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Evolution of a method for quantitative supercritical fluid extraction of Ethanox 330 antioxidant from high-density polyethylene

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Abstract

Supercritical fluid extraction (SFE) was employed prior to the HPLC assay of the additive Ethanox® 330 from high-density polyethylene (HDPE). The effects of temperature, various modifiers and modifier concentration were investigated. The use of extraction temperatures above 95°C for the additive-containing polymer resulted in less than quantitative recovery and the appearance of a degradate peak in the extract chromatogram. A 70-min extraction was found to be optimum for HDPE when using greater than 10% methylene chloride- or methanol-modified CO_2. After discovering the optimal extraction temperature, we found that rinsing the octadecylsilica solid-phase trap with methylene chloride rather than methanol improved the recovery efficiency. Recoveries of greater than 90% can be achieved in all cases when the primary antioxidant, Ethanox 330, appears in the presence of secondary antioxidants.

Keywords: Ethanox 330; High-density polyethylene; Antioxidants

1. Introduction

In order to ensure that the specified amount of an additive has been incorporated into a polymer following extrusion, a rapid and accurate analytical method for each additive is required. Furthermore, quantification of degradable additive(s) in the polymer is necessary, since the amount of additive(s) can influence the physical nature of the polymer [1]. Conventional extraction techniques for polymer additive(s), such as liquid–solid extraction and dissolution/precipitation are laborious, time consuming, and expensive. The optimal recovery is usually significantly less than 90%. During Soxhlet (e.g. liquid–solid) extraction, thermal decomposition of certain additive(s) may result from heating potentially a reactive organic solvent to temperatures as high as 110°C. In addition, a large amount of organic solvent, such as toluene or decalin, must be eliminated in order to concentrate the sample prior to chromatographic separation and analysis.

Dissolution/precipitation extraction minimizes the chance of additive decomposition since in many situations there is no heated solvent. Monteiro and Matos [2] used sonication in a cold solvent bath to extract certain additives from polyolefins. The minimum extraction time in the ultrasonic bath was 30–45 min depending on the additive and polymer. Although, they were able to minimize the extraction time, subsequent steps were still needed to filter and to remove the large amount of solvent. Sonication in a cold solvent bath to extract additives from high-

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density polyethylene was also used by Yagoubi et al. [3]. The process required milling the pellets before sonication. In all the cases reported [4–6], the quantity of solvent was relatively large. Filtering the extract solution through a PTFE membrane was also required prior to chromatographic analysis.

Supercritical fluid extraction (SFE) has recently become a favorable means of analytical sample preparation for various applications. The expectation of SFE is to provide faster and more efficient extraction. Ashraf-Khorassani et al. [7] have employed on-line SFE–SFC to extract and analyze for polystyrene additives. They found that higher extraction efficiencies of *N*,*N*-ethyl bis(stearamide) (EBS) could be obtained at elevated temperatures (150°C). Thus, a 15-min extraction time was found to be optimal for high percent recovery of EBS from milled polystyrene. Lou et al. [8] studied the extraction of Irganox® 1010, Irganox® 1076 and Irgafos® 168 from polyethylene by on-line SFE–SFC. After discovering the optimal flow-rate, density, and pressure, they also found that increasing the extraction temperature improved the recovery efficiency. The maximum extraction temperature, however, had to remain below the melting point of the polymer to avoid plugging the restrictor from carry-over of the melted polymer. On-line SFE–SFC was also used by Tikuisis and Cossar, [9] to quantitatively determine the antioxidant content of high-density polyethylene. Their results showed an average recovery of greater than 97% for all antioxidant additives. The total analysis time for each sample was less than 90 min. It has also been shown in a number of publications that similar results with polymer additives can be obtained by off-line SFE in conjunction with either HPLC or GC [10–12].

The work presented in this paper employs SFE for the removal of the antioxidant Ethanox® 330 from high-density polyethylene followed by HPLC–UV analysis. Spiking experiments onto sand were performed as the first part of our study, in order to determine the effect of temperature and modifier type upon extraction and trapping efficiency of Ethanox 330. The second part of our study involved determination of the extraction efficiency of Ethanox 330 from HDPE in the absence of other additives using previously determined optimum extraction conditions. The third part of our study concerned the determination of the extraction efficiency of Ethanox 330 from HDPE in the presence of co-additives. Fig. 1 shows the structure of Ethanox 330 and various co-additives.

2. Experimental

2.1. Calibration

The amount of Ethanox 330 additive extracted from the HDPE polymer was determined via high-performance liquid chromatography using an external calibration curve that was constructed using four concentrations of Ethanox 330 standard (Albemarle Corp., Baton Rouge, LA, USA). A 1000-ppm stock solution of the antioxidant Ethanox 330 in spectrograde 95:5 (v/v) methanol–tetrahydrofuran was initially prepared. The chromatographic standards ranged in concentration from 50 to 1000 ppm which covered the expected concentration levels of Ethanox 330 additive in the polymer.

2.2. Spiking study

A 100-μl aliquot of the 1000-ppm Ethanox 330 stock solution was spiked onto Ottawa sand which was contained in a 7-ml extraction vessel. The spiked matrix was then subjected to the identical extraction and subsequent chromatographic parameters as the individual polymer samples.

2.3. Extraction

The HDPE samples for extraction were obtained from Albemarle. The various concentration levels of Ethanox 330 were incorporated into the HDPE during extrusion in their laboratory. Prior to extraction, the HDPE pellets were ground with a Wiley Mill, obtained from the Forestry Department at Virginia Tech., at room temperature, in order to increase particle surface area. Since loss of additive(s) may occur due to thermal decomposition during the milling process, the chamber was cooled by blowing house air inside the chamber between samples. In addition, only a few pellets were ground at a time.

Extractions were performed on a Hewlett-Packard

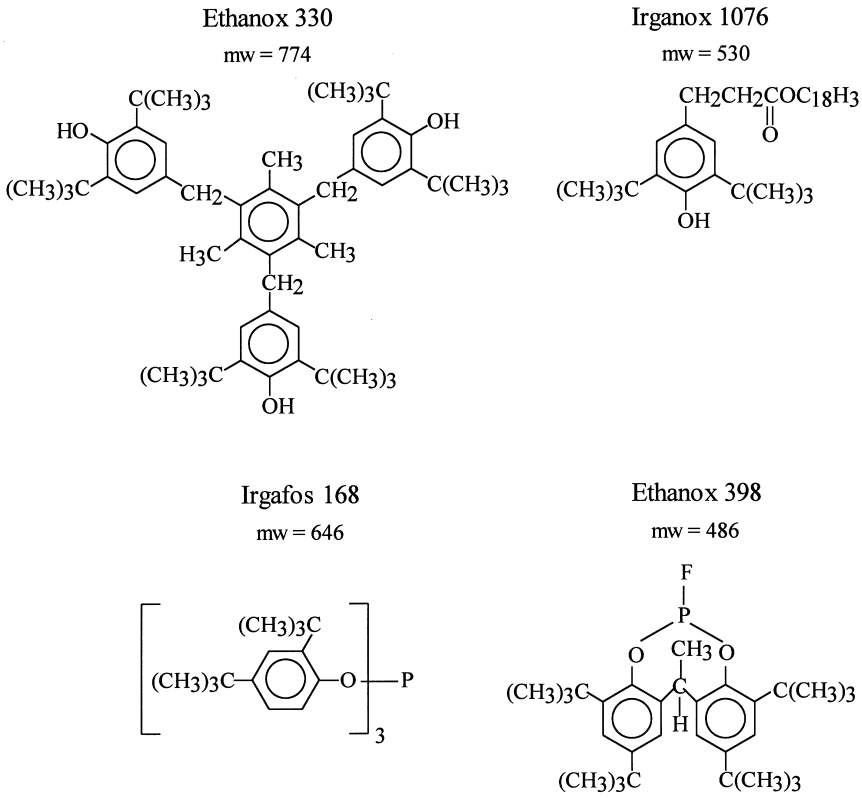

Fig. 1. Structures of antioxidants.

7680T (Wilmington, DE, USA) extractor. A 7-ml extraction vessel was filled with 1.0 g of ground HDPE sample. Ottawa sand (Fischer Scientific, Fair Lawn, NJ, USA) was used to fill approximately 80% of the remaining vessel volume for all extractions. It was necessary to leave a small percentage of dead volume in the vessel due to expansion of the polymer during extraction. A liquid phase tandem trap was initially used along with an octadecylsilica solid-phase trap as a precaution to ensure high trapping efficiency. The liquid tandem trap was filled with 5 ml of methanol. Carbon dioxide (SFE/SFC grade) without helium headspace was obtained from Air Products and Chemicals Co. (Allentown, PA, USA). The optimum extraction conditions were:

Extraction fluid	CO_2
Flow-rate	1.0 ml/min liquid
Modifier	20% (v/v) $MeCl_2$ added in-line to CO_2
Pressure	350 bar
Chamber temp.	110°C
Nozzle extraction temp.	55°C
Nozzle rinsing temp.	30°C
Static time	20 min
Dynamic time	50 min
Trap	Octadecylsilica solid phase+5 ml of liquid MeOH
Solid phase trap extraction temp.	80°C
Solid-phase trap rinsing temp.	30°C
Rinse solvent	$MeCl_2$
Trap rinse volume	5.4 ml (3×1.8 ml)

2.4. Chromatographic analysis

A Hewlett-Packard Series 1050 HPLC was used for all extract analyses. The mobile phase consisted

of 90:5:5 (v/v/v) acetonitrile–methanol–tetrahydrofuran. A 20-μl injection of the combined solid-phase trap rinse solvent and liquid methanol tandem trap after reduction in volume to 1.0 ml was introduced. The flow-rate was set at 1.0 ml/min. The column was an ODS Hypersil (150×4.6 mm, 5 μm dp) with a C_{18} (Varian, Sunnyvale, CA, USA) guard column. UV detection at 280 nm was used for all analyses.

3. Results and discussion

3.1. Ethanox 330 extraction

The main objective of this study was to obtain high recoveries of Ethanox® 330 at different levels from HDPE employing supercritical fluid extraction. Because Ethanox 330 exhibited at least 10 times higher solubility in methylene chloride than in methanol, methylene chloride was used as the CO_2 modifier (e.g. 10–20% (v/v)). For a successful polymer additive extraction, the temperature must be above the polymer T_g (e.g. glass transition) and below the polymer T_m (e.g. melting). The T_g of HDPE is sub-ambient and we determined the melting point of the polymer with additive to be near 130°C. The optimal extraction temperature based on the thermal properties of the polymer was therefore initially deemed to be 110°C. Any higher temperature would not be feasible since the HDPE would melt and plug the extraction vessel. Replicate HDPE samples at 100, 500, and 1000 ppm doped levels of Ethanox 330 were extracted with 20% CH_2Cl_2 and analyzed. The best recovery of Ethanox 330 from all three HDPE samples was approximately 80% regardless of additive level. Our failure to achieve 100% recovery of Ethanox 330 from the polymer matrix at all additive levels with methylene chloride at 100°C was puzzling. Lower recoveries were obtained with 10% CH_2Cl_2. Similar results were obtained with 20% methanol-modified CO_2. It should be noted that liquid chromatography with detection at 280 nm of the neat additive standard suggested less than 1% impurities were present; therefore, an impurity in the Ethanox 330 could not account for the relatively low percent recovery from HDPE.

Numerous extraction experiments were next performed on Ethanox 330 spiked on Ottawa sand to determine optimum extraction/trapping conditions for the additive exclusive of the polymer. When the extraction chamber temperature was 110°C with either 20% methanol- or methylene chloride-modified CO_2, we noticed the appearance in our extract of a second HPLC peak at a retention time of 11 min. Ethanox 330 eluted at 8 min (Fig. 2). The second peak was not present in the HPLC trace of either aged or fresh Ethanox 330 standard dissolved in methanol. Therefore, the second peak was believed not to be due to oxidation of the standard solution prior to the spiking experiments. To confirm that the second peak was also not due to extracted impurities from the Ottawa sand, an extraction of sand by itself was performed at an extraction chamber temperature of 110°C with 20% methylene chloride-modified CO_2. In this case the second unknown peak did not appear in the extract HPLC trace.

As the extraction chamber temperature was de-

Fig. 2. HPLC of an Ethanox 330 polymer extract (20-μl injection). (1) Ethanox 330; and (2) degradate. Extracted with either 20% methylene chloride or 20% methanol at chamber temperature, 110°C; 350 bar; extraction time, 70 min; rinse solvent, MeCN–MeOH–THF (90:5:5, v/v/v).

creased from 110 to 80°C, the percent recovery of Ethanox 330 from sand increased (Fig. 3). At an extraction chamber temperature of 80°C, for example, 103% recovery of Ethanox 330 was achieved with 20% methanol and 101% with 20% methylene chloride. For the set of experiments conducted at 80°C, the unknown peak was absent from the extract HPLC trace. These results implied that the additive degradation was promoted at a higher temperature and was not dependent on the presence of the polymer.

Having discovered that 80°C was the optimal extraction chamber temperature for extraction of the additive from an inert matrix, these conditions were then applied to HDPE containing Ethanox 330. Unfortunately, only 10% of the additive was recovered from the polymer at a chamber temperature of 80°C. Next, a 95°C chamber temperature was investigated. In this case, 70% of the additive was recovered. At 110°C, we obtained only 80–85% recovery. It is interesting to note that the degradate created during SFE constitutes approximately 15% of the HPLC total chromatographic peak area, and our SFE recoveries are also low by 15–20%. Recall earlier that approximately 80% recoveries were obtained regardless of the doping level at 110°C. Furthermore, the degradate peak was found in each extract chromatogram.

Attempts were made to identify the degradate compound by isolating the separated material and performing mass spectrometric analysis on it by direct probe insertion. Mass spectrometric determinations were obtained in single quadrupole mode (70 eV) on a Fisons VG Quattro Mass Spectrometer (Manchester, UK). Two major ions of m/z 556 and 509 were observed. The ion at m/z 556 (2.6 min) can be envisioned to be a fragment of Ethanox 330. The second ion sharing a m/z 556 (2.0 min) is thought to be the degradate. Employing an equation taken from Watson [13], we can calculate the number of rings and double bonds for the species at m/z 556. Fig. 4 illustrates the possible chemical structure from the

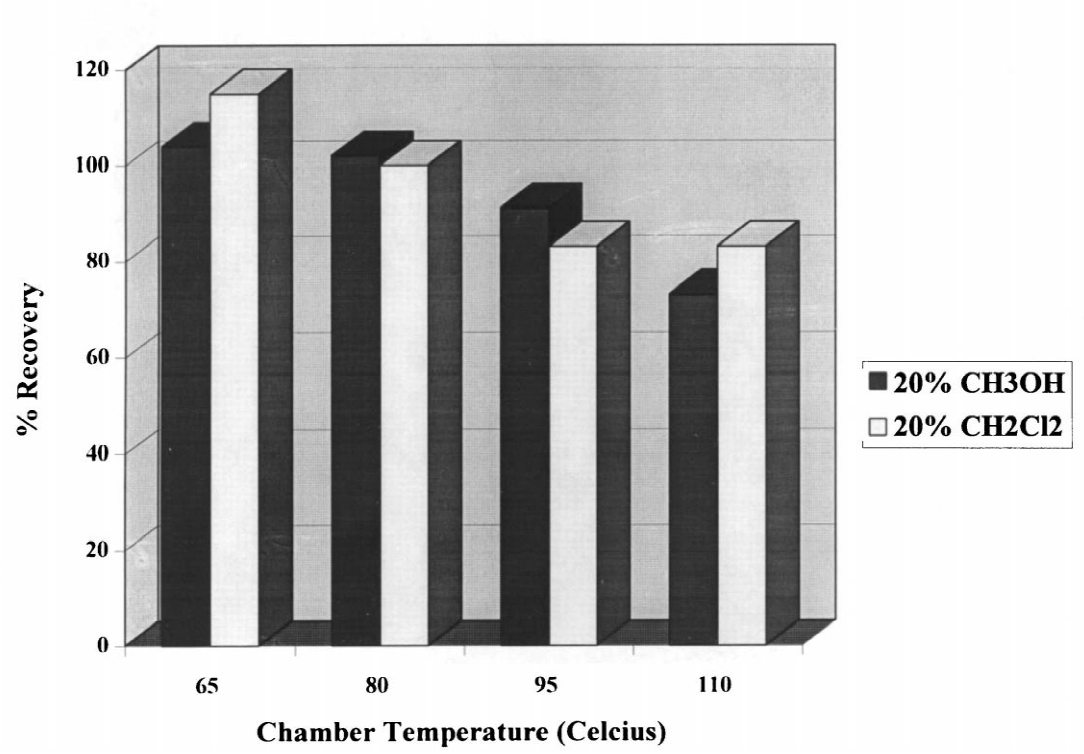

Fig. 3. Effect of temperature on Ethanox 330 recovery spiked on sand. Extracted with either 20% methylene chloride or 20% methanol; 350 bar; extraction time, 70 min; rinse solvent, MeCN–MeOH–THF (90:5:5, v/v/v).

Formula for calculation of # of rings and double bonds:

$C_X H_Y N_Z O_n$ (halogens treated as hydrogen)

$R + db = x - y/2 + z/2 + 1$

m/z 556

$C_{39}H_{56}O_2$ $R + db = 39 - 56/2 + 1 = 12$

x = 39
y = 56
z = 0

9 double bonds
3 rings

Could be the structure:

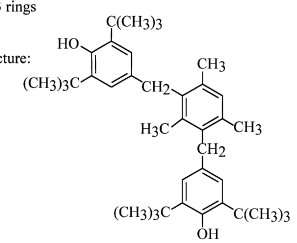

Fig. 4. Formula calculation of the number of rings and double bonds for possible degradate species.

number of rings and double bonds calculated for *m/z* 556. Attempts were made to determine the chemical structure of the ion at *m/z* 509; however, the component of *m/z* 509 could not be related to Ethanox 330. Our mass spectral findings are supported by a previous report by Koch [14], who identified 13 products of the oxidative degradation of 1,3,5-trimethyl-2,4,6-*tris* (3,5-di-*tert*-butyl-4-hydroxybenzyl)-benzene in autooxidized polypropylene (e.g. Ethanox 330). One of the suggested structures was our tentative structure for *m/z* 556.

3.2. Ethanox 330 extraction in the presence of co-additives

The next phase of our study involved the determination of the extraction efficiency of Ethanox 330 from HDPE samples containing co-additives, such as other primary and secondary antioxidants. Table 1 lists the composition and additive level of HDPE samples studied. In order to rinse the nozzle and trap more efficiently and in turn to free the analyte from the co-extracted polymer, methylene chloride, in which the oligomers were very soluble was chosen as the more effective rinse solvent. Extraction recoveries, thereby, improved from 60–70% to near 100% in going to methylene chloride as the rinse solvent.

The polymer samples listed in Table 1 were then extracted in triplicate using the revised optimum SFE extraction technique. Recoveries greater than 90% were found regardless of the sample. A number of co-additives were also extracted in our study, however, they did not co-elute with Ethanox 330. Furthermore, the co-additive combinations appeared to preserve the integrity of Ethanox 330 under the SFE extraction conditions (e.g. 110°C) since no significant degradate peak appeared in the extract HPLC.

We were interested to determine which co-additive was responsible for the high recoveries of Ethanox 330 at 110°C. A series of HDPE samples containing various doped levels of Ethanox 330 and only

Table 1
HDPE sample composition (μg/g) and additive level

Sample no.	Ethanox 330	Ethanox 398	Irgafos 168	Irganox 1076	CaSt[a]	DHT[b]	$CaCO_3$ (%)
4	500		1000		500		
5	1000		1000		500		
6	500	1000				500	
7	1000	1000				500	
8	500		1000	100			2
9	1000		1000	100			2
10	100		300				
11	500		1000				
12	1000		1000				

[a]Calcium stearate.
[b]Dihydrotalcite.

Irgafos 168 were subsequently studied. By eliminating the calcium stearate, we should be able to determine if the secondary antioxidant by itself or the combination of secondary antioxidant and acid scavenger led to the high recoveries of Ethanox 330. Employing the same optimum SFE extraction conditions, the average percent recovery of Ethanox 330 was surprisingly only 70% for these samples. At first glance one might therefore have concluded that the presence of the acid scavenger was critical to getting 100% recovery. However, we noticed extensive precipitation in the rinse solution. The use of a methylene chloride rinse required its removal prior to HPLC analysis. This solvent exchange was performed by gently blowing nitrogen over the rinse solution to eliminate most of the methylene chloride. Due to the cooling afforded by the evaporating solvent, the oligomers precipitated out of solution. While this step was carried out with all other samples that had been recovered with methylene chloride, in the case of the samples being discussed here, a greater amount of oligomers seemed to have been extracted and subsequently precipitated. The precipitated oligomer was therefore believed to have trapped significant quantities of Ethanox 330. HPLC analysis of the polymer extract solution with ambient injection represented only 56.0% recovery of Ethanox 330. HPLC analysis of that same solution but with the temperature of the injection near 50°C yielded 95.0% recovery of Ethanox 330. We next concluded that the presence of Irgafos 168 was critical to our achieving quantitative recovery of Ethanox 330 from HDPE.

Having now insured no Ethanox 330 occlusion by co-extracted oligomer the remaining HDPE samples containing only Ethanox 330 and Irgafos 168 were extracted in triplicate using the optimum SFE extraction technique and heating (50°C) the diluted extract prior to LC analysis. Recoveries greater than 90% were found regardless of the ratio of Ethanox 330 to Irgafos 168 additive level (μg/g). Samples were unavailable to test the extraction efficiency of Ethanox 398 in the exclusive presence of Ethanox 330. No doubt Ethanox 398 is just as effective as Irgafos 168 since samples 6–7 (Table 1) did not contain Irgafos 168, yet recoveries of Ethanox 330 were quantitative at 110°C.

4. Conclusion

For analysis of Ethanox 330 in HDPE, a low extraction chamber temperature is needed to ensure the stability of Ethanox 330 minus the presence of additives. However, a high extraction chamber temperature is required to swell the polymer and achieve high extraction efficiency. The optimal extraction efficiency of Ethanox 330 without the presence of co-additives was approximately 80% regardless of the additive concentration at 110°C. A high recovery of greater than 90% can be achieved at 110°C in all cases when the Ethanox 330 is in the presence of secondary antioxidants such as Irgafos 168 or Ethanox 398. The co-additive combination appeared to improve the stability of Ethanox 330. Proper trap rinsing and careful assay control was, moreover, essential to achieve quantitative results in spite of quantitative extraction.

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References

[1] R.H. Elmore, J.L. Hedrick, Hewlett-Packard Application Note 228-281, June, 1994.
[2] M.G. Monteiro, V.F. Matos, Int. GPC Symp. '87, 1987, pp. 437–446.
[3] N. Yagoubi, A. Baillet, C. Murana, D. Baylocq-Ferrier, Chromatographia 35 (1993) 455–458.
[4] D. Dilettato, P.J. Arpino, K. Nguyen, A. Bruchet, J. High Resolut. Chromatogr. 14 (1991) 335–342.
[5] J.F. Schabron, L.E. Fenska, Anal. Chem. 52 (1980) 1411–1415.
[6] M.C.A. Esperidiao, F. Galembeck, Eur. Polym. J. 29(7) (1993) 993–997.

[7] M. Ashraf-Khorassani, D.S. Boyer, J.M. Levy, J. Chromatogr. Sci. 29 (1991) 517–521.
[8] X.W. Lou, H.G. Janssen, C.A. Cramers, J. Microcol. Sep. 7 (1995) 303–317.
[9] T. Tikuisis, M. Cossar, Antec '93, 1993, pp. 270–276.
[10] J.H. Braybrook, G.A. Mackay, Polym. Int. 27 (1992) 157–164.
[11] H. Engelhardt, J. Zapp, P. Kolla, Chromatographia 32 (1991) 527–537.
[12] A. Clifford, K. Bartle, S. Zhu, Anal. Proc. Anal. Commun. 32 (1995) 227–230.
[13] T.J. Watson, Introduction to Mass Spectrometry, 3rd ed., Lippincott-Raven, New York, 1997.
[14] V.J. Koch, Angew. Makromol. Chem. 20 (1971) 21–33.