Alpha tocopherol as an antioxidant for extrusion coating polymers

Peter F. Zambetti, Sharon L. Baker, and David C. Kelley

ABSTRACT: Bottle and film packaging applications use alpha tocopherol as an antioxidant. The higher temperatures of an extrusion coating process present a more oxidative environment, however. This paper explores alpha tocopherol in a low-density polyethylene extrusion coating application with special emphasis on sensory performance and sealing characteristics. There is also data substantiating alpha tocopherol's effectiveness in high-density polyethylene bottles.

KEYWORDS: Antioxidants, bottles, extrusion coating, food wrap film, high density polyethylene, low density polyethylene, odors, plastic containers, polymers, taste, tocopherols, vitamins.

Alpha tocopherol, vitamin E, has been extensively researched in the human and animal arenas as an important free radical scavenger *(1)*. Its chemical structure belies the fact that it is 250 times more reactive toward peroxy radicals in styrene than the commonly used butylated hydroxy toluene (BHT) antioxidant *(1)*.

The use of vitamin E in the plastics arena is relatively new. Its commercial use began in the middle of the 1980s as a replacement for BHT in food packaging for the Far East market *(2)*. Vitamin E has since gained commercial acceptance in the United States as a hindered phenol to prevent oxidative degradation of many polymers *(3)*.

Earlier work demonstrated that low levels of vitamin E offered enhanced processability of a material after repeated extrusions as measured by change in melt flow and color *(4)*. **Figure 1** shows use of vitamin E in HDPE to reduce gels in blown films. The use of phenolic antioxidants alone in applications where taste and odor are critical is commonplace. A typical example is high-density polyethylene (HDPE) dairy and water bottles. In low-density polyethylene (LDPE) for extrusion coating, there is almost no use of antioxidants. LDPE extrusion coating depends on a certain amount of oxidation for good adhesion to the substrate. "Off-taste" in these applications has challenged resin producers, converters, and end-users for years.

Unacceptable odors and flavors come from a variety of materials commonly used in food packaging and from environmental factors. These include monomers, oligomers, plasticizers, slip additives, solvents, antioxidants, antistat agents, and antifog agents *(5)*. In addition, oxidative reactions that produce aldehydes, acids, ketones, and alcohols can cause unacceptable taste and odor *(6)*.

Koszinowski and Piringer have demonstrated that aldehydes can be the most potent compounds responsible for unacceptable taste and odor *(7)*. These compounds and several others present at the ppb level produce substances contributing to strong odors.

This paper discusses the effect of vitamin E in reducing unacceptable taste and odor in a LDPE coating resin and compares its use to a low temperature (400°F) molding application using HDPE. This experiment specifically addresses the use of vitamin E in a particular extrusion coating grade of LDPE. There is a review of parameters such as taste and odor reduction and the impact on adhesion and heat seal performance. In addition, there is a comparison of the effectiveness of vitamin E compared to other antioxidants in HDPE blow-molded bottles.

Zambetti is manager, industrial products, for Hoffmann-La Roche, 340 Kingsland St., Nutley, NJ 07110. Baker and Kelley are development chemist and development associate, respectively, for The Dow Chemical Co., Bldg. B-1607, 2301 Brazosport Blvd., Freeport, TX 77541.

Experimental

Low-density polyethylene

Production of the sample structures used a laboratory pilot extrusion laminator equipped with a 3.5-in. diameter extruder, a 30:1 length/diameter screw, and a 30-in. coat-hanger die deckled to 24 in. with a 6-in. air gap. The chill roll had a matte finish. Dry blending added different concentrations of a 1% vitamin E concentrate in LDPE to an extrusion coating resin with melt index of 8 and density of 0.916. Sample coating used 90 rpm at 615°F onto 48 gauge primed polyester film. Coating onto 50 lb kraft paper determined extrusion coating performance. Neck-in evaluation was at 440 ft/min. This is equivalent to a coating of 1.0 mil thickness. There was also measurement of drawdown or minimal coating thickness.

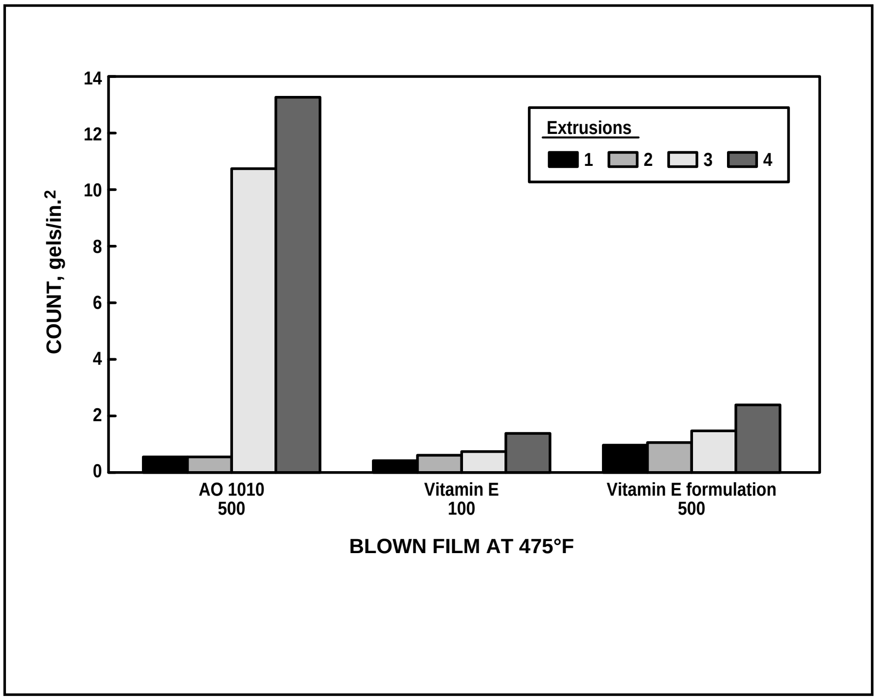
Formation of laboratory heat seals used 1 in. wide strips of substrate sealed at 40-psi bar pressure with a 0.5-s dwell using heated bars at temperatures of 120–230°C on a commercial hot tack tester. The sealed samples aged for 24 h at ambient temperature. A tensiometer at 10 in./min crosshead speed with 90° "T" peel measured the force required to pull apart the seal. Delaminating a 1-in. sample using a tensiometer at 10 in./min crosshead speed determined adhesion values.

A vertical form/fill/seal machine produced pouches for sensory evaluation. The bag size was 7.125 in. x 5.875 in. For taste evaluation, the pouches contained 100 mL of a purchased brand of drinking water. Sealing temperature was 220°F. Evaluation of the filled pouches occurred one day after storage at room temperature for 20 h. Production of the pouches filled with air for odor evaluation used the same machine and seal temperatures. Sample evaluation was also one day after storage at room temperature for 20 h.

Sensory data came from 24 trained panelists who evaluated the samples in a ranking format. Presentation of the samples coded with random three digit numbers used a balanced block design to minimize bias. Data analysis used Friedman Analysis of Variance for ranking the data followed by Duncan Multiple Range Comparisons *(8)*.

Rutgers Center for Advanced Food Technology conducted the gas chromatography/mass spectrometry (GC/MS). The samples of the film underwent matrix spiking with internal standards followed by heating to 80°C for 30 min to promote outgassing of volatile components. During this time, nitrogen purged the volatiles from the films for trapping with adsorbent tubes. The adsorbent traps then thermally desorbed into the GC/MS system for separation and identification.

1. HDPE film gel study



High-density polyethylene

A 30-mm twin screw extruder compounded 100 ppm of vitamin E antioxidant into a commercial HDPE homopolymer used for water/dairy bottle applications. The same conditions compounded two other antioxidants. Blow molding used a commercial single-head machine at 400°F with 8-s cycle time. Data from this experiment will show the effect of vitamin E at processing temperature lower than that of the 615°F extrusion coating temperature.

HDPE water/dairy bottle taste evaluations involved storing the water in the test bottles at 38°C for 24 h and 96 h in an environmental test chamber. The panelists received the samples 30 mL at a time. These samples also had random three digit codes. Panelists received a reference sample and two coded samples. Instructions were to identify which coded sample matched the reference. To indicate their preference in the duo-trio tests, they entered their responses using light pens onto computer screens.

Results

LDPE coating evaluation

Table I shows the measurement of extrusion coating performance for the LDPE control and the LDPE

I. Vitamin E extrusion performance data for LDPE using temperature profile of 350, 450, 550, 620, and 620°F with 3.5 in. extruder with 30:1 length/diameter screw

Vitamin E, ppm	*Melt temp., °F*	*Amperage reading*	*Pressure, ext., psig*	*Neck-in @ 440 fpm, in.*	*Neck-in @ 880 fpm, in.*	*Drawdown, fpm*	*Min. coating thickness, in.*
0	616	98	930	1.875	1.75	1730	.25
100	616	97	920	2.125	2	>2100	<.21

II. LDPE adhesion data using vitamin E using 3.5 in. laboratory extruder with 30 in. die deckled to 24 in.

Sample designation	*Vitamin E, ppm*	*Speed, fpm*	*Extruder, rpm*	*Rate, lb/h*	*Melt temp., °F*	*Pressure, psig*	*Amperage reading*	*Foil adh., lb/in.*	*Kraft paper adh. rating*	*Bleached paper adh. rating*	*Polyester adh., lb/in.*
A	0	220	45	125	619	690	71	0.6	4	4	-
B	100	220	45	125	620	710	73	0.1	1	1	-
C	0	440	90	250	618	1080	96	0.4	5	4	CNS
D	50	440	90	250	618	1070	95	0.1	1	2	CNS
E	100	440	90	250	619	1070	95	0.1	1	1	0.04
F	200	440	90	250	619	1060	94	0.1	1	1	0.04
G	0	880	180	500	616	1590	125	0.1	1	1	-
H	100	880	180	500	617	1590	125	0.1	1	1	-

III. Effect of vitamin E on heat seal data at varying seal temperatures in lb/in. using primed polyester film

Vitamin E, ppm	*90°F*	*95°F*	*100°F*	*105°F*	*110°F*	*115°F*	*120°F*	*125°F*	*135°F*	*150°F*
0	0.09	-	2.93	8.29	7.72	9.06	8.66	8.81	9.73	-
50	0.05	0.11	2.51	8.37	6.09	-	-	-	-	-
100	0.05	0.57	1.43	1.74	1.98	2.36	-	2.07	2.01	1.73
200	0.06	0.29	1.5	1.62	1.89	1.57	1.65	-	-	-

with 100 ppm of vitamin E at a melt temperature of 615°F. The presence of vitamin E resulted in a 0.25 in. increase in neck-in and an increase in drawdown of 300 ft/min. There was no difference in the amperage reading or the pressure. The increase in neck-in and drawdown is due to the suppression of crosslinking reactions.

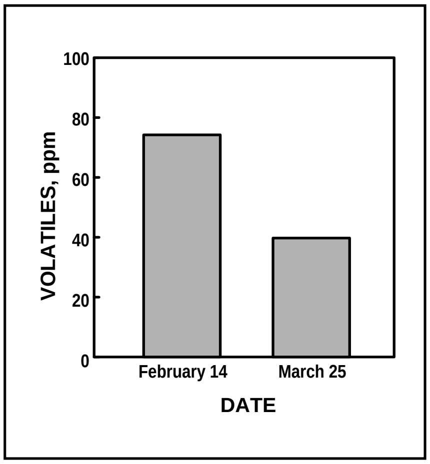
Table II shows that the presence of vitamin E reduced the adhesion to the various substrates. In this table, the paper adhesion ranking is from 1 to 5 with 5 being the best. A rating of 5 exhibited much fiber tear. The designation CNS means it was not possible to separate the sample. Good adhesion to the polar substrates requires a certain level of oxidation. At 50 ppm, there was good adhesion to the primed polyester film. This adhesion decreased as the concentration of vitamin E increased, however. At 50 ppm, there was an adverse effect to kraft paper. **Table III** presents the heat seal data for primed polyester film. Here again the loss of adhesion to the primed polyester film affected the heat seal strength.

The data from this work suggests using coextrusion to address adhesion problems. With coextrusion, a tie layer could achieve the desired adhesion to the substrate when the sealant layer contains vitamin E. A tie layer of 30–50% would also help carry the web and reduce neck-in of the coating.

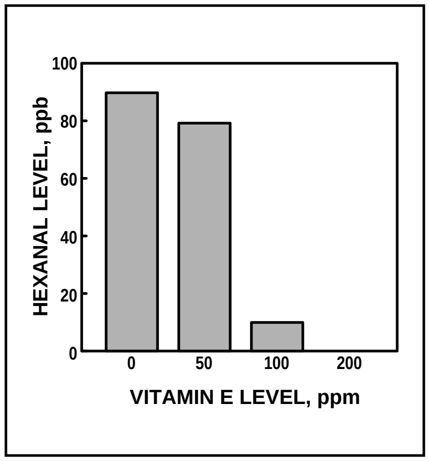
Taste and odor

This work evaluated the effectiveness of vitamin E as an antioxidant in LDPE extrusion coated on primed polyester film at 615°F at 1-mil thickness. The tests showed that addition of 50 ppm of vitamin E to LDPE gives a significant improvement in the taste and odor performance of the polymer. Additional improvements are possible at higher loadings. Taste and odor evaluations conducted by a trained panel show that the best odor performance (least intense odor) occurs at 100-ppm loading. At 200 ppm, no significant odor improvements occurred. At this level, there is less taste contribution to water, however.

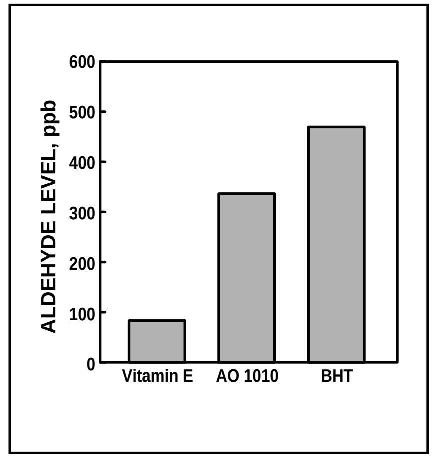
2. LDPE volatiles study showing effect of time



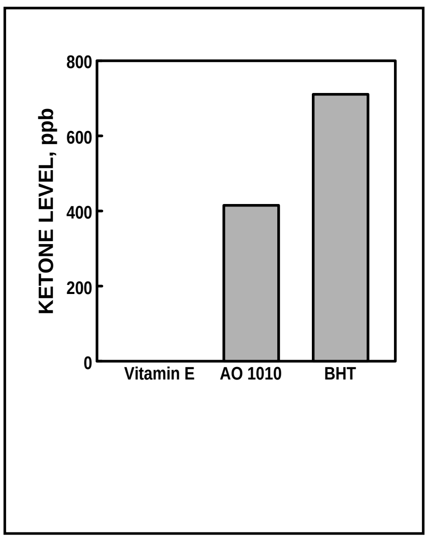
3. LDPE aldehyde study showing effect of vitamin E level



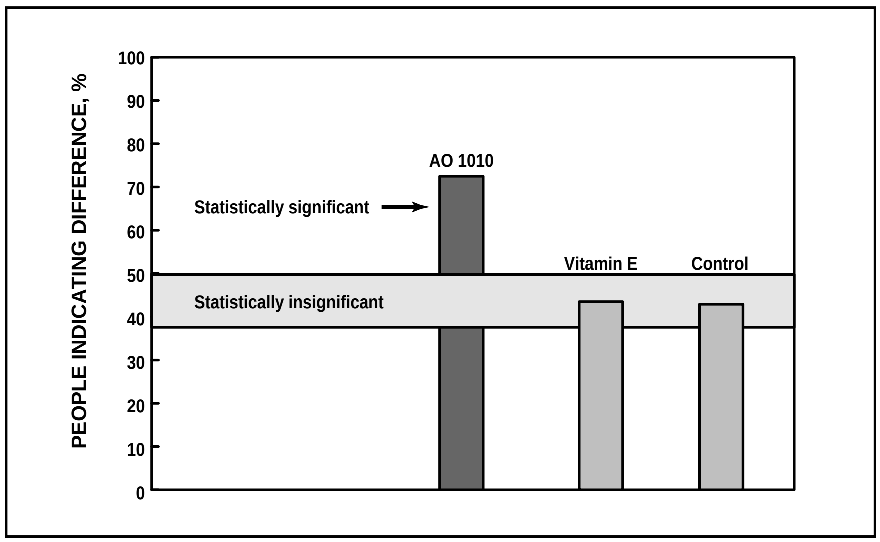
4. HDPE aldehyde study showing effect of different antioxidants



5. HDPE ketone study showing effect of different antioxidants



6. Matching taste tests with control in vitamin E in HDPE



Gas chromatography/mass spectrometry

Samples of primed polyester film and LDPE with varying levels of vitamin E underwent determination of volatile out-gassing products by purge and trap, thermal desorption, and GC/MS. Samples coated in late October 1993 received first analysis on Feb. 14, 1994, with some treatments repeated on March 25, 1994. The second analysis showed that film samples analyzed closer to the October coating date would have had higher levels of volatiles. **Figure 2** shows a decrease of 47% in total volatiles between the two dates.

Aldehydes at low ppb levels are the most potent volatiles responsible for objectionable taste and odor. **Figure 3** shows the reduction of these compounds. Note that there are 90 ppb of hexanal found in the sample not containing any vitamin E. The olfactory sense can detect hexanal at a level below 1.0 ppb. There is a 11% reduction in hexanal when adding 50 ppm of vitamin E. That level decreases further by 89% and 100% when introducing 100 ppm and 200 ppm of vitamin E, respectively. The taste and odor panel data noted above also validated this result—taste of water decreases with increasing vitamin E.

High-density polyethylene

The objective with HDPE was to quantify volatile components of such bottles with emphasis on only the most potent compounds causing taste and odor problems. **Figure 4** shows the difference in the generation of aldehydes when using other antioxidants in HDPE water bottles. Vitamin E provides a 76–83% reduction in the aldehyde level. **Figure 5** shows no detection of ketone levels in the vitamin E sample.

After storing the HDPE bottles for 96 h at 38°C, 75% of the panelists could identify the bottle stabilized with Tetrakis (methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)) methane) (AO 1010) as being different from the control. **Figure 6** indicates there were no differences with the bottles stabilized with 100 ppm of vitamin E vs. control at 96 h for water filled one gallon HDPE jugs.

Conclusions

The use of vitamin E as an antioxidant in both LDPE for extrusion coating and HDPE for extrusion blow-molding of bottles offers improvements in sensory performance and prevents oxidation of the substrates. The data for LDPE suggests the use of a coextruded tie layer may be necessary for better adhesion. Vitamin E also can increase shelf life of food in film packages *(9)* and reduce the odor associated with other polymers used in food packages.

Literature cited

1. Burton, G. W. and Ingold, K. U., *Acc. Chem. Res.* 19, 570:7(1986).
2. Urata, Y., *Packaging Japan* 7:49(1988).
3. Laermer, S. F. and Nabholz, F., *Plastics and Rubber Processing and Applications* 14(4): 235(1990).
4. Laermer, S. F. and Zambetti, P. F., *Journal of Plastic Film and Sheeting* 8(3):228(1992).
5. Culter, J., *Journal of Plastic Film and Sheeting* 8(3):208(1992).
6. Baker, S. L., Potts, M. W., and Hughes, M. M., *TAPPI 1991 Polymers, Laminations and Coatings Conference Proceedings*, TAPPI PRESS, Atlanta, p. 259.
7. Koszinowski, J. and Piringer, O., *Journal of Plastic Film and Sheeting* 2(2):40(1986).
8. Kelley, D. and Baker, S., *TAPPI 1993 Polymers, Laminations and Coatings Conference Proceedings*, TAPPI PRESS, Atlanta, p. 421.
9. Anon., *European Packaging* 4(2): 21(1993).

This paper is the result of a joint effort by The Dow Chemical Co., Hoffmann-La Roche Inc., and Ampacet Corp. The authors thank the following for their assistance: Dow Polyolefin Taste and Odor Panel, Rutgers Center for Advanced Food Technology, Dr. T. Hartman of Rutgers GC/MS Laboratory, and the Vitamins R & D and Analytical Services functions within Hoffmann-La Roche.

Received for review June 23, 1994.

Accepted Oct. 11, 1994.

Presented at the TAPPI 1994 Polymers, Laminations and Coatings Conference.