

# Polymer Processing and Characterization of LLDPE Films Loaded with $\alpha$ -Tocopherol, Quercetin, and Their Cyclodextrin Inclusion Complexes

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**ABSTRACT:** Natural antioxidant additives were compounded into linear low-density polyethylene (LLDPE) using a twin-screw counter-rotating mixer and compression molded into films. Manufactured LLDPE films contained 2715 mg kg<sup>-1</sup>  $\alpha$ -tocopherol in its free and  $\beta$ -cyclodextrin complexed form and 1950 mg kg<sup>-1</sup> quercetin in its free and  $\gamma$ -cyclodextrin complexed form. Both cyclodextrin complexes were loaded into films at 1.5% by weight. These natural antioxidants were incorporated into LLDPE resins with two different catalyst types, Ziegler-Natta and metallocene. Films were characterized by optical microscopy, oxidation induction time (OIT), oxygen transmission rate, contact

angle analysis, and atomic force microscopy (AFM). All antioxidant additives increased the oxidative stability of LLDPE as measured by increased OIT, particularly quercetin. Natural antioxidants and their cyclodextrin inclusion complexes may provide a dual function in packaging to protect the polymer from oxidative degradation during melt processing and to delay the onset of oxidation of the packaged food during storage. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2299–2309, 2010

**Key words:** additives; antioxidants; cyclodextrin; inclusion complex; polyethylene

## INTRODUCTION

During package manufacturing, many antioxidants and stabilizers within a polymer act sacrificially and are converted into oxidation products as they function to protect the polymer from degradation. The toxicity of these synthetic antioxidant transformation products is either not well known or suspected to be greater than the parent additive.<sup>1</sup> Current worldwide trends to avoid or reduce the use of synthetic food additives have given way to investigations of using natural antioxidants in food and packaging systems. Natural antioxidants continue to receive attention in the food industry because of their presumed safety, given that they are sourced primarily from plant materials and have been in use for centuries.

The first natural antioxidant incorporated into synthetic polymers was  $\alpha$ -tocopherol.<sup>2</sup>  $\alpha$ -Tocopherol

exhibits an excellent melt stabilization to polyethylene and polypropylene at low concentrations in the range of 100–300 mg kg<sup>-1</sup>, which surpasses that of the stabilization provided by some of the best synthetic hindered phenol antioxidants traditionally used for this purpose.<sup>3</sup> Therefore,  $\alpha$ -tocopherol can be used cost effectively at only a small fraction of the concentration typically required for polyolefin stabilization by synthetic hindered phenols.  $\alpha$ -Tocopherol is also a superior antioxidant for reducing off-odor and off-taste from high-density polyethylene bottles compared with the typical synthetic antioxidants, Irganox 1010 and butylated hydroxytoluene (BHT).<sup>4–6</sup> Flavonoid antioxidants, such as quercetin, have not been investigated for incorporation into polymer packaging materials.

The natural antioxidants may have a dual function in the polymer packaging to protect the polymer from oxidative degradation during melt processing and to delay the onset of oxidation of the packaged food during storage.<sup>7</sup> Considerable losses of  $\alpha$ -tocopherol have been reported in low-density polyethylene (LDPE) films likely due to thermo-oxidative effects during extended polymer processing.<sup>7,8</sup> Cyclodextrins (CDs) are known for their ability to act as host molecules to form inclusion

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complexes with a wide variety of guest molecules.<sup>9,10</sup> The advantages of CD inclusion complex formation with natural antioxidants are potential thermo-oxidative protection during polymer melt processing and a provision of controlled release. CD inclusion complexes may be embedded directly into polymer films by melt processing, and the antioxidant is protected both from the environment and its processing into polymers by the thermally stable crystalline lattice provided by the host CD. CDs can decrease the effective guest mobility in a controlled manner allowing for a continuous, more uniform level of antioxidant release for extended shelf life foods.

Linear low-density polyethylene (LLDPE) has the fastest growth rate of the three major polyethylene families and is used in the flexible film food market. Polymer additive transport depends on the structural variations and complexity of the polymer backbone in addition to the type and nature of the diffusing additives. Different catalysts in the production of LLDPE can be used to obtain polymers with different molecular weight distributions, crystalline structure morphologies, and diffusion path networking arrangements, which may allow differences in additive release rates for active packaging materials.

Multiple-site catalysis of polyethylene leads to polymer chains with varying structures across the chains and a broad molecular weight distribution. Conventional multisite Ziegler-Natta LLDPEs are characterized by broad molecular weight distributions and broad comonomer distributions. Ziegler-Natta LLDPE has more comonomer in the lower molecular weight fraction and less in the high molecular weight fraction.<sup>11</sup>

Single-site catalyzed LLDPE has comonomer much more uniformly distributed along the polymer backbone than do conventional resins. Metallocene catalysts are highly active catalysts exhibiting an exceptional ability to polymerize olefin monomers and have advantages over the conventional Ziegler-Natta catalysts. Metallocenes produce extremely uniform polymers and copolymers of narrow molecular weight distribution and narrow comonomer distribution and simultaneously control the resulting polymer chain architectures. A narrower comonomer distribution results in a narrower crystallite size distribution in the crystalline morphology. This narrower crystalline size distribution will have a significant impact on additive diffusion and release rate through the material. Control of crystalline morphology translates into control of diffusion path tortuosity.

This study compares a Ziegler-Natta LLDPE and a metallocene LLDPE having the same density (crystallinity) but different crystalline structure morphologies and diffusion path networking arrangements

that may allow for differences in release rate. LLDPE resins were selected after surveying the patent literature,<sup>12-16</sup> which describes a range of recommended and preferred resin characteristics for packaging film sealant layers. Regardless of whether the sealant layer polyethylene copolymer is produced by heterogeneous catalysis (Ziegler-Natta LLDPE) or homogeneous catalysis (metallocene LLDPE), the preferred range for the melt index is 1.3–8.1 dg min<sup>-1</sup> (ASTM D 1238 Condition 190°C/2.16 kg) with a density in the range of 0.88–0.94 g cm<sup>-3</sup>.

A more complete understanding of the incorporation of active compounds and their CD inclusion complexes into polymer packaging is necessary to develop and tailor future packaging systems to specific foods. In future applications of this technology, additives will be incorporated into the innermost layer of the film structure, which generally functions as the food contact layer and the sealant layer, for controlled release to a food product. The purpose of this research was to compound  $\alpha$ -tocopherol, quercetin, and their CD inclusion complexes into Ziegler-Natta LLDPE and metallocene LLDPE while maintaining their relative antioxidant activity and stability. LLDPE films loaded with these natural antioxidants were characterized and will be used in future studies to measure their antioxidant release rates into a model food system.

## EXPERIMENTAL

### Materials

( $\pm$ )- $\alpha$ -Tocopherol of 98% purity and quercetin dihydrate of 99% purity were supplied by Sigma-Aldrich (St. Louis, MO). Preparation of inclusion complexes of  $\alpha$ -tocopherol with  $\beta$ -CD and quercetin with  $\gamma$ -CD was performed as described previously.<sup>17</sup> These CD complexes in unhydrated form were stored in a desiccator after the lyophilization stage. Solid  $\alpha$ -tocopherol :  $\beta$ -CD complexes with 18.1% (w/w)  $\alpha$ -tocopherol content and quercetin :  $\gamma$ -CD complexes with 13.0% (w/w) quercetin content were used as antioxidant additives in LLDPE. high-performance liquid chromatography (HPLC)-grade water was obtained from Fisher Scientific (Pittsburgh, PA).

Two commercially available LLDPE resins were selected as comparable materials with different catalyst systems. Ziegler-Natta LLDPE had a density of 0.918 g cm<sup>-3</sup> 1-hexene (C6) comonomer, and a melt flow index of 3.2 dg min<sup>-1</sup> (ASTM D 1238 Condition 190°C/2.16 kg). Metallocene LLDPE had a density of 0.918 g cm<sup>-3</sup> 1-hexene (C6) comonomer, and a melt flow index of 3.5 dg min<sup>-1</sup> (ASTM D 1238 Condition 190°C/2.16 kg). Both LLDPE resin grades contained a typical antioxidant stabilizer package added by the manufacturer but no antiblock or slip agents.

**TABLE I**  
**Concentration Levels of Natural Antioxidant Additives Compounded into LLDPE**

Antioxidant Additive	Concentration Level <sup>a</sup>			
	Antioxidant (wt %)	Additive in LLDPE (wt %)	Additive in LLDPE (mg kg <sup>-1</sup> )	Antioxidant in LLDPE (mg kg <sup>-1</sup> )
$\alpha$ -Tocopherol	98.0	0.28	2770	2715
$\alpha$ -Tocopherol : $\beta$ -CD complex	18.1	1.50	15000	2715
Quercetin	99.0	0.20	1970	1950
Quercetin : $\gamma$ -CD complex	13.0	1.50	15000	1950

<sup>a</sup> Natural antioxidant concentrations listed are in addition to the typical stabilizer system in commercial LLDPE resins.

The degree of crystallinity (mass fraction,  $W_{c,d}$ ), based on density ( $\rho$ ) was calculated using the following equation:

$$W_{c,d} = \frac{1/\rho_s - 1/\rho_a}{1/\rho_c - 1/\rho_a} \times 100,$$

where  $\rho_s$ ,  $\rho_c$ , and  $\rho_a$  are the density of the sample, completely crystalline (1.00 g cm<sup>-3</sup>), and completely amorphous (0.852 g cm<sup>-3</sup>) polyethylene, respectively.<sup>18</sup> Both Ziegler-Natta and metallocene LLDPE resins were estimated to have 49% crystallinity.

### Compounding of additives into LLDPE

LLDPE resins were compounded with additives and compression molded into films at the Advanced and Applied Polymer Processing Institute in Danville, VA. A Plasti-Corder twin-screw counter-rotating mixer type EPL-V5501 (C.W. Brabender Instruments, South Hackensack, NJ) with a measuring head type C.E.E.6-230V8. 5AMP, temperature control console type 808-400-DTI, and electronic Plasti-Corder torque rheometer was used to compound antioxidant additives into Ziegler-Natta and metallocene LLDPE resins. Before compounding, both LLDPE resin types were purged with a positive pressure of N<sub>2</sub> through the material for at least 24 h to reduce oxidative degradation of the polymer during processing. The concentration levels of natural antioxidants and their inclusion complexes compounded into Ziegler-Natta and metallocene LLDPE resins are summarized in Table I.

Control runs were used to determine the time to fusion peak torque, and a minimum of 5 min was added to this time to ensure adequate and equal mixing time in melt shear. Torque readings were continuously measured with a torque rheometer and provided an estimate of the melt viscosity for the two LLDPE resin types. Resin pellets were added to the 50-mL mixing bowl at a temperature of 190°C and mixed at a speed of 100 rpm for a residence time of 5 min. Control Ziegler-Natta LLDPE had a maximum torque of 1450 m-g at initial time with an end torque of 1130 m-g after 5 min. Control metallo-

cene LLDPE had a maximum torque of 1510 m-g at initial time with an end torque of 1250 m-g after 5 min. A N<sub>2</sub> bleed was applied to the opening of the small bowl during shear mixing of LLDPE and additives to limit O<sub>2</sub> exposure during compounding. Three compounded batches of each additive treatment and two control batches of each LLDPE resin type were produced. Control batches received the same thermal exposure by melting and mixing the resin pellets. A purge material was used to clear the bowl between different additive treatments. Each compounded LLDPE batch in the melt state was manually pressed between two polytetrafluoroethylene (PTFE)-coated platens into preforms of <10-mm thickness and ~43 g weight for subsequent compression molding.

### Compression molding of LLDPE into films

The compression molding method was modified from ASTM D 4703-03.<sup>19</sup> A compression molding press Genesis Series G100H-18-CX (Wabash MPI, Wabash, IN) was used to compression mold the preforms of LLDPE into films. A brass picture frame mold with inner dimensions of 23.5 cm × 23.5 cm and thickness of 820  $\mu$ m was used with aluminum foil (20- $\mu$ m thickness) as the parting agent. The mass of the preform was sufficient to fill the mold volume (45.3 cm<sup>3</sup>) when it was melted and provided an excess of about 3% (w/w) for flash. Manually pressed LLDPE preforms were placed in the picture-frame mold between two, aluminum foil parting agents and then the assembly was inserted between the PTFE-coated platens. The mold assembly was preheated between both platens and set at a process temperature of 190°C by closing the press with application of contact pressure for 5 min. The press platens at 190°C were closed with 6 tons of ram force in three cycles to remove entrapped air in the material and prevent the development of voids in the films: (1) 10-s press, (2) 10-s press, and (3) 5-min press. At the low pressure of ~140 psi, the presence of any entrapped air was more easily observed. Films were cooled by air, followed immediately by

circulated water cooling under compression to 40°C at an average cooling rate of 23°C min<sup>-1</sup>. The press was opened, and films were removed from the mold at a temperature <40°C. LLDPE films containing each antioxidant additive and control films of each resin type were produced in triplicate and duplicate, respectively. Films were punched with a 45-mm diameter steel blanking die resulting in 45.2-mm diameter sample discs to perform future controlled-release studies. LLDPE film thickness of 10 sample discs from four different batches were measured with a micrometer at four locations across the film as 870 ± 2 μm (*n* = 160). All sample films were stored at refrigeration temperatures and protected from light to minimize additive migration and maintain additive stability.

### Optical transmission microscopy

An Eclipse series 80i advanced research microscope (Nikon Instruments, Melville, NY) with a DS-Fi1 digital imaging head and CFI Plan Fluor series objective lens at 20× magnification was used to observe particulate antioxidant additives and their qualitative degree of dispersion in LLDPE films. NIS Elements Imaging Software BR 2.30 (Nikon Instruments, Melville, NY) was used to process images.

### Oxidation induction time

LLDPE films with additives were cut into 3.2-mm diameter discs of 870 ± 2-μm thicknesses using a bore-hole cutter to obtain sample weights of 6.5 ± 0.2 mg. Sample discs were placed in an open standard aluminum differential scanning calorimetry (DSC) pan. A DSC Q1000 instrument (TA Instruments, New Castle, DE) was used with a sample purge flow of N<sub>2</sub> at 50 mL min<sup>-1</sup>. The DSC was equilibrated at 50°C, ramped to 200°C at 20°C min<sup>-1</sup>, held isothermal for 5 min, and then the gas was switched to O<sub>2</sub> at 12.5 min. Samples were held under O<sub>2</sub> isothermally at 200°C until stopping the run after the maximum slope of the exotherm was observed in the real-time DSC curve. Universal Analysis 2000 (TA Instruments, New Castle, DE) software was used to analyze the oxidation induction time (OIT) of each sample (*n* = 2) by the tangent method. This method follows ASTM Standard D 3895-04.<sup>20</sup>

### Oxygen transmission rate

An 8001 oxygen permeation analyzer (Illinois Instruments, Johnsburg, IL) was calibrated at 23.0°C and 0% relative humidity with a standard Mylar film of known oxygen transmission rate (OTR) of 64.8 cm<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>. N<sub>2</sub> flow through the bottom chamber was 19 cm<sup>3</sup> min<sup>-1</sup>, and O<sub>2</sub> flow through the top chamber

was 20 cm<sup>3</sup> min<sup>-1</sup>. A masking plate with a diameter of 2.5 cm (4.91 cm<sup>2</sup> surface area) was used. LLDPE control and antioxidant additive films (*n* = 2) of 870 ± 2-μm thickness were measured for OTR (cm<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>) at 23.0°C, 0% relative humidity, and atmospheric pressure until an equilibrium condition was present at 360 min.

### Contact angle measurements

Static water contact angle measurements were performed at room temperature using a FTA200 dynamic contact angle analyzer (First Ten Angstroms, Portsmouth, VA) connected to a B/W CCD camera (Sanyo North America, San Diego, CA) above a benchtop vibration isolation system with Stabilizer Technology (Newport, Irvine, CA). A constant sessile droplet volume of water was used and delivered to the surface of each LLDPE film by an 18-gauge needle with a pump out rate of 0.20 μL s<sup>-1</sup>. Contact angles of water droplets with good symmetry were reported as a mean of the left and right angles on control LLDPE films (*n* = 6) and LLDPE films with antioxidant additives (*n* = 9).

### Atomic force microscopy (AFM)

A MultiMode scanning probe microscope (Veeco Instruments, Santa Barbara, CA) with a type E piezoelectric scanner was used at ambient temperature to image the surface morphology of selected LLDPE films. Antimony (n) doped silicon probes (Veeco model TESP7) with nominal tip radius of 8 nm, force constant of 42 N m<sup>-1</sup>, and resonance frequency of 320 kHz were used. LLDPE film samples with dimensions of 10 mm × 10 mm were scanned in several different areas to obtain a representative surface image. The atomic force microscope (AFM) was operated in tapping mode with a scan area of 3.0 μm<sup>2</sup>, a scan rate of 1.0 Hz, and 512 lines per image. The free air amplitude (*A*<sub>0</sub>) and set-point amplitude (*A*<sub>sp</sub>) were set at target values of 6.5 and 4.5 V, respectively. Therefore, the set-point amplitude ratio (*r*<sub>sp</sub>) represented moderate tapping with a value of 0.7. Raw height and phase images were processed for background removal (flattening) by using the MultiMode's image analysis and presentation software.

### Statistical analysis

Statistical analysis of the antioxidant additives in each individual LLDPE resin type was performed by a one-way analysis of variance with the general linear model supported by SAS (Version 9.1.3, 2003, SAS, Cary, NC). Multiple comparisons were adjusted for the Tukey-Kramer method of the general linear model procedure to test for least-squares mean separation. Effects were considered significant



at  $P < 0.05$ . Data values were reported as mean  $\pm$  standard error.

## RESULTS AND DISCUSSION

### Physical appearance of additive-loaded LLDPE films

All natural antioxidants and their CD complexes were observed to be uniform and consistent throughout the LLDPE without any particulates observed on the macroscale. The manufactured Ziegler-Natta and metallocene LLDPE films contain 2715 mg kg<sup>-1</sup>  $\alpha$ -tocopherol in its free and  $\beta$ -CD complexed form and 1950 mg kg<sup>-1</sup> quercetin in its free and  $\gamma$ -CD complexed form as summarized in Table I. At 0.20 and 0.27% natural antioxidant concentrations, these are at the typical concentration levels used with commercial synthetic hindered phenols.<sup>21</sup>

Control metallocene LLDPE films are observed to have greater clarity than the conventional Ziegler-Natta LLDPE control. Free  $\alpha$ -tocopherol and its  $\beta$ -CD complex loaded into LLDPE films exhibit a slight amber color. Films loaded with quercetin are observed as an intense yellow color, but this yellow intensity is noticeably subdued in films containing the quercetin :  $\gamma$ -CD complex.

### Additive dispersion in LLDPE films

The relatively polar structure of the CD molecule has presented difficulties in distributing this additive and its inclusion complexes into nonpolar matrices, such as polyolefins. Siró et al.<sup>22</sup> observed the visible inhomogeneous distribution of  $\alpha$ -tocopherol :  $\beta$ -CD complexes in LDPE film. Their materials were processed with a single-screw extruder and were observed to have CD agglomerates that appeared as white spots in the LDPE matrix. Single-screw extrusion has also produced LDPE films containing uncomplexed  $\beta$ -CD in the form of aggregates.<sup>23</sup> Other processing techniques, including melt pressing and solution casting, seem to have limited effectiveness in uniformly distributing inclusion complexes throughout the polymer.<sup>24</sup>

In this study, the dispersion of natural antioxidant : CD complexes within LLDPE was optimized by mixing the resin and additive in the melt state with a twin-screw counter-rotating mixer. No visual aggregation of additives was observed as had been reported by previous researchers, which indicates that polymer and additive were mixed efficiently and only additive solubility within the polymer was a limiting factor. The solubility of additives is dependent on the volume of amorphous fraction and the polymer structure. Many additives are compounded into the polymer at levels above their

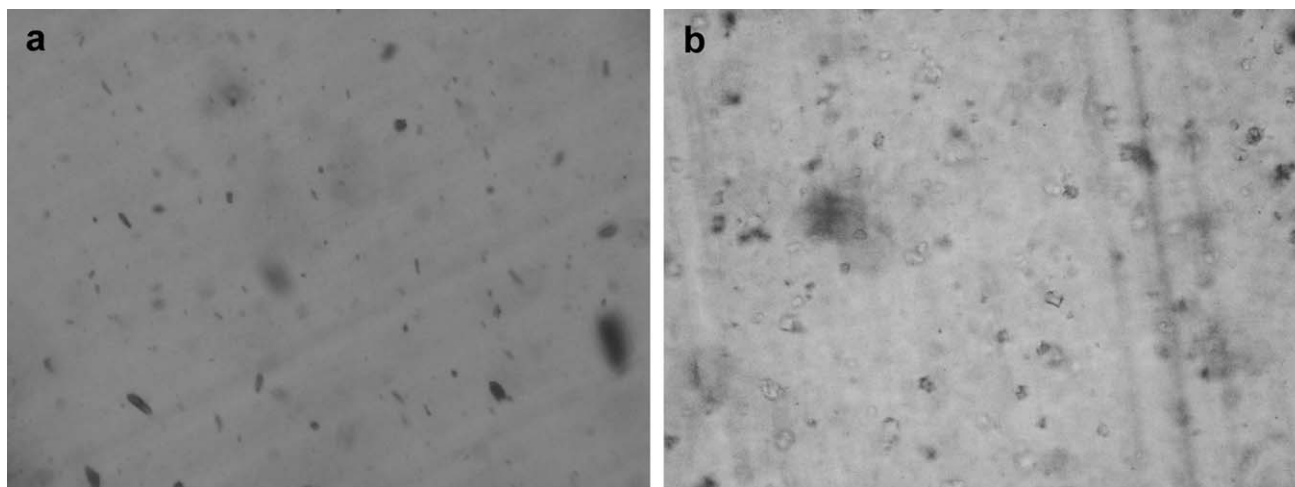
intrinsic solubility and, therefore, exist in a supersaturated solution. Such additives have low diffusion coefficients and migration is thereby minimized, or a two-phase system is formed, which consists of a saturated solution of additive in polymer and a separate additive phase.

Additives dissolved in a polymer are primarily located in the amorphous phase in zones around knots, folds and various chain entanglements where there is sufficient free volume to hold the molecule.<sup>25</sup> Uniform dispersion of the antioxidants during compounding is critical for obtaining optimal performance of higher molecular weight antioxidants, which are expected to have relatively slow diffusion rates. The temperature of processing the polymer may play an important role in the type of dispersion obtained.<sup>26</sup> Quercetin has a melting point (323°C<sup>27</sup>) above the process temperature of 190°C, and its resulting dispersion is of the particulate type, in which quercetin exists as separate phases in the LLDPE matrix.  $\alpha$ -Tocopherol exists as a liquid at room temperature, so its melting temperature is clearly below 190°C, and it forms a more solution-like dispersion in which  $\alpha$ -tocopherol molecules are homogeneously dispersed in the polymer matrix.

### Optical transmission microscopy

The LLDPE films containing natural antioxidant additives were viewed under 200 $\times$  magnification to obtain a qualitative measure of each additives solubility in the bulk polymer. The  $\alpha$ -tocopherol and  $\alpha$ -tocopherol :  $\beta$ -cyclodextrin complex were not observed throughout the thickness of the LLDPE films, which indicates that these additives were both soluble in the amorphous phase. This observation was rather remarkable because the relatively polar  $\beta$ -CD host molecule is not miscible within the LLDPE.<sup>23</sup> The  $\alpha$ -tocopherol :  $\beta$ -CD complex seems to have much less polarity than its free  $\beta$ -CD host, which was indicated previously by its lack of water solubility.<sup>17</sup>  $\alpha$ -Tocopherol also may have retained its ability to act as a plasticizer from within its  $\beta$ -CD inclusion complex thereby increasing the additive solubility.

Figure 1 shows evenly distributed composites of both quercetin and quercetin :  $\gamma$ -cyclodextrin complex in LLDPE, indicating their insolubility in the amorphous phase. These films possess a discernable phase boundary between the polymer bulk and the domains of both quercetin and its  $\gamma$ -CD complex. Surface antioxidant concentrations were observed to be equivalent compared with concentrations in the bulk LLDPE, qualitatively indicating that there was not an affinity for the polymer-air interface. Quercetin appears as opaque short, needle-like crystals. The crystal structure of quercetin exists as hydrogen-bonded dimers connected by water molecules.<sup>28</sup> In



**Figure 1** Optical transmission microscopy of (a) quercetin and (b) quercetin :  $\gamma$ -cyclodextrin inclusion complex localization within Ziegler-Natta LLDPE at  $\times 200$  magnification.

contrast, quercetin's  $\gamma$ -CD complex appears as translucent, thin, tetragonal crystals.  $\gamma$ -CD inclusion complexes are known to form channel-type crystalline structures with either tetragonal or hexagonal packing.<sup>29,30</sup> LLDPE films loaded with quercetin :  $\gamma$ -CD complex are of lighter yellow intensity than the equivalent weight percent of quercetin. This reduction in color intensity may be explained by the presence of quercetin within the crystalline channel structure of  $\gamma$ -CD.

### Oxidation induction time

The OIT method is an antioxidant performance test that is also useful for characterizing the degree of dispersion of antioxidants. In polymer matrices containing fairly uniform antioxidant dispersions, the OIT increases approximately linearly with increasing antioxidant concentration.<sup>26</sup> The OIT is a measure of when the onset of oxidation of the polymer matrix occurs. The OIT is generally considered the time at which the active antioxidant in the polymer has been completely consumed.

Antioxidant performance is expected to improve as the antioxidant becomes more uniformly dispersed in the polymer matrix because to inhibit the oxidation reaction, the additive must chemically contact the peroxyradical on the polymer chains.<sup>26</sup> The contact between the dispersed additive and the peroxyradical occurs by diffusion processes. As the degree of dispersion of the antioxidant increases, the average required diffusion path length and, therefore, diffusion time is shortened. The termination reaction rate of immobile macroradicals attached to the polymer chain is directly proportional to the concentration of mobile antioxidant molecules.<sup>25</sup> At a constant average antioxidant concentration, the OIT increases as the degree of dispersion increases.

In Table II, the OIT of the control films at 200°C vary considerably between Ziegler-Natta and metallocene LLDPE with values of  $24.4 \pm 0.4$  and  $81.4 \pm 1.1$  min, respectively. These commercial resin grades contain a typical antioxidant stabilizer package, but differences in OIT may be due to differences in polymerization processes and residual metal catalysts. The antioxidant concentrations of  $2715 \text{ mg kg}^{-1}$   $\alpha$ -tocopherol and  $1950 \text{ mg kg}^{-1}$  quercetin in LLDPE are nearly equivalent on a molar basis and all additives resulted in increased OIT of the polymer. Free  $\alpha$ -tocopherol provides considerable additional oxidative protection to Ziegler-Natta and metallocene LLDPE by extending the OIT by 59.3 and 14.8 min, respectively. The  $\beta$ -CD complex of  $\alpha$ -tocopherol is even more effective than free  $\alpha$ -tocopherol with the OIT extended by 68.1 and 38.9 min in Ziegler-Natta and metallocene LLDPE, respectively. This added protection of the  $\beta$ -CD complex is either because  $\alpha$ -tocopherol is stabilized during polymer processing or experiences increased antioxidant effectiveness within the CD cavity.

Quercetin exhibited excellent performance by extending the OIT of Ziegler-Natta and metallocene LLDPE by 128.4 and 124.7 min, respectively. This result is remarkable because quercetin exists as a particulate dispersion in LLDPE. Several studies have shown that antioxidants, including quercetin,<sup>31,32</sup> can function effectively in suspension in bulk vegetable oils.<sup>33</sup> The reported solubility limit of quercetin in soybean oil is  $\sim 100 \text{ }\mu\text{M}$  ( $34 \text{ mg L}^{-1}$ ),<sup>34</sup> which is likely on the order of its solubility in polyethylene. The activity of partially soluble, suspended quercetin may be attributed to its more favorable orientation at the air-polymer interface where surface oxidation occurs.<sup>33</sup> Low solubility with an effective antioxidant is not a disadvantage if the diffusion or dissolution rates are not determining factors.<sup>35</sup> The quercetin :  $\gamma$ -CD complex extended the OIT by

**TABLE II**  
Oxidation Induction Time (OIT) of LLDPE Films with Antioxidant Additives at 200°C

Antioxidant Additive	OIT (min) <sup>a</sup>	
	Ziegler-Natta LLDPE	Metallocene LLDPE
Control	24.4 ± 0.4 e	81.4 ± 1.1 e
α-Tocopherol <sup>b</sup>	83.7 ± 0.5 c	96.2 ± 0.8 d
α-Tocopherol : β-CD complex <sup>b</sup>	92.5 ± 1.4 b	120.3 ± 1.3 c
Quercetin <sup>c</sup>	152.8 ± 0.0 a	206.1 ± 0.9 a
Quercetin : γ-CD complex <sup>c</sup>	36.6 ± 0.3 d	125.8 ± 0.4 b

<sup>a</sup> Values were reported as mean ± standard error ( $n = 2$ ).

<sup>b</sup> A measure of 2715 mg kg<sup>-1</sup> α-tocopherol.

<sup>c</sup> A measure of 1950 mg kg<sup>-1</sup> quercetin.

12.2 and 44.4 min in Ziegler-Natta and metallocene LLDPE films, respectively, relative to their controls. The performance of quercetin in its γ-CD complex has been greatly suppressed relative to quercetin in its free form but remains comparable with the α-tocopherol : β-CD complex in metallocene LLDPE. In its γ-CD complex, quercetin is expected to have a lower diffusion coefficient due to a large increase in molecular weight from the γ-CD host molecule. Such a decrease in mobility would not allow quercetin to contact macroradicals and peroxyradicals on the polymer chains as effectively.

### Oxygen transmission rate

OTR was measured as an indicator of antioxidant additive location within the free volume of the amorphous phase of the polymer. In Table III, LLDPE films were observed to have high oxygen permeability as expected with both Ziegler-Natta and metallocene types having respective OTR values of 163.0 ± 6.0 and 150.5 ± 0.5 cm<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>. The relatively broad molecular weight distribution of Ziegler-Natta LLDPE results in more overall mobility of molecules, which may have contributed to this slightly higher OTR. α-Tocopherol is soluble in the LLDPE and is likely to plasticize the film, which increases the diffusion coefficient for oxygen. This plasticizing effect is small because the α-tocopherol loading is at a low level of 0.28% (w/w) and may be

observed in Ziegler-Natta LLDPE with an increase in OTR to 173.5 ± 0.5 cm<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>. Wessling et al.<sup>7</sup> observed a trend of increasing OTR through LDPE films containing increasing levels of α-tocopherol.

Additives in the form of platelets can lower the permeability more than additives of compact geometries. Platelets that are oriented in the plane of the polymer film will reduce the effective diffusion coefficient by creating a tortuous path for the oxygen molecules traversing the film. Quercetin loaded into LLDPE at 0.20% (w/w) resulted in improved oxygen barrier properties with decreased OTR values of 147.5 ± 2.5 and 129.5 ± 3.5 cm<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup> in Ziegler-Natta and metallocene LLDPE, respectively. Free CDs have been reported to exhibit improved barrier properties of diffusion and transmission rate when dispersed in HDPE films.<sup>36</sup> CD complexes of both α-tocopherol and quercetin loaded at the 1.5% (w/w) level resulted in decreased OTR values in metallocene LLDPE but no difference in Ziegler-Natta LLDPE films.

### Contact angle measurements

Static water contact angle experiments were performed on control and loaded LLDPE films to characterize the effect of natural antioxidant additives on the hydrophobicity of the polymer surface. In Table IV, the LLDPE control films had water contact angles of 94.2 ± 0.8° and 92.9 ± 0.7° for Ziegler-Natta and metallocene LLDPE, respectively. The

**TABLE III**  
Oxygen Transmission Rate (OTR) of LLDPE Films with Antioxidant Additives

Antioxidant Additive	OTR (cm <sup>3</sup> m <sup>-2</sup> d <sup>-1</sup> ) <sup>a</sup>	
	Ziegler-Natta LLDPE	Metallocene LLDPE
Control	163.0 ± 6.0	150.5 ± 0.5
α-Tocopherol <sup>b</sup>	173.5 ± 0.5	147.0 ± 3.0
α-Tocopherol : β-CD complex <sup>b</sup>	160.0 ± 7.0	139.0 ± 3.0
Quercetin <sup>c</sup>	147.5 ± 2.5	129.5 ± 3.5
Quercetin : γ-CD complex <sup>c</sup>	159.5 ± 2.5	133.5 ± 6.5

<sup>a</sup> Values were reported as mean ± standard error ( $n = 2$ ).

<sup>b</sup> A measure of 2715 mg kg<sup>-1</sup> α-tocopherol.

<sup>c</sup> A measure of 1950 mg kg<sup>-1</sup> quercetin.



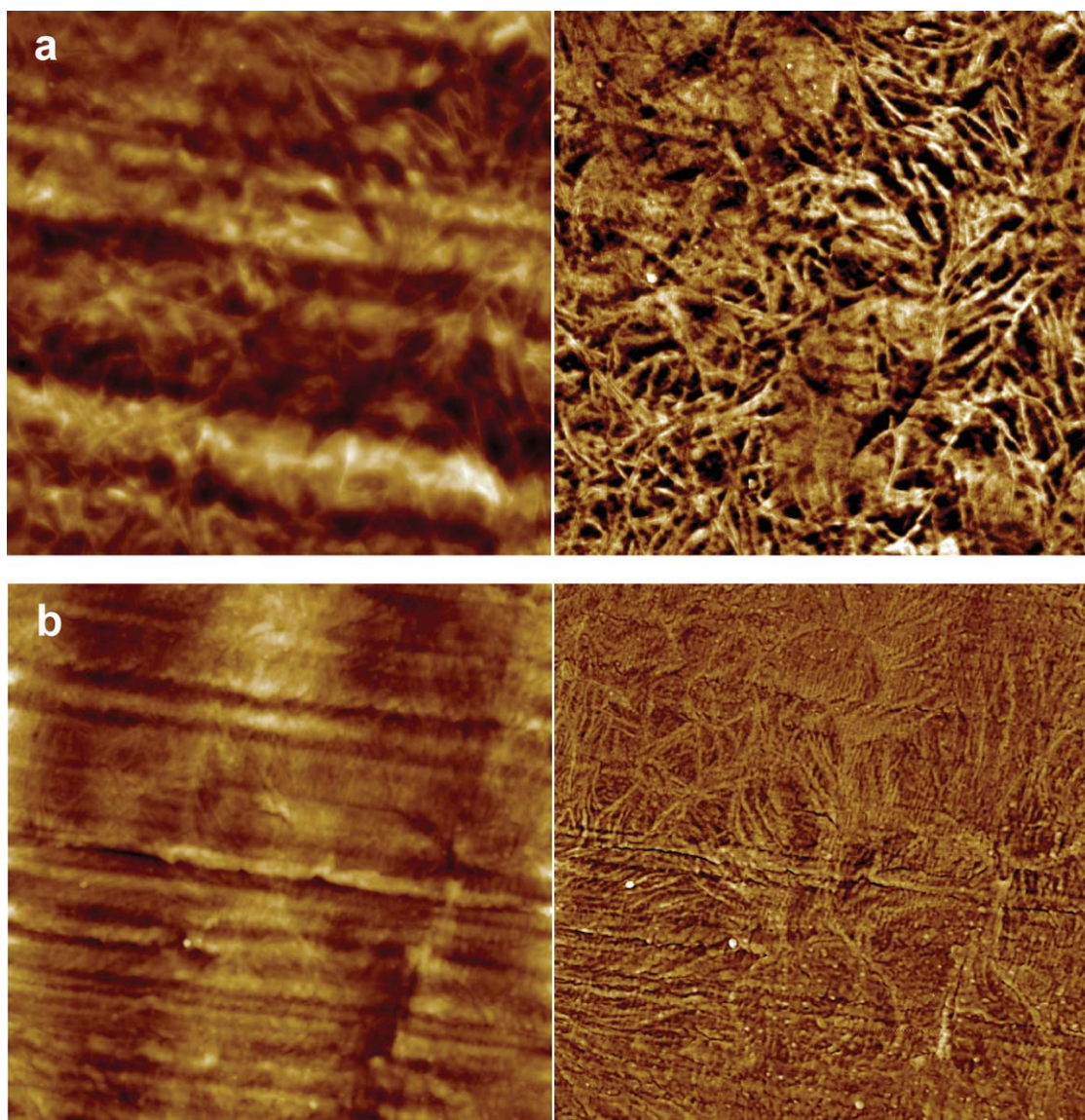
**TABLE IV**  
**Static Water Contact Angle Measurements of LLDPE Films**  
**with Antioxidant Additives**

Antioxidant Additive	Water Contact Angle (°) <sup>a</sup>	
	Ziegler-Natta LLDPE	Metallocene LLDPE
Control	94.2 ± 0.8 b	92.9 ± 0.7 bc
α-Tocopherol <sup>b</sup>	96.2 ± 0.6 ab	91.9 ± 0.5 c
α-Tocopherol : β-CD complex <sup>b</sup>	97.2 ± 0.7 a	94.5 ± 0.6 abc
Quercetin dihydrate <sup>c</sup>	97.1 ± 0.5 a	96.5 ± 1.0 a
Quercetin : γ-CD complex <sup>c</sup>	96.8 ± 0.8 ab	95.0 ± 0.6 ab

<sup>a</sup> Values were reported as mean ± standard error for control ( $n = 6$ ) and antioxidant additives ( $n = 9$ ).

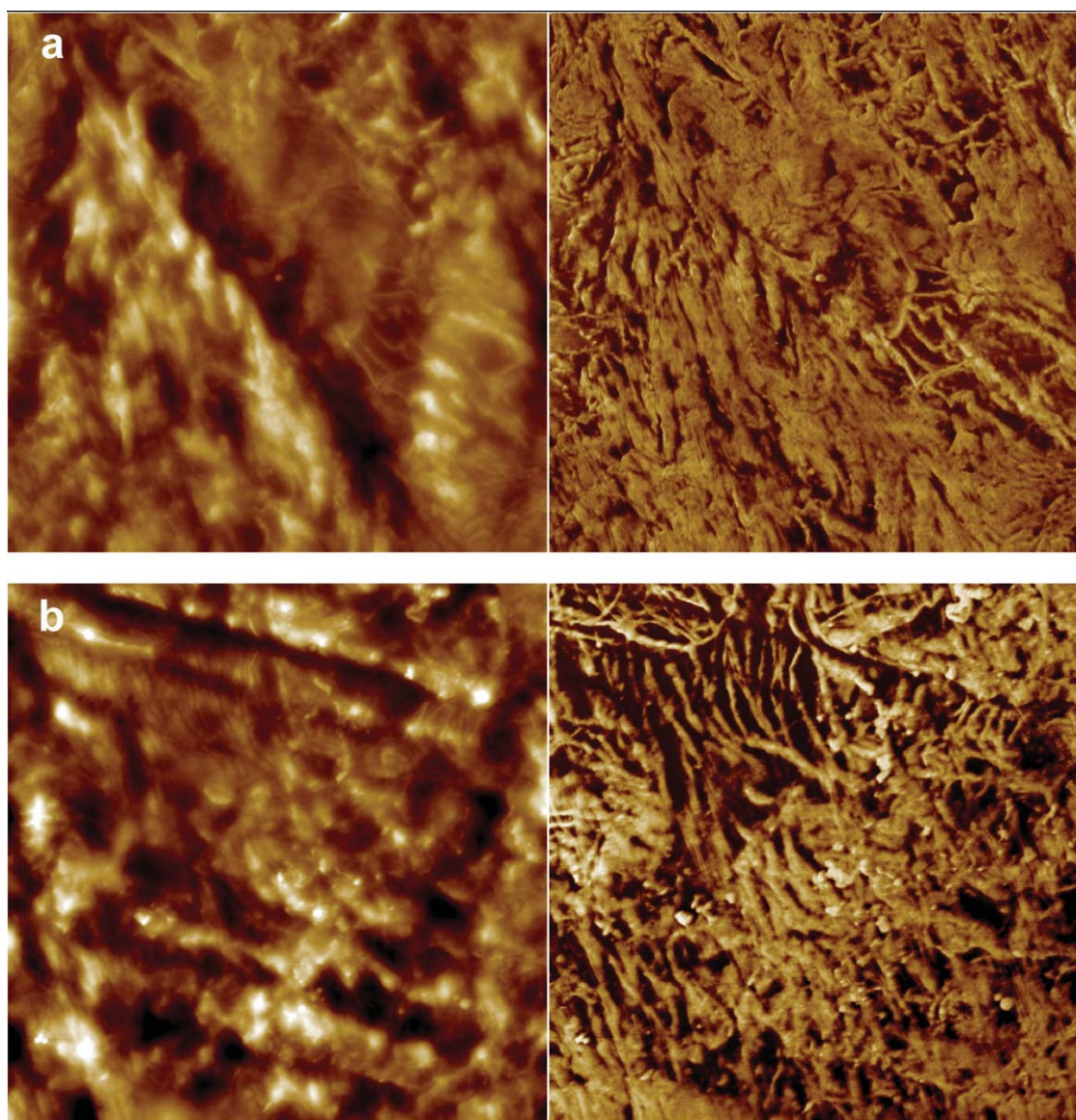
<sup>b</sup> A measure of 2715 mg kg<sup>-1</sup> α-tocopherol.

<sup>c</sup> A measure of 1950 mg kg<sup>-1</sup> quercetin.



**Figure 2** AFM height (left) and phase (right) images ( $3.0 \mu\text{m}^2$ ) 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)  $20^\circ$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 3** AFM height (left) and phase (right) images ( $3.0 \mu\text{m}^2$ ) of (a)  $\alpha$ -tocopherol and (b)  $\alpha$ -tocopherol :  $\beta$ -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 covers phase shifts of (a)  $30^\circ$  and (b)  $70^\circ$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

mean water contact angles across all antioxidant additive treatments were significantly different between the Ziegler-Natta ( $96.3^\circ$ ) and the metallocene ( $94.1^\circ$ ) LLDPE. The topography of the surface roughness can strongly influence the configuration of the three-phase contact line between the solid, air, and liquid droplet.<sup>37,38</sup> The optical microscopy images created the expectation that both quercetin and its  $\gamma$ -CD complex would have greater contact angles because of the increased surface roughness of these additives as particulate dispersions in LLDPE. Increasing water contact angle indicates either increased hydrophobicity or greater roughness imparted to the polymer surface by the additives. In

Ziegler-Natta LLDPE films, the water contact angles for both  $\alpha$ -tocopherol :  $\beta$ -CD complex and quercetin loadings were significantly greater than those for the control. In metallocene LLDPE films, the quercetin loadings had a significantly higher contact angle than its control.

#### AFM

AFM image interpretation requires great care because the image is not solely a function of the sample surface but represents a convolution of the forces between the tip and surface. Small sections of the macroscopic surface are scanned, which are

not necessarily representative of the entire sample. The structure and morphology of the uppermost polymer surface layers, usually several nanometers thick, generally differ from those of the bulk.<sup>39</sup> The height profile provides an estimate of the nature of the surface roughness. In Figure 2, the height images of both LLDPE control films do not show much variation, and the surface topography of linear striations is simply because of the aluminum foil parting agent used during compression molding. The height images of Ziegler-Natta LLDPE loaded with  $\alpha$ -tocopherol and its  $\beta$ -CD complex in Figure 3 show an apparent increase in surface roughness on the film.

Phase imaging provides a method of distinguishing surface features of different moduli. The phase images provide a map of stiffness variation on the sample surface such that a stiffer region has a more positive phase shift and, therefore, appears brighter in a phase image.<sup>40</sup> In Figure 2, the surface morphology of both neat LLDPE films seems to exist as a fringed micelle model. Small crystallites and amorphous phases co-exist in the semicrystalline LLDPE. The long molecular chains meander from one micelle to another, passing through amorphous regions, and the fringes represent transition materials between the crystalline and amorphous phases.<sup>41</sup> The darker regions of the phase image correspond to the softer, amorphous phase of LLDPE, whereas the brighter regions correspond to the surface lamellae. In Figure 3, both Ziegler-Natta LLDPE surfaces were observed to be partially covered with natural antioxidant additive, but the lamellae and amorphous regions can still be observed between gaps of the additive. These results are generally similar to AFM images showing surface coverage of the slip agent erucamide on LLDPE films.<sup>42</sup>

### CONCLUSIONS

Natural antioxidants and their CD complexes were successfully incorporated into LLDPE films in a uniform distribution without any visual aggregation of these additives. All antioxidant additives increased the oxidative stability of LLDPE, notably the flavonoid quercetin. The flavonoids have not previously been investigated as polymer additives, but they seem to have great potential to stabilize polymers from oxidative degradation if their added color is either not a concern or desired as a natural colorant. Natural antioxidants could fill the widespread need for additives that can be used in a variety of direct food contact applications or packaging. These natural antioxidant additives may have a dual function in the packaging to protect the polymer from oxidative degradation during melt processing and to delay the onset of oxidation of the packaged food during storage.

### References

1. Scott, G. *Biochem Soc Symp* 1995, 61, 235.
2. Laermer, S. F.; Nabholz, F. *Plast Rubber Process Appl* 1990, 14, 235.
3. Al-Malaika, S.; Goodwin, C.; Issenhuth, S.; Burdick, D. *Polym Degrad Stab* 1999, 64, 145.
4. Yam, K. L.; Ho, Y. C.; Young, S. S.; Zambetti, P. F. *Polym-Plast Technol Eng* 1996, 35, 727.
5. Ho, Y. C.; Yam, K. L.; Young, S. S.; Zambetti, P. F. *J Plast Film Sheeting* 1994, 10, 194.
6. Ho, Y. C.; Yam, K. L. *Plast Rubber Compos Process Appl* 1997, 26, 83.
7. Wessling, C.; Nielsen, T.; Leufvén, A. *Packaging Technol Sci* 2000, 13, 19.
8. Al-Malaika, S.; Ashley, H.; Issenhuth, S. *J Polym Sci Part A: Polym Chem* 1994, 32, 3099.
9. Connors, K. A. *J Pharm Sci* 1995, 84, 843.
10. Szejtli, J. *Chem Rev* 1998, 98, 1743.
11. Simpson, D. M.; Vaughan, G. A. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons: New York, 2003, p 441.
12. Farley, J. M.; Meka, P.; Stehling, F. C.; Trudell, B. C.; Kurtzman, M. B. U.S. Pat. 5,530,065 (1996).
13. Hodgson, W. J., Jr. U.S. Pat. 5,206,075 (1993).
14. Longo, E.; Forloni, R.; Cesare, G. D. U.S. Pat. 7,063,885 (2006).
15. Breidt, P., Jr.; Higgins, T. W.; Nahmias, A. M.; Weiner, M. L. U.S. Pat. 4,147,827 (1979).
16. Su, T.-K.; Poirier, R. V. U.S. Pat. 5,885,721 (1999).
17. Koontz, J. L.; Marcy, J. E.; O'Keefe, S. F.; Duncan, S. E. *J Agric Food Chem* 2009, 57, 1162.
18. Munaro, M.; Akcelrud, L. *J Polym Res* 2008, 15, 83.
19. Annual Book of ASTM Standards (D 4703 - 03. Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets); ASTM International: West Conshohocken, 2006, p 612.
20. Annual Book of ASTM Standards (D 3895 - 04. Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry); ASTM International: West Conshohocken, 2006, p 237.
21. Al-Malaika, S.; Issenhuth, S. *Polym Degrad Stab* 1999, 65, 143.
22. Siró, I.; Fenyvesi, É.; Szente, L.; De Meulenaer, B.; Devlieghere, F.; Orgoványi, J.; Sényi, J.; Barta, J. *Food Addit Contam* 2006, 23, 845.
23. Fenyvesi, É.; Balogh, K.; Siró, I.; Orgoványi, J.; Sényi, J. M.; Otta, K.; Szente, L. *J Inclusion Phenom Macrocyclic Chem* 2007, 57, 371.
24. Huang, L.; Taylor, H.; Gerber, M.; Orndorff, P. E.; Horton, J. R.; Tonelli, A. *J Appl Polym Sci* 1999, 74, 937.
25. Mar'in, A. In *Specialty Polymer Additives: Principles and Applications*; Al-Malaika, S., Golovoy, A., Wilkie, C. A., Eds.; Blackwell Science: Oxford, 2001, p 195.
26. Cobb, W. T.; Cooke, T.; Semen, J. *Polyolefins 2000: The International Conference on Polyolefins*; Society of Plastics Engineers: Houston, TX, 2000.
27. da Costa, E. M.; Filho, J. M. B.; do Nascimento, T. G.; Macêdo, R. O. *Thermochim Acta* 2002, 392-393, 79.
28. Rossi, M.; Rickles, L. F.; Halpin, W. A. *Bioorg Chem* 1986, 14, 55.
29. Ding, B. J.; Steiner, T.; Saenger, W. *Acta Crystallogr Sect B* 1991, 47, 731.
30. Uyar, T.; Hunt, M. A.; Gracz, H. S.; Tonelli, A. E. *Crystal Growth Design* 2006, 6, 1113.
31. Nieto, S.; Garrido, A.; Sanhueza, J.; Loyola, L. A.; Morales, G.; Leighton, F.; Valenzuela, A. *J Am Oil Chem Soc* 1993, 70, 773.
32. Harris, G. K.; Willcox, J. K.; Catignani, G. L. *J Food Biochem* 2004, 28, 337.

33. Frankel, E. N.; Huang, S.-W.; Kanner, J.; German, J. B. *J Agric Food Chem* 1994, 42, 1054.
34. Azuma, K.; Ippoushi, K.; Ito, H.; Higashio, H.; Terao, J. *J Agric Food Chem* 2002, 50, 1706.
35. Uri, N. In *Autoxidation and Antioxidants*; Lundberg, W. O., Ed.; Interscience: New York, 1961, p 133.
36. Wood, W. E. *Polymers, Laminations, and Coatings Conference Proceedings*, Atlanta, GA, 2001.
37. Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* 1999, 15, 3395.
38. Walters, K. B.; Schwark, D. W.; Hirt, D. E. *Langmuir* 2003, 19, 5851.
39. Magonov, S. N.; Whangbo, M.-H. *Surface Analysis with STM and AFM: Experimental and Theoretical Aspects of Image Analysis*; VCH: Weinheim, 1996, p 277.
40. Magonov, S. N.; Elings, V.; Whangbo, M.-H. *Surf Sci* 1997, 375, L385.
41. Lu, W.; Debelak, K. A.; Witt, A. R.; Collins, W. E. *Polym News* 2000, 25, 365.
42. Ramírez, M. X.; Hirt, D. E.; Wright, L. L. *Nano Lett* 2002, 2, 9.