

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

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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.

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TABLE OF CONTENTS

ABSTRACT	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS AND TERMS	xiii
CHAPTER 1: INTRODUCTION	1
Current Strategies to Prevent Oxidation in Foods	1
Oxidation Remains Problematic	2
Active Food Packaging Technologies	3
Research Objectives	5
References	6
CHAPTER 2: REVIEW OF LITERATURE	7
α -Tocopherol	7
Quercetin	9
Antioxidants as Prooxidants: A Paradox	11
Properties of Cyclodextrins	12
Hydration State	14
Antioxidant Activity	15
Preparation of Cyclodextrin Inclusion Complexes	16
Solvent Effects	16
Benefits of Cyclodextrins	17
Cyclodextrin Inclusion Complexes of Natural Antioxidants	17
Analytical Methods of Cyclodextrins and Their Inclusion Complexes	19
^{13}C CP/MAS NMR	19
Thermoanalytical Characterization	23
Synthetic Antioxidant Release from Food Packaging	23
Natural Antioxidants in Polymers	26
Cyclodextrin Interaction with Polymers	28
Cyclodextrin Inclusion Compounds in Polymer Matrices	29
Linear Low Density Polyethylene	30
Controlled Release of Active Ingredients in Foods	31
Diffusion in Polymers	32
Diffusion in a Plane Sheet	33

Diffusion from a Stirred Solution of Limited Volume	33
Tables	35
Figures	36
References	41
CHAPTER 3: FORMATION AND CHARACTERIZATION OF CYCLODEXTRIN INCLUSION COMPLEXES OF α -TOCOPHEROL AND QUERCETIN	52
Abstract	52
Introduction	53
Materials and Methods	54
Results and Discussion	59
Literature Cited	68
Tables	73
Figures	77
Appendix	83
CHAPTER 4: POLYMER PROCESSING AND CHARACTERIZATION OF LLDPE FILMS CONTAINING α -TOCOPHEROL, QUERCETIN, AND THEIR CYCLODEXTRIN INCLUSION COMPLEXES	110
Abstract	110
Introduction	111
Materials and Methods	112
Results and Discussion	116
Literature Cited	125
Tables	129
Figures	133
Appendix	136
CHAPTER 5: CONTROLLED RELEASE OF α -TOCOPHEROL AND ITS β - CYCLODEXTRIN INCLUSION COMPLEX FROM LLDPE INTO COCONUT OIL ..	139
Abstract	139
Introduction	140
Materials and Methods	141
Results and Discussion	146
Literature Cited	154
Tables	158
Figures	161
Appendix	164
CHAPTER 6: OXIDATIVE PROGRESSION STUDY OF UNSTABILIZED CORN OIL DURING THE CONTROLLED RELEASE OF α -TOCOPHEROL AND ITS β - CYCLODEXTRIN INCLUSION COMPLEX FROM LLDPE	167
Abstract	167
Introduction	168
Materials and Methods	169
Results and Discussion	171

Literature Cited	176
Tables	179
Figures	181

LIST OF TABLES

Table 2.1. Physical and Chemical Properties of α -, β -, and γ -Cyclodextrin	35
Table 3.1. Characteristics of Reactants and Products in the Preparation of Solid, Natural Antioxidant:CD Inclusion Complexes	73
Table 3.2. Colorimetric Analyses in the CIE L*a*b* Color Space	74
Table 3.3. Water Content and Thermal Decomposition Temperature (T_d) in Air Atmosphere	75
Table 3.4. Enthalpy of the Measured Effect (ΔH_{meas}) and Peak Temperature during Dehydration and Vaporization of Water	76
Table 4.1. Concentration Levels of Natural Antioxidant Additives Compounded into LLDPE	129
Table 4.2. Oxidation Induction Time (OIT) of LLDPE Films with Antioxidant Additives at 200 °C	130
Table 4.3. Oxygen Transmission Rate (OTR) of LLDPE Films with Antioxidant Additives	131
Table 4.4. Static Water Contact Angle Measurements of LLDPE Films with Antioxidant Additives	132
Table 5.1. Hildebrand Solubility Parameters (δ) of Solvents, Polyethylene, Coconut Oil, and Natural Antioxidants at 25 °C	158
Table 5.2. Extraction of Antioxidant Additives from LLDPE Films into Tetrahydrofuran	159
Table 5.3. Curve-Fit Parameters of Active Concentration Fraction (f), Diffusion Coefficient (D), and Concentration Mass Ratio (α) Selected to Minimize the Sum of Squares Error ($\Sigma \varepsilon^2$) of the Migration Model	160
Table 5.4. Various Solvent Extraction Efficiencies of Antioxidant Additives from Metallocene LLDPE Films (45.2-mm diameter and 870- μ m thickness)	164
Table 6.1. Peroxide Values of Ten Stripped Corn Oil Bottles Received in Three Different Shipments (A, B, and C)	179
Table 6.2. Oxidation Induction Time (OIT) of Natural Antioxidants in Stripped Corn Oil at 150 °C	180

LIST OF FIGURES

Figure 2.1.	Structures of various natural antioxidants	36
Figure 2.2.	(a) The truncated cone shape and the functional structural scheme of the β -cyclodextrin molecule. (b) The glucose units are connected through glycosidic α -1,4 bonds. The C-2-OH group of one glucose unit forms an intramolecular hydrogen bond with the C-3-OH group of the adjacent glucose unit	37
Figure 2.3.	Synthetic antioxidants used in polymers for food packaging	38
Figure 2.4.	(a) Zero-order, (b) first-order, and (c) $t^{-1/2}$ release patterns from devices containing the same initial active agent content	39
Figure 2.5.	Comparison of different models for predicting the diffusion coefficient as a function of migrant molecular weight with experimental data for LLDPE and LDPE. Experimental data (\times), deterministic approach (—), worst-case approach (---), and stochastic approach (---) with approximate 95% confidence interval (.....)	40
Figure 3.1.	Structure and carbon numbering of the natural antioxidants (a) α -tocopherol and (b) quercetin	77
Figure 3.2.	ATR/FT-IR spectra of (a) free α -tocopherol, (b) β -CD, (c) α -tocopherol and β -CD physical mixture, and (d) α -tocopherol: β -CD inclusion complex	78
Figure 3.3.	ATR/FT-IR spectra of (a) quercetin dihydrate, (b) γ -CD, (c) quercetin and γ -CD physical mixture, and (d) quercetin: γ -CD inclusion complex	79
Figure 3.4.	^{13}C NMR spectrum of (a) α -tocopherol. ^{13}C CP/MAS NMR spectra of (b) β -CD, (c) α -tocopherol and β -CD physical mixture, and (d) α -tocopherol: β -CD inclusion complex. Asterisks indicate spinning sidebands	80
Figure 3.5.	^{13}C CP/MAS NMR spectra for (a) quercetin dihydrate, (b) γ -CD, (c) quercetin and γ -CD physical mixture, and (d) quercetin: γ -CD inclusion complex. Asterisks indicate spinning sidebands	81
Figure 3.6.	DSC curves showing the glass transition of α -tocopherol in its (a) free α -tocopherol form, (b) α -tocopherol and β -CD physical mixture, and (c) α -tocopherol in β -CD inclusion complex under N_2 at a temperature rate of $5\text{ }^\circ\text{C}/\text{min}$	82
Figure 3.7.	Hydration time of (a) β -cyclodextrin and (b) γ -cyclodextrin cavity from ambient to 100% relative humidity as measured by water activity at $25\text{ }^\circ\text{C}$. Water activity measurements were performed on an Aqua Lab Model Series 3TE. Samples at ambient relative humidity were placed in a glass desiccator with deionized, distilled water placed in the base of the container to achieve a 100% relative humidity environment	83

Figure 3.8. Molar ratio of β -CD: α -tocopherol inclusion complex product with (a) 16:1 β -CD: α -tocopherol and (b) 1:1 β -CD: α -tocopherol reactant ratios during equilibration shaking at 250 rpm and 25 °C (n = 2)	84
Figure 3.9. Quercetin content in its γ -cyclodextrin inclusion complex product when different molar ratios of reactants were varied after 24-hour equilibration shaking at 250 rpm and 25 °C (n = 2)	85
Figure 3.10. Physical appearance of (a) α -tocopherol, (b) β -CD, (c) α -tocopherol and β -CD physical mixture, and (d) α -tocopherol: β -CD inclusion complex. Solid inclusion complexes of natural antioxidants with CD differ in appearance from their same weight percent physical mixtures	86
Figure 3.11. Physical appearance of (a) quercetin dihydrate, (b) γ -CD, (c) quercetin and γ -CD physical mixture, and (d) quercetin: γ -CD inclusion complex. Solid inclusion complexes of natural antioxidants with CD differ in appearance from their same weight percent physical mixtures	86
Figure 3.12. ATR/FT-IR spectrum of α -tocopherol	87
Figure 3.13. ATR/FT-IR spectrum of β -CD	88
Figure 3.14. ATR/FT-IR spectrum of α -tocopherol and β -CD physical mixture	89
Figure 3.15. ATR/FT-IR spectrum of α -tocopherol: β -CD inclusion complex	90
Figure 3.16. ATR/FT-IR spectrum of quercetin dihydrate	91
Figure 3.17. ATR/FT-IR spectrum of γ -CD	92
Figure 3.18. ATR/FT-IR spectrum of quercetin dihydrate and γ -CD physical mixture	93
Figure 3.19. ATR/FT-IR spectrum of quercetin dihydrate: γ -CD inclusion complex	94
Figure 3.20. TG and DTG curves of β -CD with a temperature ramp of 5 °C/min under air atmosphere	95
Figure 3.21. TG and DTG curves of α -tocopherol with a temperature ramp of 5 °C/min under air atmosphere	96
Figure 3.22. TG and DTG curves of α -tocopherol and β -CD physical mixture with a temperature ramp of 5 °C/min under air atmosphere	97
Figure 3.23. TG and DTG curves of α -tocopherol: β -CD inclusion complex with a temperature ramp of 5 °C/min under air atmosphere	98
Figure 3.24. TG and DTG curves of γ -CD with a temperature ramp of 5 °C/min under air atmosphere	99
Figure 3.25. TG and DTG curves of quercetin dihydrate with a temperature ramp of 5 °C/min under air atmosphere	100
Figure 3.26. TG and DTG curves of quercetin dihydrate and γ -CD physical mixture with a temperature ramp of 5 °C/min under air atmosphere ...	101
Figure 3.27. TG and DTG curves of quercetin: γ -CD inclusion complex with a temperature ramp of 5 °C/min under air atmosphere	102
Figure 3.28. DSC curve of β -CD showing the dehydration and vaporization enthalpies of water	103

Figure 3.29. DSC curve of α -tocopherol and β -CD physical mixture showing the dehydration and vaporization enthalpies of water	104
Figure 3.30. DSC curve of α -tocopherol: β -CD inclusion complex showing the dehydration and vaporization enthalpies of water	105
Figure 3.31. DSC curve of quercetin dihydrate showing the dehydration and vaporization enthalpies of water	106
Figure 3.32. DSC curve of γ -CD showing the dehydration and vaporization enthalpies of water	107
Figure 3.33. DSC curve of quercetin dihydrate and γ -CD physical mixture showing the dehydration and vaporization enthalpies of water	108
Figure 3.34. DSC curve of quercetin: γ -CD inclusion complex showing the dehydration and vaporization enthalpies of water	109
Figure 4.1. Optical transmission microscopy of (a) quercetin and (b) quercetin: γ -cyclodextrin inclusion complex localization within Ziegler-Natta LLDPE at 200 \times magnification	133
Figure 4.2. Atomic force microscopy height (<i>left</i>) and phase (<i>right</i>) images (3.0 μm^2) of (a) Ziegler-Natta LLDPE and (b) metallocene LLDPE. In both height images, the contrast covers variations in the 0–50 nm range. In the phase images, the contrast covers phase shifts of (a) 30 $^\circ$ and (b) 20 $^\circ$	134
Figure 4.3. Atomic force microscopy height (<i>left</i>) and phase (<i>right</i>) images (3.0 μm^2) of (a) α -tocopherol and (b) α -tocopherol: β -CD complex in Ziegler-Natta LLDPE. In the height images, the contrast covers variations in the (a) 0–100 nm and (b) 0–50 nm range. In the phase images, the contrast cover phase shifts of (a) 30 $^\circ$ and (b) 70 $^\circ$	135
Figure 4.4. (a) Ziegler-Natta and (b) metallocene LLDPE films containing natural antioxidant additives. Visual appearance of optical translucence and color indicated by logo design with black text and white background	136
Figure 4.5. Example of water contact angle characterization on the surface of a metallocene LLDPE control film	137
Figure 4.6. Example of oxidation induction time (OIT) determination of Ziegler-Natta LLDPE containing 1950 mg/kg quercetin by DSC	138
Figure 5.1. Mass fraction of α -tocopherol released from Ziegler-Natta LLDPE film into coconut oil during 4-week storage at 30 $^\circ\text{C}$ in its (a) free and (b) β -cyclodextrin complexed forms. Solid curves represent the migration model fitted to experimental data points	161
Figure 5.2. Mass fraction of α -tocopherol released from metallocene LLDPE film into coconut oil during 4-week storage at 30 $^\circ\text{C}$ in its (a) free and (b) β -cyclodextrin complexed forms. Solid curves represent the migration model fitted to experimental data points	162
Figure 5.3. Mass fraction of α -tocopherol released from Ziegler-Natta and metallocene LLDPE into 95% ethanol at 4 weeks of storage at 30 $^\circ\text{C}$ in its free and β -cyclodextrin complexed forms	163

Figure 5.4.	HPLC chromatograms of standards of (a) α -tocopherol (10 mg/L) and (b) quercetin dihydrate (8 mg/L) in sample solvent of 75:25 isopropanol:methanol	165
Figure 5.5.	HPLC chromatograms of α -tocopherol released from Ziegler-Natta LLDPE films containing the additives (a) free α -tocopherol and (b) α -tocopherol: β -CD complex into coconut oil at 28 days of storage at 30.0 °C	166
Figure 6.1.	(a) Pentane, (b) hexanal, and (c) <i>trans</i> -2-heptenal are secondary oxidation products of linoleic acid, a primary component of corn oil ..	181
Figure 6.2.	Peroxide value of stripped corn oil with different natural antioxidant treatments in Ziegler-Natta LLDPE during 4 weeks of storage at 30 °C	182
Figure 6.3.	Peroxide value of stripped corn oil with different natural antioxidant treatments in metallocene LLDPE during 4 weeks of storage at 30 °C	183
Figure 6.4.	Conjugated dienoic acid of stripped corn oil with different natural antioxidant treatments in Ziegler-Natta LLDPE during 4 weeks of storage at 30 °C	184
Figure 6.5.	Conjugated dienoic acid of stripped corn oil with different natural antioxidant treatments in metallocene LLDPE during 4 weeks of storage at 30 °C	185
Figure 6.6.	SPME/ GC-MS chromatogram of mixed standards of pentane (26.0 mg/kg), hexanal (10.1 mg/kg), and <i>trans</i> -2-heptenal (2.1 mg/kg) spiked into a stripped corn oil matrix	186
Figure 6.7.	SPME/ GC-MS chromatogram of pentane, hexanal, and <i>trans</i> -2-heptenal in stripped corn oil (peroxide value of 20.6 meq O ₂ /kg) at initial time	187

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- <i>tert</i> -butyl-4-methoxyphenol)
BHT	butylated hydroxytoluene (2,6-di- <i>tert</i> -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