especially helpful. He was always willing to take the time to talk through and help formulate solutions to difficulties along the research path. I also would like to thank my graduate committee members, Susan Duncan and Timothy Long, who graciously provided me with their expertise and time.

Thanks to Ron Moffitt for his guidance, expertise, and allowing me to have an internship experience at the Advanced and Applied Polymer Processing Institute (AAPPI); thanks to Sungsool Wi for his generous help with running solid-state NMR samples; thanks to Herve Marand for his time and expertise in interpreting DSC curves; and thanks to Stephen McCartney, at the Institute for Critical Technology and Applied Science (ICTAS) for his help with AFM.

A very special thanks to the Food Science staff, John Chandler, Harriet Williams, and Joell Eifert who always gave freely of their time; thanks to my fellow Food Science graduate students for their support, especially Kevin Holland, Dina Romano, Becky Baker, and Denise Gardner who were a great source of encouragement, fun, and good laughs; thanks to my fellow MILES trainees, especially Andy Whelton who helped me with more research questions than I can count.

A warm thanks to my family, who have always believed in me and supported me with their love. My parents, Lowell and Marie Koontz, are simply the best parents I could have ever asked for and are a continual source of encouragement. My brother Mike and his wife Julie and my aunts, Lynn and Lois, have all cheered me on along the way.

This research is based upon work supported by the Macromolecular Interfaces with Life Sciences (MILES) Integrative Graduate Education and Research Traineeship (IGERT) of the National Science Foundation under Agreement No. DGE-0333378. I would also like to recognize ConAgra Foods Inc. for financially supporting this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND TERMS

α	concentration mass ratio
A_0	free air amplitude
A_{sp}	set-point amplitude
AAPPI	Advanced and Applied Polymer Processing Institute
AFM	atomic force microscopy
ATR/FT-IR	attenuated total reflectance/Fourier transform–infrared spectroscopy
β-CD	β-cyclodextrin
BHA	butylated hydroxyanisole (2,6-di-*tert*-butyl-4-methoxyphenol)
BHT	butylated hydroxytoluene (2,6-di-*tert*-butyl-4-methylphenol)
BDE	bond dissociation enthalpy
^{13}C NMR	carbon-13 nuclear magnetic resonance
CAR	Carboxen
CD	cyclodextrin
CMD	comonomer distribution
CP/MAS	cross polarization/magic angle spinning
ΔE^*_{ab}	magnitude of the total color difference
ΔH_{dehyd}	enthalpy of dehydration
ΔH_{meas}	enthalpy of the measured effect
ΔH_{vap}	enthalpy of vaporization
δ	Hildebrand solubility parameter
D	diffusion coefficient
DAD	diode array detector
DSC	differential scanning calorimetry
DTG	derivative thermogravimetric
DVB	divinylbenzene
ϕ	volume fraction
f	active concentration fraction
γ-CD	γ-cyclodextrin
G	group molar attraction constant

GC-MS	gas chromatography–mass spectrometry
GRAS	generally recognized as safe
HDPE	high density polyethylene
HPLC	high performance liquid chromatography
HP-β-CD	hydroxypropyl-β-cyclodextrin
HP-LDPE	high pressure low density polyethylene
K	partition coefficient
K_{11}	binding constant of 1:1 complex
k	capacity factor
L_P	half thickness of polymer film
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
LOD	limit of detection
LOQ	limit of quantification
met LLDPE	metallocene-catalyzed linear low density polyethylene
M	molecular weight
$M_{F,\infty}$	total amount of additive transferred from polymer film to food at infinite time
$M_{F,t}$	total amount of additive transferred from polymer film to food at time t
m	mass
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
n	index variable
OIT	oxidation induction time
OTR	oxygen transmission rate
PDMS	polydimethylsiloxane
PE	polyethylene
PET	polyethylene terephthalate
PTFE	polytetrafluoroethylene
PP	polypropylene
q_n	non-zero positive roots of $\tan q_n = -\alpha q_n$
ρ	density

R	gas law constant
r_{sp}	set-point amplitude ratio
SPME	solid-phase microextraction
SPVD	short-path vacuum distillation
T	absolute temperature
$T_{1\rho}$	spin-lattice relaxation time in the rotating frame
T_d	decomposition temperature
T_g	glass transition temperature
t	time
t_R	retention time
TG	thermogravimetric
TGA	thermogravimetric analysis
THF	tetrahydrofuran
UV	ultraviolet
V	volume
$W_{c,d}$	mass fraction degree of crystallinity
X	mole fraction
ZN LLDPE	Ziegler-Natta-catalyzed linear low density polyethylene