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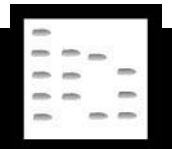
POLYMER ADDITIVES: SUPERCRITICAL FLUID CHROMATOGRAPHY



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Introduction

Commercial polymers contain small quantities of low molecular weight additives which are evenly dispersed throughout the polymer matrix. They are typically present at concentrations in the order of 0.1–1.0% (w/w) but can be as high as 60% w/w in certain formulations. They make an important contribution to the properties and suitability of particular polymer grades.

The analysis of polymer additives is a two-stage process. The additives are first separated from the polymer by solvent extraction or reprecipitation. The extracted additives are then separated and quantified by a suitable chromatographic technique. This article is concerned with the application of supercritical fluid chromatography (SFC) to this second stage. However this also involves a discussion of coupled supercritical fluid chromatography–supercritical fluid extraction (SFE-SFC) in which both stages are combined into a single analysis.

Polymer Additives

The most common polymer additives are stabilizers, plasticizers, lubricants and flame retardants. Stabilizers are added to prolong the useful life of a polymer formulation by protecting it from thermal and light-assisted oxidation. This process is caused by the formation in the polymer chain of free radical sites which can react with oxygen to form unstable peroxy radicals and ultimately cause polymer chain scission. Stabilizers are divided into four main classes: UV absorbers, primary antioxidants, secondary antioxidants and quenchers.

UV absorbers such as benzophenones and triazoles screen the polymer from harmful photons by absorbing them and then dissipating the excitation energy as heat so there is no radical formation. Primary antioxidants are typically hindered phenols. They react with free radicals to prevent further propagation. Secondary antioxidants destroy the hydroperoxide sites on the polymer chain which could otherwise be converted to peroxy radicals. They tend to be sulfur- or phosphorus-containing compounds. Quenchers are usually organonickel compounds and their function is to take over the energy absorbed by the chromophores in the polymer and dissipate it as heat.

Lubricants are added to make the polymer easier to process by controlling the melt rheology during thermoplastic moulding. They optimize the properties of the finished article to create smooth and unblemished surfaces and minimize stress fractures. External lubricants are compounds that are added to a polymer blend to control the degree of adhesion and friction between the polymer melt and hot processing equipment. Internal lubricants are added to polymer blends to reduce the melt viscosity to facilitate lower processing temperatures and to improve heat dissipation. Many lubricants posses a combination of internal and external characteristics. Lubricants are typically fatty alcohols, acids and esters and hydrocarbon waxes.

Plasticizers are high-boiling, organic chemicals which are often present at high concentrations, solvating the polymer chains to form stable gels. As a result,

intermolecular forces are reduced and this leads to a lower polymer glass transition temperature. The polymer is consequently less brittle and more easily worked. Typical plasticizers are phthalates, adipates and polychlorinated hydrocarbons. Flame retardants are typically chlorinated organophosphates.

It is evident then that a vast number of chemical species are used as polymer additives. They have widely varying volatilities with molecular weights potentially varying from 200 to 1000 Da. They tend to be of low to medium polarity and many do not have UV chromophores. Polymer formulations contain unique combinations of additives (called additive packages) which often contain 10 or more compounds. Thus the identification and quantitation of these additive packages is a challenging chromatographic problem.

Advantages of SFC for Polymer Additive Analysis

The analysis of extracted polymer additives by means of chromatographic separation has been reviewed by Handley. Gas chromatography (GC) has been used to analyse plasticizers and some stabilizers. It has the advantage of employing the near-universal flame ionization detector (FID) as the standard detector. Many additives, however, are not volatile enough to be efficiently separated by GC and, although high temperature GC has made recent advances, this approach is not suitable for most stabilizers because they tend to be thermally labile. This has led toliquid chromatographic techniques being favoured. Gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC) methods have been developed. GPC has the wider molecular weight range but its use is severely limited by its inferior resolution compared to HPLC. Unfortunately, HPLC separations tend to employ gradient elution and this necessitates the use of UV detectors. This means that conventional HPLC is not applicable to the analysis of additives which lack a UV chromophore.

SFC has been widely applied in the analysis of polymer additives. It is a potentially attractive alternative because it can combine a compatibility with the universal FID detector with a capability to elute high boiling components at lower temperatures than GC. This capability arises from the properties of the supercritical fluid (SF) which is the mobile phase in SFC. This is a dense fluid which is above or near its critical temperature and pressure. It has solvating properties, which are similar to those of a liquid, and transport properties which approach those of a gas. The enhanced solubility of high-boiling polymer additives in a SF compared with their solubility in a gas enables them to be eluted at much lower temperatures than is possible for GC. SFC also compares favourably with LC because of the higher binary diffusion coefficients and the lower viscosities of the SF compared to the liquid phase. The higher diffusion coefficients of polymer additives in an SF give enhanced resolution. The lower viscosity results in a lower pressure drop across an analytical column and this means that higher flow rates can be used to give faster separations. SF mobile phases have been used with both packed and capillary columns to achieve polymer additive separations.

Capillary Column Separations

Capillary SFC separations of polymer additives are performed using conventional GC columns with modified polysiloxane-bonded stationary phases. Unmodified carbon dioxide is used as the mobile phase. Reported separations typically use columns of 50 or 100 μm internal diameter (i.d.) with typical film thicknesses varying from 0.05 to 0.5 μm. These narrow-bore columns are required to achieve an equivalent resolution to the 250–320 μm columns, which are used in conventional GC, because the diffusivity range of supercritical carbon dioxide is lower than that of a GC carrier gas. Similarly, the relatively short 10 m column length reflects the higher viscosity of supercritical carbon dioxide.

Capillary columns in SFC tend to be characterized by better resolution than packed columns; however, they also have an inferior sample capacity and produce longer analysis times.

Capillary SFC is carried out using GC analysers which are modified by the addition of a high pressure pump to deliver liquid carbon dioxide to the top of the column. The other end of the column is connected to the FID via a pressure restrictor which accounts for most of the pressure drop in the system. This allows the column pressure to be controlled by increasing the flow rate until the required level is achieved. The earliest restrictors were approximately 10 cm lengths of 5–10 μm fused silica but these have subsequently been replaced by frit and integral restrictors. The limitation of this type of fixed restrictor is that independent control of both flow and pressure is impossible. The pressure is controlled by changing the flow rate and vice versa. Pressure programming is always used for polymer additive separations. Typical flow rates are very low and this means that syringe pumps with their superior performance are routinely used. Capillary SFC is compatible with all GC detectors, including the FID; however, the depressurization of carbon dioxide through the restrictor results in Joule–Thompson cooling of the detector and relative-

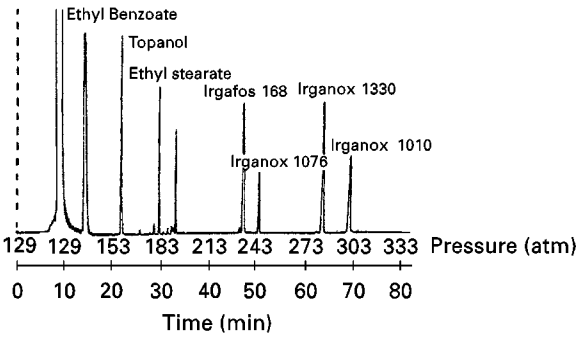

Figure 1 Chromatogram of polymer additive standards on a 10 m × 50 μm i.d. Octyl column at 110°C. Mobile phase: carbon dioxide pressure programmed from 129 atm (12 min) to 350 atm at 3 atm min^{-1}. (Reproduced with permission from Moulder *et al.* (1989).)

ly high FID temperatures (300–400°C) are required to compensate for this effect.

Polymer additive separations tend to be performed isothermally at temperatures between 80 and 140°C. The additives are eluted by means of a pressure/density gradient. The column pressure is initially held at a low pressure (8–15 MPa) for 5–10 min to allow the solvent to elute through the system while the less soluble additives are retained at the top of the column. The pressure is then increased at a rate of between 0.25 and 1 MPa min^{-1} to reach a final pressure of 35–45 MPa. Those additives which have the highest solubility in the mobile phase are solvated at lower pressures and consequently are eluted first. Additives with lower solubilities elute later. Many additive packages are composed of components with similar polarities and their solubilities and hence their retention times are largely determined by their molecular weights, with lighter molecules eluting first. A typical chromatogram is shown in **Figure 1**.

A wide range of additives have separated using polysiloxane phases. These include phenolic antioxidants, benzotriazoles, thioesters, organophosphite and organometal stabilizers; fatty acid, ester and amide lubricants; and organophosphate flame retardants. Methyl, octyl, phenyl and biphenyl substituted stationary phases have been used. Biphenyl columns have been found to give better separations than methyl columns and their use has dominated in later publications.

Packed Column Separations

These are divided into two distinct categories: separations on 1 mm (i.d.) columns of lengths between 10 and 40 cm; and separations on conventional 4.6 mm (i.d.) × 20–25 cm (length) HPLC columns. The stainless-steel columns are packed in both cases with 5 μm particles of bonded silica. Packed column SFC has been used to elute phenolic antioxidants, benzotriazoles, thioesters and organophosphite stabilizers, fatty ester and amide lubricants and phthalate plasticizers.

Separations on 1 mm columns are similar to those on capillary columns. They are performed using capillary SFC instrumentation with the pressure restrictor adjusted to give a higher flow rate range. Unmodified carbon dioxide is used as the mobile phase, the column is operated isothermally at 100–150°C and the additives are eluted with a pressure programme. The pressure is initially held at 10–15 MPa and then increased at 0.5–1.2 MPa min^{-1} to a final pressure of 35–45 MPa. Nonpolar octadecyl phases are most commonly used for these separations; however, more polar octyl, phenyl and polyethylene glycol phases have also been used. A typical separation is shown in **Figure 2**. Packed columns are more active than capillaries and this can lead to peak tailing for more polar additives. This tailing can be minimized by adding a polar modifier to the carbon dioxide mobile phase at approximately 1% (v/v). Formic acid is commonly used for this purpose it has a low FID response. An alternative approach is to use 250–320 μm (i.d.) fused silica columns which are packed with bonded silica particles. These packed capillary columns exhibit lower activity than conventional packed columns and they generate flow rates which are more compatible with the FID.

Separations on 4.6 mm columns resemble normal-phase HPLC separations. The column is operated isothermally at the lower temperature range of 40–60°C and isobarically with the pressure set to 10–20 MPa with the flow rate set to 2–4 mL min^{-1}. The additives are eluted by means of a composition

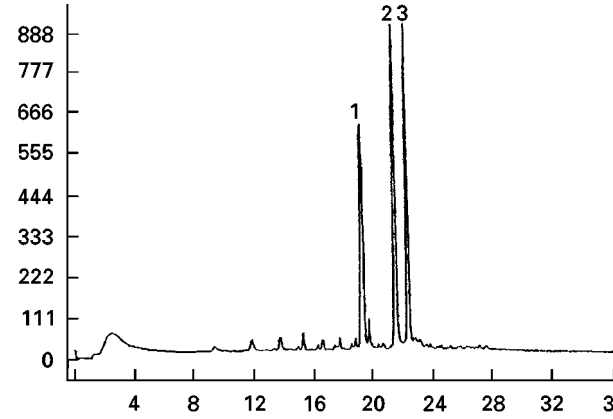

Figure 2 Chromatogram of polyethylene additives on a 25 cm × 1 mm i.d. C_{18} column at 150°C. Mobile phase: carbon dioxide pressure programmed from 1500 psi (6 min) to 6000 psi at 200 psi min^{-1}. Peaks: 1, Tinuvin 326; 2, Irgafos 168; 3, Irganox 1076. (Reproduced with permission from Ryan *et al.* (1990).)

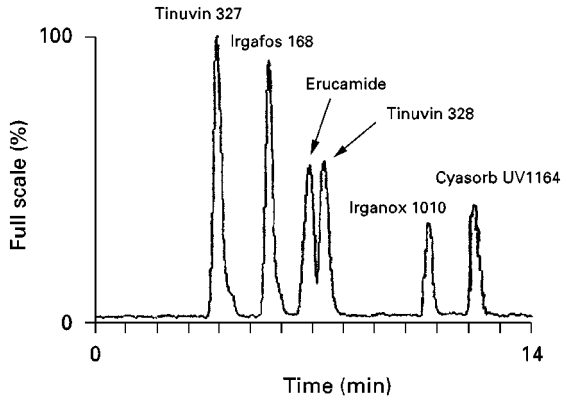

Figure 3 Chromatogram of polymer additives on a 25 cm × 4.6 mm i.d. C_{18} column. Mobile phase: carbon dioxide methanol at 200 bar and 2 mL min^{-1}. Methanol concentration programmed from 2% (1 min) to 10% (5 min) at 0.89% min^{-1}. (Reproduced with permission from Carrot *et al.* (1998).)

gradient of a polar modifier (usually methanol) in carbon dioxide. They are sequentially desorbed from the stationary phase as the polarity of the mobile phase increases. The elution order in such separations is determined by the relative adsorption strengths of the additives which in turn are determined by their functional groups and polarities. Hence, the least polar additives elute first and more polar additives elute later. Polar cyano, amino and diol phases are best suited to this mechanism; however, octadecyl columns can also be used due to the presence of residual silanol groups. A typical composition gradient separation is shown in **Figure 3**.

Composition gradient separations are performed using modified HPLC instrumentation. The high flow rates necessitate the use of binary piston pump systems. The larger system volume allows the use of back-pressure regulators which give independent control of both pressure and flow rate. UV detectors are used because organic modifiers are not compatible with the FID.

Offline Analysis: Sample Injection and Calibration

Sample introduction in SFC is achieved using HPLC-type high pressure injection valves. A fixed-volume injection loop is filled with the additive solution, then switched into the SF flow path and swept on to the column. A 200 nL loop is typically used in capillary SFC; however, even this volume is sufficient to overload a 50 μm column. Hence, flow split and time split techniques are used so that only a fraction of the 200 nL aliquot is introduced into the column.

Time split injection is a convenient procedure for routine analysis. It does not suffer from the problem of additive molecular weight discrimination, which is associated with flow split injection, but it gives poor additive peak area repeatabilities (10–20%) and the low sample capacity also leads to relatively poor sensitivity. The lower limit of detection (using FID) for a single additive solution, which is injected in time-split mode on to a 50 μL coulumn, is approximately 100 p.p.m. (w/v). For a 5 mL extract of a 5 g polymer sample this is equivalent to 100 p.p.m. (w/w) concentration of the additive in the polymer. This detection limit should be an adequate characterization of most polymer additive packages; however, it is not sufficient for studies on the migration of additives into food simulants where there is a requirement to detect additives in food simulants at p.p.b. levels. Greater sensitivity can be achieved by means of large volume injection/solvent venting techniques.

The sample capacity of a packed column in SFC compares favourably with HPLC and a similar range of sample volumes (5 μL–1 mL) is employed. This means that it is possible with packed column SFC to achieve the p.p.b. (w/v) level limits of detection which are required for additive migration work.

The sample injection repeatability is similar to that obtained in HPLC and this means that multi-level external standards can be used for the additive peak area–concentration calibration. The poor repeatability of capillary SFC injection, conversely, means that in this case an internal standard must be used for calibration.

Online SFE-SFC

Online SFE-SFC has been reviewed by Levy and Ashraf-Khorassani. The polymer is analysed in a single process without any intermediate preparation. It involves the transfer of the whole of the SFE extract on to the SFC analyser and this means that online SFE is more sensitive than equivalent offline procedures where the extract is diluted in an aliquot of solvent for subsequent injection on to an analyser. Hence it is ideally suited for trace analysis or for applications where there is little available sample. However the counterpoint of this argument is that the sample size is limited by the capacity of the interfaced analyser. This can be a disadvantage. Additives should be evenly dispersed throughout a batch of polymer chips. However, in practice, process faults can cause localized variations so that the additives are more concentrated in some chips than in others. In this circumstance it is clearly important for a representative analysis to be able to sample from more than one chip.

The most widely used coupling system is called cryotrapping. This involves feeding the SFE outflow

into a vented collection tee or retention gap which is cooled by adiabatically vaporizing liquid CO_2 through it. The extracted analytes are deposited in the retention gap during the extraction whilst the SF is vented to the atmosphere. When the extraction is complete the vent is closed and deposited analytes are eluted by the SF into the column.

Calibration curves for quantitative analysis can be obtained from online extractions on known amounts of free additive. These are then used to convert the online additive peak areas from the polymer extraction into concentration values. However, the validity of this approach depends on the complete removal of the additives from the polymer during the SFE step. Alternatively, the system can be calibrated using similar polymer samples of known additive concentration. It is not necessary with this procedure completely to extract all of the polymer additives so long as the extraction conditions for the polymer sample and standard are identical.

Identification of Unknown Additives

FID and UV detection are sufficient for the analysis of an additive package of known composition. The order of the eluting peaks is determined in this case by comparing their retention times with those of the pure additives, eluted under identical conditions; however, this procedure is clearly impossible for the identification of a mixture unknown additives. Hence there is a requirement for the SFC separation to be coupled with a spectroscopic technique which records sufficient structural and fingerprinting data on the eluting additive to enable it to be identified either by deduction or by comparison with library records.

Fourier transform infrared (FTIR) spectroscopy can be coupled indirectly to capillary SFC by depositing the additive on to an infrared disc or directly by passing the column outflow through a flow cell. The latter technique is possible because carbon dioxide exhibits just two narrow absorption bands in the near infrared spectrum. Alternatively xenon, which is completely transparent to infrared, can be used as the mobile phase. Both interfaces have been successfully used to identify a wide range of stabilizers; however, they lack sensitivity and quantitative measurements have not been achieved. The poor sensitivity necessitates the use of 100 μm i.d. columns.

Carbon dioxide is a nonprotonated solvent and this makes SFC the ideal chromatographic technique to couple with ^1H nuclear magnetic resonance (NMR). The relatively large dead volume of the NMR probe means that it can only be interfaced with packed column SFC with flow rates $>1\,mL\,min^{-1}$ and sample loadings of 20–120 μL. This procedure has ben used to analyse phthalate plasticizers. Unfortunately, SFC-NMR signals have been found to be pressure-dependent and exhibit increased spin-lattice relaxation times.

SFC has been most successfully coupled to mass spectroscopy (MS). MS detectors can be used in several modes to give molecular ion data and structural data from fragmentation patterns which can be compared with library records to identify an unknown additive. Total ion chromatograms can also be used for quantitative analysis. Capillary SFC is interfaced directly by feeding the end of the column into the ionization chamber of the MS. The MS signal is not affected by the SFC pressure gradient. This has been used for the identification and quantitation of flame retardants from polyurethane foams. Several interfaces (moving belt, thermospray, particle beam) have been used to couple packed-column SFC and MS. These tend either to inhibit the range of compatible SFC conditions or result in the loss of volatile components. The most promising system is currently atmospheric pressure chemical ionization MS which has been used with a carbon dioxide–methanol composition gradient to identify and quantify benzotriazoles and phenolic stabilizers.

Conclusion

SFC is a useful technique for the analysis of a wide range of polymer additives. It can elute nonvolatile and thermally labile additives which are not suitable for analysis by GC and it gives better resolution and faster separations compared with HPLC. Useful separations are obtained with both packed and capillary columns. Capillary separations generally involve 50 μm i.d. columns and FID detection with unmodified carbon dioxide used as the mobile phase. The additives are eluted with a pressure/density gradient. Packed columns with i.d. < 1 mm can also be operated in this way; however, separations on 4.6 mm i.d. columns employ composition gradients at a fixed temperature and pressure with UV detection. Capillary SFC generally gives separations of superior resolution but with longer analysis times and poor sensitivity.

The flexibility of SFC as a technique for the analysis of polymer additives is further enhanced by the ease with which it is interfaced to other techniques. SFE-SFC enables the detection of trace levels of additives which could not be analysed by offline procedures. SFC-FTIR, SFC-NMR and SFC-MS give the capability to determine the chemical structures of additives from polymer samples of unknown compositions.

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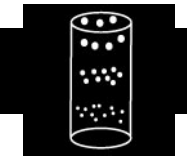
POLYMERS



Field Flow Fractionation

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Introduction

Two subtechniques of the field-flow fractionation (FFF) family are used to separate polymers with high resolution on an analytical scale; these are thermal FFF (ThFFF) and flow FFF (FlFFF). For lipophilic polymers, ThFFF excels in the analysis of high-molecular-weight-polymers ($M > 10^6\,\mathrm{g\,mol^{-1}}$) and gel-containing polymers. ThFFF can also separate polymer blends and copolymers according to chemical composition. For hydrophilic polymers, FlFFF compares well with size-exclusion chromatography (SEC) for the analysis of polymers with $M > 10^3\,\mathrm{g\,mol^{-1}}$, and like ThFFF, excels when $M > 10^6\,\mathrm{g\,mol^{-1}}$. By varying factors that control retention, each FFF application can be optimized, and programming such factors allows highly polydisperse samples to be analysed with unparalleled precision in a single run. FFF channels are more expensive than SEC columns, but with proper maintenance, channel lifetimes are virtually unlimited.

FFF, like liquid chromatography, relies on the differential migration of dissolved or suspended materials as they are flushed through a conduit. Unlike chromatography, however, the FFF separation relies on interactions of the analyte with an applied field rather than a stationary phase. As a result, the FFF separation occurs in a single phase (see **Figure 1**) with minimal exposure to surfaces, and the flowing liquid has a laminar profile. These features make for a gentle separation, so that fragile molecules and molecular complexes can be characterized with little disruption.

FFF instrumentation (**Figure 2**) is similar to that for chromatography, and consists of a pump to drive the carrier liquid, an injection port, the separation channel, and a detector to monitor the channel effluent.