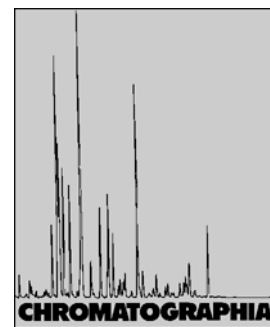


Extraction of Various Additives from Polystyrene and Their Subsequent Analysis



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Summary

The extraction of fifteen polymer additives which are used as antioxidants, uv stabilizers, process lubes, flame retardants, and antistats from eight formulations of polystyrene is demonstrated with supercritical carbon dioxide and compared to traditional dissolution/precipitation extractions. The purpose of the study was two fold: 1) the development of a high performance liquid chromatography method(s) for the additives and 2) the determination of the viability of supercritical fluids for extraction of the additives from polystyrene. Nine of the additives were assayed via reversed phase liquid chromatography while, the remaining six additives could not be assayed in this manner. In order to develop an extraction method for the additives, the effects of static extraction time, CO₂ density, and temperature were first investigated. These preliminary extractions revealed that a static period which afforded an opportunity for the polymer to swell combined with a high CO₂ density and temperature above the polymer glass transition yielded quantitative recoveries of the additives. Triplicate extractions of the various polystyrene formulations matched additive recoveries obtained by the traditional dissolution/precipitation method but the former method was faster and used less organic solvent.

Introduction

Polystyrene (PS) was first introduced on a commercial scale in Germany in 1930 and then in the United States in 1937. [1] PS has subsequently grown to be a multibillion-dollar industry. [2] PS is clear, transparent, easily fabricated, and has reasonable mechanical and thermal properties. It is slightly brittle and softens near 100 °C; and therefore, may not be used in formulations requiring sterilization. It will

degrade at elevated temperatures into a mixture of low molecular weight compounds and styrene. Specific additives are incorporated to achieve product characteristics that depend on the end usage.

Polystyrene additives include antioxidants, uv stabilizers, processing lubes, antistats, and flame retardants. With polystyrene, the additives create a difficult matrix for extraction and subsequent identification using conventional solvents and chromatographic methods. Three major

factors must be considered when developing an analytical method for polymer additives: 1) the additives themselves are not pure compounds, 2) they are insoluble in the polymer matrix, and 3) they are in low concentration. The analytical technique, therefore, must first separate the additive from the polymer. The resulting extract must then be cleaned up to remove any low molecular weight oligomers that were extracted from the polymer and that may interfere with analysis. The extract must also be handled carefully to avoid any additive decomposition. For instance, antioxidants are labile, unstable compounds that often contain complex decomposition products. [3]

Numerous publications and research papers [4–6] outline polymer additive extraction with subsequent analysis using high performance liquid chromatography (HPLC). The major deficiency noted in these reports is that they typically address only a few additive types. Published research seldom addresses the entire additive package in a given polymer. This is partially due to HPLC separation difficulties where additives possessing similar structures and similar retention times result in overlapping peaks. Other publications discuss supercritical fluid extraction (SFE) coupled with SFC. [7–11] SFE combined with chromatography has also been used to determine oligomer content. [12, 13] In another study, Jordan [14] used HPLC in combination with a mobile phase elimination interface to assay standard mixtures of polymer additives by FT-IR. By eliminating the mobile phase and depositing the additives on a germa-

Table I. Polystyrene Formulations*.

Resin	R %	M. O. %	ZnSt ppm	StAc ppm	Irg1076 %	TinP %	Tin770 %	TNNP %	AC ppm	BT93 %	DE83 %	S. O. %	HS %	E %
201			1000											
208		3.0	1000											
334	8.5	2.5	1000		0.1				200					
765	8.8	1.5		1000	0.1	0.2	0.2							
779	10.0	1.5		2500	0.2	0.3	0.5			13				
1119	10.0	2.0			0.1			0.2						
F7000	10.0	2.0			0.2						11.7			0.4
P8001	7.0	1.5	1800									1.2	2.9	

Legend: R: Butadiene Rubber; TNNP or Wytex:Tris nonyl phenyl phosphite; M. O. Mineral Oil; AC: Acrawax; ZnSt: Zinc Stearate; BT93: 1,2-bis tetra-bromophthalimido ethane; StAc: Stearic Acid; DE83: decabromodiphenyl oxide; Irg1076: Irganox 1076; S.O.: Silicone Oil; TinP: Tinuvin P; HS: Hostastat; Tin770: Tinuvin 770; E: Erucamide; * Reference 20.

Table II. HPLC Chromatographic Conditions^a Used for the Separation of Additives.

HPLC Method Number	Mobile Phase ^b	HPLC Gradient Program
1	MeOH: Water	20–70% MeOH @ 24% per min. 70–80% MeOH @ 13% per min. 80–100% MeOH @ 2.4% per min.
2	ACN: Water	20–70% ACN @ 24% per min. 70–80% ACN @ 13% per min. 80–100% ACN @ 2.4% per min.
3	ACN: Water	50:50 linear
4	MeOH	Isocratic
5	MeOH: Water	95:5

^a The column was an ODS-2 Keystone Spherisorb, 5 μ m, 250 mm \times 4.6 mm. Temperature was ambient. Detection was UV @280 nm and ELSD. ^b The mobile phase was modified with 2% triethylamine or n-butylamine.

nium disk, it was possible to positively identify the additives by their characteristic infrared spectrum. Thus, there are numerous hyphenated techniques that have proven useful for the analysis of polymer additives. Many laboratories, however, do not have the instrumentation available or funding to obtain specialized equipment. Therefore, many manufacturing plants want to establish simple methods for laboratory technicians using existing laboratory equipment.

The purpose of the study reported here was to first develop a HPLC method for fifteen additives. The HPLC development included attempts to find a “universal” method for the polystyrene additive package. The second phase of the study was to determine whether supercritical CO₂ was capable of extracting a variety of additives quantitatively from eight different polystyrene resins. The SFE method development concerned the effects of supercritical fluid density, extraction temperature, static extraction time, and dynamic extraction time.

Experimental

Huntsman Chemical Company (Chesapeake, VA) supplied the additives, PS dimer/trimer fractions, and the polymer re-

sins. The polystyrene resin formulations used in this study are outlined in Table I. The HPLC instrument used was a Hewlett Packard Model 1050 (Little Falls, DE) equipped with an automatic injector and UV detector. An evaporative light scattering detector (ELSD), (Alltech, MK III) was used in tandem after the UV detector. Solvents were reagent grade and consisted of 1, 2-dichloromethane (CH₂Cl₂), acetonitrile (ACN), tetrahydrofuran (THF), and methanol (MeOH). The water was ultrapure HPLC grade.

HPLC Method Development

HPLC method development began by determining the solubility of the fifteen additives in various solvents and combination of solvents at ambient and higher temperature. Four additives (acrawax, zinc stearate, silicone fluid, and BT-93) were not soluble in any of the organic solvents studied. The aforementioned four additives and mineral oil were therefore not assayed using reversed phase chromatography. During preliminary HPLC method development, analysis centered on synthetic mixtures of additives. Chromatograms of single additives exhibited several peaks due to residual by-products and contaminants in the synthetic mixtures.

Refer to Table II for a listing of the column, gradients, and conditions that were used successfully or semi-successfully to establish HPLC reversed phase methods for the additives.

Preliminary HPLC separations used an ODS-2 Keystone Spherisorb, 5 μ m, 250 mm \times 4.6 mm column. The mobile phase began with 78% MeOH/2% n-butylamine and increased at a rate of 1.2% MeOH per minute under ambient conditions. Three additives, Irganox 1076, Tinuvin 770, and Wytex, exhibited good separations. To separate the remaining seven additives the mobile phase began with 20% MeOH and increased at 24% per minute to 70% MeOH, then a 13% increase per minute to 80%, and finally a 2.4% increase per minute to 100% MeOH in 18 minutes. This mobile phase scheme resulted in the separation of five of the seven additives: Larostat, Hostastat, Great Lakes 59, Mold Pro 830, and Mold Pro 678. However, the dimer/trimer fractions masked one of the Mole Pro 830 peaks. Tinuvin P and Great Lakes 83R did not separate in this chromatographic run. Figure 1 depicts the separation using HPLC Method 1.

HPLC Method 2 began with 20% ACN with an increase of 24% per minute to 70% ACN, then a 13% increase per minute to 80%, and finally a 2.4% increase per minute to 100% ACN in 18 minutes. This gradient resulted in a separation of only three of the additives: Hostastat, Larostat, Great Lakes 59 plus the dimer/trimer fraction. Figure 2 depicts the separation using HPLC Method 2.

Considering the separation problems encountered with both HPLC method #1 and #2 and the limited solubility of the additives in organic solvents, we decided to raise the temperature the column. Nielson [16, 17] had shown improved peak shape in his study of polymer additives by using 40 °C to 55 °C column temperatures for polyethylene additives. HPLC Method 3

used a 50:50 ACN: water linear gradient and a column temperature of 50 °C. The additives in solution were heated to 50 °C before injection. Unfortunately, this linear gradient resulted in a poor separation. The dimer/trimer fractions masked the majority of the additives. Hostastat and Larostat peaks overlapped one another, and Great Lakes 59 exhibited two peaks.

HPLC Method 4 used 100% MeOH. This method was adequate for several of the resin packages. It was not valid however, for the two antistats (Hostastat or Larostat), and when the uv stabilizer (Tinuvin 770) or the antioxidant (Wytox) were present. These additives required a mobile phase containing water. When both of the antistats were present, HPLC Method 1 had to be used. For Tinuvin 770 or Wytox, HPLC Method 5 was (Isocratic MeOH/H₂O (95/5) satisfactory.

In summary, HPLC Method 4 that used a methanol isocratic scheme proved to be efficient for the majority of the resin packages. The overall preferred method would be the methanol: water gradient at ambient temperature (method 1). In retrospect, we realized that trying to develop a single method to identify all the additives was not practical, and would probably not be needed for real world samples and applications. Typically, the resin packages contain only three to four additives. With that in mind, the chromatography of extracts used the best gradient for the analyte(s) of choice.

Extraction

All extractions were performed using a Hewlett Packard (Little Falls, DE) Model 7680T supercritical fluid extractor employing carbon dioxide (CO₂) as the supercritical fluid. Carbon dioxide without helium headspace was donated by Air Products and Chemicals, Inc. (Allentown, PA). The SFE system used a cryogenically cooled (4 °C) dual head reciprocating pump. The extraction vessels were 7 mL and were packed in a layered fashion. The first layer consisted of Ottawa sand (20–30 mesh, Fisher Scientific) followed by the ground polymer, and finally Celite. The solid phase trap contained stainless steel beads. The trapped analytes were rinsed from the stainless steel bead trap using a mixture of HPLC grade methanol and chloroform (EM Science). The trap rinses were collected in 2 mL capped amber vials.

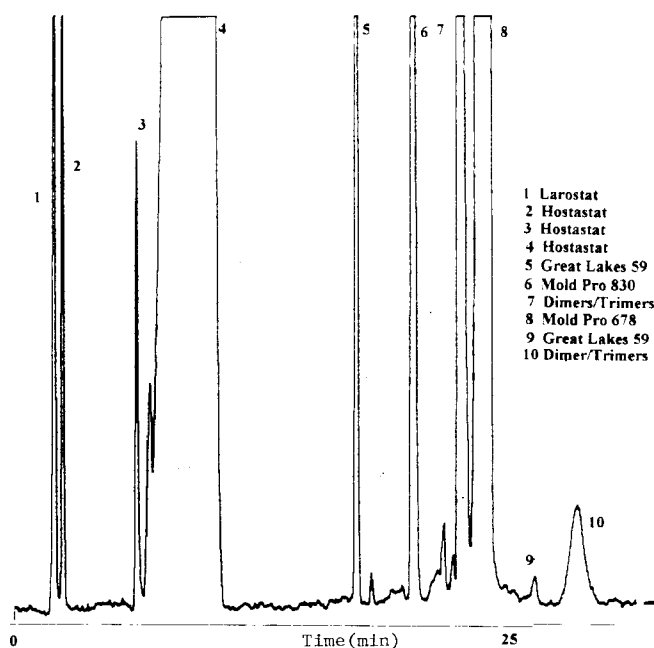


Figure 1. HPLC Chromatogram of Additives using HPLC Method No. 1. Conditions: Methanol: Water 20:80 (24%/minute), 70:30 (13%/minute), 100:0 (8%/minute), ambient temperature, and UV detection at 280 nm.

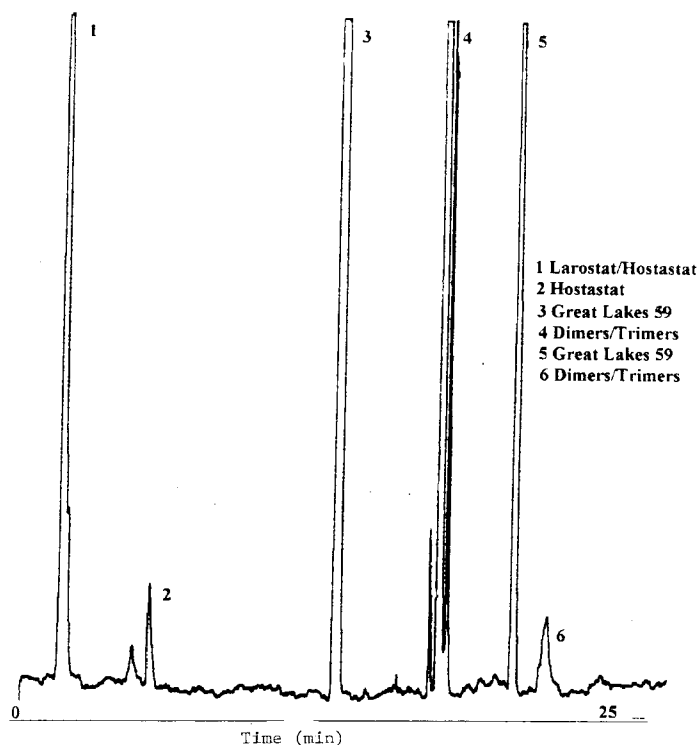


Figure 2. HPLC Chromatogram of Additives using HPLC Method No. 2. Conditions: Acetonitrile: Water 20:80 (24%/minute), 70:30 (13%/minute), 100:0 (8%/minute), ambient temperature, and UV detection at 280 nm.

Results and Discussion

Polystyrene Additives

Additives function by contributing to the quality, life, and usefulness of the resin. Additives are typically present in small

quantities, somewhat dependent upon their desired function. Their concentrations are typically less than a percent, but may range from 0.1% upwards to 10% for some flame retardants.

Antioxidants function by blocking chain reactive oxidative degradation me-

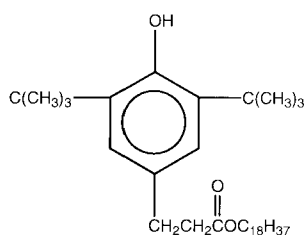


Figure 3. Structure of Irganox 1076, Octadecyl 3,5-di-tert-butyl-4-hydroxycinnamate.

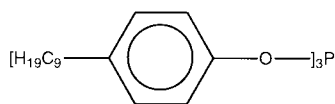


Figure 4. Structure of Wytox, Tris Nonyl Phenyl Phosphite.

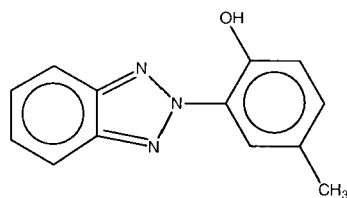


Figure 5. Structure of Tinuvin P, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole.

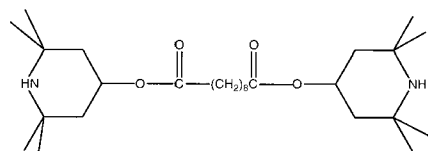


Figure 6. Structure of Tinuvin 770, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate.

chanisms. Polymers not protected by antioxidants are subject to oxidative attack that may shorten the polymer's life due to discoloration, cracking, brittleness, and loss of mechanical properties. Primary acting antioxidants are structurally hindered phenols, phosphites, and secondary aromatic amines, Figures 3 and 4.

Decomposition initiated by heat and light also contributes to the oxidative process. UV absorbers (Figure 5 and 6) commonly classified as hindered amine light stabilizers can absorb energy and impede bond cleavage. Processing lubricants are added to enhance extrusion, injection molding, and casting. Lubricants are typically fatty acids such as stearic acid or salts of fatty acids such as zinc stearate. Other lubricants, sometimes referred to as slip agents, include waxes and silicones.

Antistats function to help bleed off static electricity that is inherent in the polymer. The antistat's function involves in-

Table III. Percent Extractables and Total Mass of Additive Extracted Using the Dissolution/Precipitation Extraction Process.

Resin No.	1 st Extraction (%)	2 nd Extraction (%)	Total µg additive extracted per gram of resin
Irganox 1076			
334	85.79	14.21	75
765	88.04	11.96	117
779	89.12	10.88	131
1119	81.67	18.33	51
7000	21.59	78.41	131
Tinuvin P			
765	84.04	15.96	83
779	86.10	13.90	112
Tinuvin 770			
765	100	0	12
779	100	0	55
Wytox			
1119	78.12	21.88	13

creasing the hydrophilic and hydroscopic nature of the surface of the polymer. Internal electrostatic dissipation is often remedied by using a conductive filler such as carbon black. External antistat agents are commonly quaternary ammonium salts. Flame retardants function by forming a layer on the surface of the polymer that serves as a barrier to oxygen penetration and protects the polymer from heat. Brominated polyaromatic compounds are frequently used in polystyrene. Other additives include substances such as rubber (butadiene) which functions to reduce the brittle properties of polystyrene. Impact grade polystyrene, for example, has polybutadiene dispersed throughout the polymer. [16]

Traditional Extraction Results

The traditional dissolution/precipitation procedure was easy, although time consuming. The resins required a minimum of an hour to completely dissolve in chloroform. The filtering step also required approximately an hour to complete. Cleanup was tedious and the resins containing rubber made it extremely difficult to clean the glassware. It is also noteworthy to mention that the resins which contained rubber required longer dissolution times (e. g. 30–40 min). In our study, recoveries ranged from 80–90% for a first pass yield. The exception was Irganox 1076 (Figure 3) from resin package 7000 where the first pass yield was only 22%. Additional additives were extracted in all the resin packages during a second pass, (Table I) except for Tinuvin 770 from two of the resin packages. Exhaustive extraction would thus require numerous dissolution/

precipitation steps, extended extraction times, or changes in solvent and temperature to obtain quantitative results. Refer to Table III for the total mass of additive extracted per gram of polymer determined by dissolution/precipitation extraction.

Although the dissolution/precipitation method has been around for years, it has numerous drawbacks. Extraction times are lengthy, requiring a minimum of one hour to three days for the extraction alone. [16] These methods are dependent upon the temperature of the extraction, solvent used, the matrix, and the additive being extracted. Analysis of the extracts is subject to numerous handling steps that contribute to error. Co-extractives such as dimers, trimers, and low molecular weight waxes are a problem. Besides the handling problems, the additives themselves are seldom pure components. The polymerization process also introduces degradation products or contaminants. Other constraints include the need for a great deal of working space inside and outside a fume hood, large quantities of glassware, re-concentration steps, and lengthy extract clean-up. Overall, the traditional extraction methods are very labor intensive and expensive. Supercritical fluid extraction (SFE) is a promising alternative technique that overcomes many of the traditional sample preparation pit falls.

Supercritical Fluid Extraction Results

The data shown in Table IV indicate that SFE is feasible for removal of PS additives. Relative standard deviations (RSD) ranged from 1.7 to 13.8%. Quoted SFE recoveries are relative to the dissolution/pre-

cipitation extractions, since there was no data available for comparison with Soxhlet or accelerated solvent extraction (ASE) methods. In three instances, SFE results were greater than 100% as compared to the dissolution/precipitation extractions. For resin 1119, the higher recoveries (greater than 100%) may indicate that there are problems with co-precipitation of additives in the dissolution/precipitation extraction. Another explanation may be that heterogeneity was created in the polymer processing that results in variability in the analytical results.

A paired t-test was used to evaluate whether there were significant differences in recoveries between the dissolution/precipitation and SFE methods at a 95% confidence level. The values determined for Irganox 1076, Tinuvin P (Figure 5), Tinuvin 770 (Figure 6) and Wytox (Figure 4) were well below the critical t-value of 3.18. It is therefore likely that observed differences in the data are due to sampling error. The data from the SFE and dissolution/precipitation extractions came from the same population therefore any observed difference is the result of chance. In conclusion, there was no significant difference in the two methods.

A comparison of conventional versus SFE solvent usage and time for typical extraction is outlined in Table V. The solvent consumption savings of 100 mL per sample and 1 hour time savings in sample preparation exemplify the attractiveness of SFE versus the conventional methods of extraction.

Acknowledgement

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Table IV. SFE Recoveries Relative to Dissolution/Precipitation Extraction.

Polymer	RSD N = 3	%Recovery Relation to Dissolution/Precipitation Extraction
Irganox 1076		
334	4.0	83
765	1.7	87
779	9.1	82
1119	8.0	113
7000	8.5	90
Tinuvin P		
765	9.4	101
779	6.4	89
Tinuvin 770		
765	13.8	99
779	1.9	93
Wytox		
1119	10.6	156

Table V. Comparison of Conventional versus SFE Extraction for a Sample.

Dissolution/Precipitation	SFE
Sample Preparation	Sample Preparation
Dissolution: 1 hour	Grinding: 5 minutes
Precipitation: 15 minutes	Extraction: 70 minutes
Analysis: 30 minutes	Analysis: 30 minutes
Organic Solvent Use	Organic Solvent Use
Extraction: 100 mL	Extraction: 2 mL
Analysis: 30 mL	Analysis: 30 mL
TOTAL TIME: 2 hours & 45 minutes	TOTAL TIME: 1 hour & 45 minutes
TOTAL SOLVENT: 130 mL	TOTAL SOLVENT: 32 mL

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