Rate and Extent of Supercritical Fluid Extraction of Additives from Polypropylene: Diffusion, Solubility, and Matrix Effects

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SYNOPSIS

Analytical extraction of additives from polymers using a supercritical fluid (SFE) is a promising alternative to liquid extraction. Factors affecting SFE with carbon dioxide of Irgafos 168 and Irganox 1010 from commercial polypropylene have been studied, with analysis of extracts by capillary supercritical fluid chromatography (SFC). A diffusion limited extraction model was investigated by measuring the rate of SFE as a function of pressure, particle size, flow rate, and temperature. The rate of extraction was found to fit the sum of exponential decays; results were also consistent with an extrapolation procedure to obtain the total mass of additive without exhaustive extraction. Derived diffusion coefficients for the additive in polypropylene differed from literature values by approximately two orders of magnitude apparently because of swelling of the polymer by sorbed carbon dioxide. The variation of extraction rate with pressure and flow rate confirmed the solubility limitation of proposed model. The rate of extraction increased between 20 and 140°C, then fell away at higher temperatures with the onset of melting. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Chemical additives are incorporated into polyolefins to prevent degradation by heat, oxygen, and ultraviolet light, to aid in the processing of the polymer, and to modify its physical properties.[1] Analysis of polymer additives can be complicated owing to their physical properties and their inclusion in a matrix that is insoluble in most solvents, so that the range of analytical techniques that can be performed without prior separation from the polymer matrix is limited. Consequently, the analysis can be considered a two-stage procedure: The extraction of the additives from the polymer followed by identification and quantitation. Soxhlet extraction is the most commonly used preseparation technique for polyolefins with solvents such as chloroform,[2,3] dichloromethane,[4] and diethyl ether,[5,6] but such extractions are time-consuming, wasteful of solvent, and difficult to reproduce.

A promising alternative to Soxhlet extraction is supercritical fluid extraction (SFE).[7] This procedure in many ways resembles a Soxhlet extraction, except the solvent is a supercritical fluid (SCF) i.e., a substance above its critical temperature and pressure. SCFs have low viscosities and high diffusivities and therefore fast mass transfer, which should lead to rapid extraction that is experimentally easier to reproduce than are Soxhlet extractions. Although many fluids have been used in SFE, nearly all extractions are performed with carbon dioxide due to its easily attainable supercritical conditions given its critical parameters of 75.3 atm and 31°C. It is available in a highly pure state and is inexpensive, of medium polarity, and nontoxic. After an extraction, CO_2 simply evaporates at atmospheric pressure, leaving behind the extracted material.

SFE can be achieved in two ways: In a static extraction, the extraction vessel is pressurized to the desired pressure with the extracting fluid and then simply left for a certain length of time. This method was popular in early SFE experiments but has decreased in importance in comparison with dynamic SFE. Here, fresh SCF is continuously passed over the sample, extracting soluble compounds and de-

positing them in a suitable solvent or on a solid trap. In this study, only dynamic SFE was carried out. The potential of SFE for the extraction of polymer additives has been demonstrated recently.[8,9]

A variety of chromatographic techniques have been applied to the identification and quantitation of the additives once they have been separated from the polymer matrix, including liquid column chromatography,[2,10] thin-layer chromatography,[11,12] and high-performance liquid chromatography (HPLC).[13,14] HPLC is now generally used to determine a range of additives but is limited by a lack of a universal detector. Progress in high-temperature gas chromatography (GC)[15] has allowed a larger range of additives to be analyzed than by conventional GC, providing that the analytes are stable at these high operating temperatures. As most of the additives in polyolefins are of medium polarity and soluble in supercritical CO_2, supercritical fluid chromatography (SFC) is suitable for their analysis. Capillary column SFC offers high resolution, approaching that of GC, with universal FID detection and the possibility of separating nonvolatile high molecular weight additives.[5,16] Packed column SFC provides lower resolution, but allows a greater sample capacity and a rapid analysis time.[17] The coupling of SFE to the various forms of chromatography allows a one-step analysis; for additives in polyolefins, on-line SFE–SFC[18–20] and on-line SFE–GC[21] have both been investigated.

Models for SFE

Two factors may limit the rate of extraction: First, the solubility of the extracted material in the SCF under the operating conditions; for many dynamic extractions, this is not usually the limiting factor as the solute is present in such small amounts in the matrix and the flow rate of the SCF large enough for the concentration of the extract in the fluid to be well below its solubility limit. The second possible limiting factor is the rate of mass transfer out of the matrix by the analyte. This may be controlled by diffusion or at least a process similar to diffusion.

For diffusion-limited extractions, a model has been suggested by Bartle et al.[21] This assumes diffusion out of a homogeneous spherical particle, radius r, into a medium in which the extracted species is infinitely dilute. Adaptation of published solutions for the differential equation, with the appropriate boundary conditions, leads to the following equation for the ratio of mass, m, of extractable compound that remains in the matrix sphere after extraction time, t, to that of the initial mass of extractable compound, m_0:

$$\frac{m}{m_0} = \left(\frac{6}{\pi^2}\right) \sum_{n=0}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(\frac{-n^2\pi^2 Dt}{r^2}\right) \quad (1)$$

where n is an integer, and D, the diffusion coefficient of the compound in the material of the sphere. The solution is the sum of exponential decays that fits experimental extraction data well.[21]

The model has been extended to include the effects of solubility for spherical particles[22] giving the following equation:

$$\frac{m}{m_0} = 6 \sum_{n=0}^{\infty} \frac{\left(\frac{hr}{a_n}\right)^2}{[hr(hr-1) + a_n^2]} \exp\left(\frac{-a_n^2\pi^2 Dt}{r^2}\right) \quad (2)$$

where a_n are the roots of the equation

$$a \cot(a) = 1 - hr \quad (3)$$

and h is given by

$$h = \frac{KSF}{AD} \quad (4)$$

where K is a constant; S, the solubility in units of concentration; F, the volume rate of flow of fluid; A, the surface area of the matrix; and D, the diffusion coefficient.

The object of this work was to determine how certain parameters affect the rate and extent of extraction of additives from a standard polypropylene. The above models are used to explain how diffusion and solubility are affected when the flow rate, pressure, and temperature are varied.

EXPERIMENTAL

The off-line SFE system is shown in Figure 1. A Lee Scientific 602 D syringe pump was used to provide carbon dioxide (CP grade, BOC, U.K.) at the required extraction pressure. A 6.94 mL extraction cell (Keystone Scientific, U.S.A.) was fitted with slip-free connectors (Keystone Scientific) for easy installation. Stainless-steel frits (3 μm) were located at either end of the cell. Stainless-steel tubing (0.01 in. i.d.) was used to connect the extraction cell, via an on/off valve to the syringe pump. The other end of the cell was connected to a length of deactivated fused silica (Polymicro Technologies, U.S.A.) using a graphitized vespel ferrule and a Swagelok union ($\frac{1}{16}$ in.). The extraction cell was placed in a ceramic tube heater to maintain the extraction cell at the
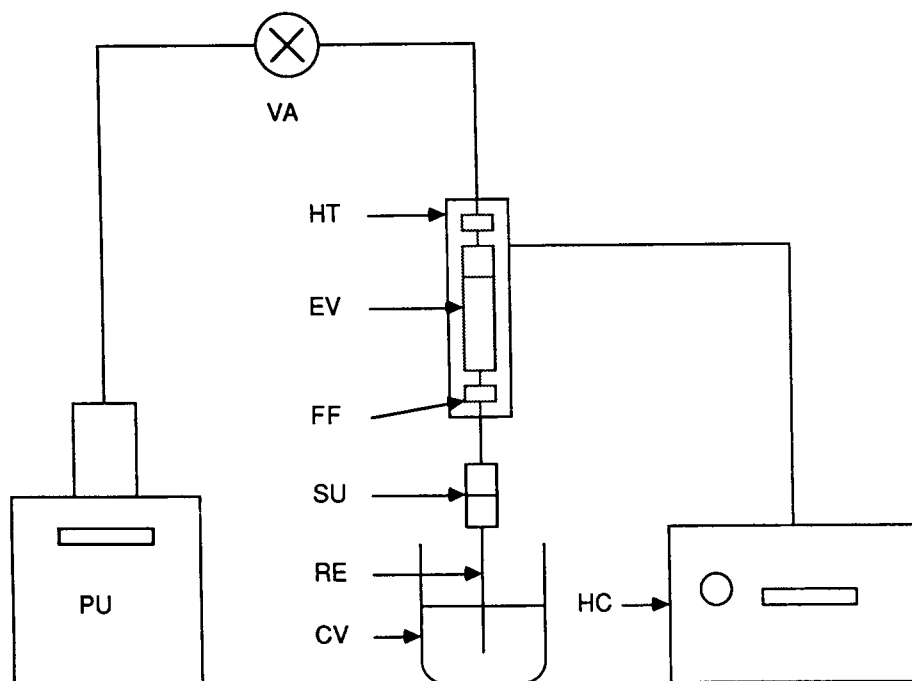
Figure 1 Off-line SFE system: PU, CO_2 pump; VA, on/off valve; HT, thermostated heating tube; FF, fingertight connectors; EV, extraction vessel; SU, swagelock union; RE, restrictor; CV, collection vial; HC, heater controller.

required temperature. The extracts were collected in a vial containing a few millilitres of HPLC-grade dichloromethane. A dichloromethane solution containing a known amount of Irganox 3114 (tris[3,5-di-*tert*-butyl-4-hydroxylbenzyl]isocyanurate) internal standard was added to the vial. The solvent was partially evaporated from the solution by passing a stream of nitrogen gas over the surface to leave an appropriate concentration for SFC. This was injected into the timed-split injector of the 602 D Lee Scientific SFC.

Polypropylene (ICI Wilton Research Centre, Wilton, U.K.) containing 1600 ppm Irgafos 168 (tris-[2,4-ditertiarybutyl phenyl]phosphite), 800 ppm Irganox 1010 (pentaerythritol tetrakis-[3-{3,5-di-*tert*-butyl-4-hydroxyphenyl}propionate]) and 3500 ppm Tinuvin 770 (bis-[2,2,6,6-tetramethyl-4-piperidinyl]sebacate) were obtained as pellets, some of which were freeze-ground to a particle size ranging from 0.6 to 1 mm diameter.

Extractions of the ground polypropylene were carried out at different pressures, ranging from 75 to 400 atm, for 30 min at 50°C. The flow rate was kept constant by changing the length and internal diameter of the fused silica linear restrictor. The flow rates were measured for gaseous CO_2 by use of a bubble flowmeter at the outlet of the restrictor. Occasionally, during an extraction, the fused silica

restrictor was blocked by deposited analyte. The blockage could be cleared rapidly by heating the end of the restrictor with a hand-held air heater. Longer extractions were then performed on the ground and pelletized polypropylene at 50°C and 400 atm. The collection vial was changed every 30 min for 5 h. These longer extractions were repeated for the ground polypropylene at different pressures, keeping the flow rate constant as described above. The effect of flow rate was investigated by extracting the ground polypropylene at 100, 200, 300, and 400 atm, using different flow rates for each pressure at 50°C and for 30 min. Using a flow rate of 7 cm^{-1} and a pressure of 400 atm, 30 min extractions were performed at different temperatures between 20 and 190°C. For the higher temperature extractions, a 50 μm i.d. restrictor was used as smaller internal diameter restrictors were found to block.

SFC was performed on a 10 m × 50 μm i.d. column with a cross-linked film of 30% biphenyl-substituted methyl polysiloxane (SB-Biphenyl-30, Dionex, U.K.). Restriction was achieved with a frit restrictor (Dionex) giving a flow of 1.7 cm/s at 75°C and 70 atm. Chromatography was performed at 130°C with either CP-grade carbon dioxide (BOC, U.K.) or SFC-grade carbon dioxide (Air Products, U.K.) as the mobile phase using a pressure ramp from 100 to 400 atm at 5 atm/min. The flame ionization detector
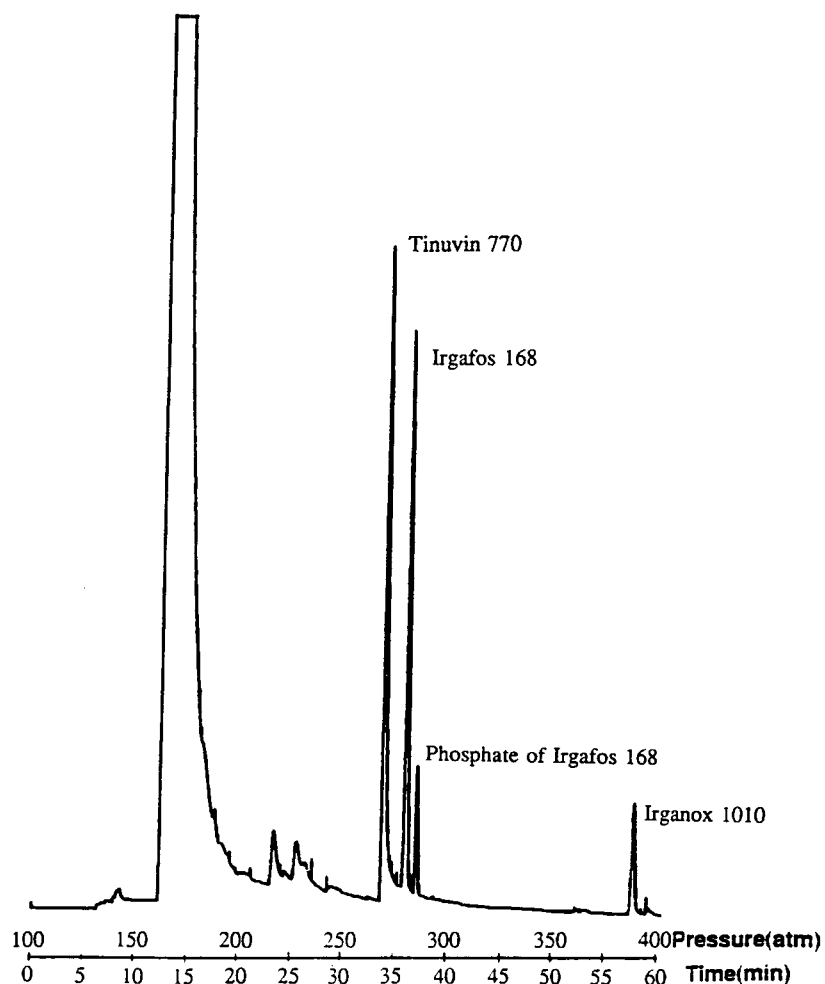
Figure 2 Capillary supercritical fluid chromatogram of an SFE extract of ground polypropylene. Extraction for 30 min with CO_2 at 400 atm and 50°C. Chromatography with the CO_2 mobile phase at 130°C. Pressure programmed from 100 to 400 atm (5 atm/min). Column 10 m × 50 μm i.d. SB, Biphenyl-30.

was maintained throughout at 400°C. Three purification traps were placed in series between the carbon dioxide cylinder and the pump: a basic alumina manifold (Dionex, U.K.), an oxygen trap (Phase-Sep, U.K.), and an activated charcoal (30–60 mesh) manifold (Dionex, U.K.).

RESULTS AND DISCUSSION

Diffusion Limited Extractions

A typical SFC chromatogram for the SFE extract of polypropylene is shown in Figure 2. All peaks exhibited good efficiency, but that of Tinuvin 770 was found to broaden excessively at lower concentrations and so was not used for these calculations. The lower

polypropylene oligomers, although present in the extract, were not eluted on the biphenyl column. After some optimization, conditions were found that gave near diffusion limited extractions. Figure 3 shows graphs of mass extracted in unit time against pressure, which are typical of solubility curves in an SCF. As the pressure is increased at constant temperature, the density of the SCF is increased, which gives rise to a greater solvent strength as the fluid becomes more "liquidlike." The solubility curve shows for both additives a threshold pressure below which the compounds are not significantly soluble. As the pressure is increased, there is an almost linear increase in solubility until a plateau is reached. It can be seen that an increase in pressure from 300 to 400 atm does not increase the amount extracted, indicating that the extraction is not limited by the

solubility of the additives in the SCF at these pressures. The flow rate, which directly affects the extraction in the same way as solubility, as shown in eqs. (2)–(4), was chosen after preliminary investigations. If this was too slow, the plateau in Figure 3 would not be reached and the solubility would limit extraction at up to 400 atm. It also follows that if the flow rate were greater the plateau would be reached sooner and extractions would be diffusion-limited at lower pressures.

The temperature was chosen for solubility reasons only, as at this temperature, the SCF is reasonably dense and the solubilities of the additives are high. The extraction profiles under these optimized conditions for Irgafos 168 and Irganox 1010 are shown in Figure 4. They exhibit typical extraction forms in which the majority of the additives are extracted during a short period at the beginning of the extraction, which then quickly tails off.

Equation (1) can be used to predict the rate of extraction from spherical particles. If the natural logarithm of this equation is taken, a characteristic time, t_c, is defined as

$$t_c = \frac{r^2}{\pi^2 D} \qquad (5)$$

and factorizing the term $\exp(t/t_c)$ gives the result

$$\ln\left(\frac{m}{m_0}\right) = \ln\left(\frac{6}{\pi^2}\right) - \frac{t}{t_c} + \ln\left[1 + \left(\frac{1}{4}\right)\exp\left(\frac{-3t}{t_c}\right)\right.$$
$$\left. + \left(\frac{1}{9}\right)\exp\left(\frac{-8t}{t_c}\right) + \cdots\right] \qquad (6)$$

A plot of $\ln(m/m_0)$, the rate of fall of extraction vs. time, falls steeply initially and the rate of fall decreases, becoming linear at longer times. This is shown in Figure 5. If the experimental data are used to plot this type of curve, m_0, the total amount of additive in the polymer must be known. An extrapolation procedure described by Bartle et al.[21] can be used, but since the sample is a carefully prepared standard polypropylene, the specified additive concentrations can be used. The extrapolation procedure would normally be used for these types of extractions. Equation (1) can also be used to predict the rate of extraction from spherical particles with different average diameters. Taking logarithms, factorizing the term-$\pi Dt/r^2$, and substituting the numerical value for $\ln(6/\pi^2)$, eq. (1) becomes
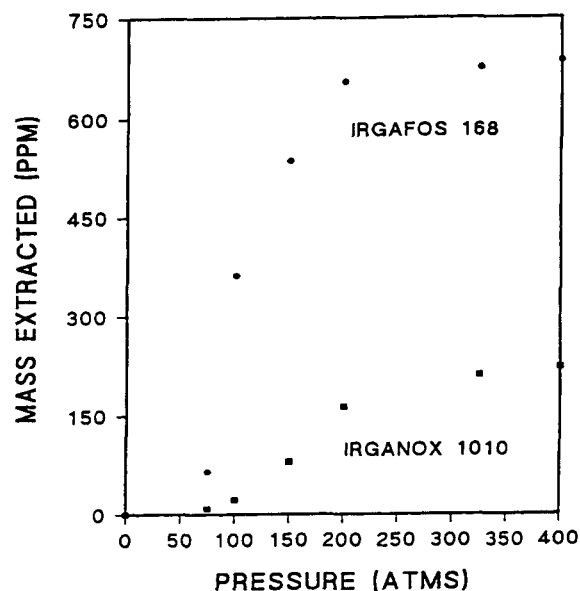

Figure 3 Mass extracted of additives in polypropylene at different pressures. SFE for 30 min at 50°C.

$$\ln\left(\frac{m}{m_0}\right) = -0.4977 - \frac{\pi^2 Dt}{r^2}$$
$$+ \ln\left[1 + \left(\frac{1}{4}\right)\exp\left(-\frac{3\pi^2 Dt}{r^2}\right)\right.$$
$$\left. + \left(\frac{1}{9}\right)\exp\left(-\frac{8\pi^2 Dt}{r^2}\right) + \cdots\right] \qquad (7)$$

At longer times, the relationship can be simplified, as the latter terms in eq. (7) tends to zero and here

$$\ln\left(\frac{m}{m_0}\right) = -0.4977 \frac{-\pi^2 Dt}{r^2} \qquad (8)$$

It can be seen the rate of fall of extraction is inversely proportional to the average particle radius squared. This can be clearly seen by letting

$$t_r = t\pi^2 D \qquad (9)$$

where t_r is a quantity proportional to time, t. Equation (7) then becomes

$$\ln\left(\frac{m}{m_0}\right) = -0.4977 - \frac{t_r}{r^2} + \ln\left[1 + \left(\frac{1}{4}\right)\exp\left(\frac{-3t_r}{r^2}\right)\right.$$
$$\left. + \left(\frac{1}{9}\right)\exp\left(\frac{-8t_r}{r^2}\right) + \cdots\right] \qquad (10)$$
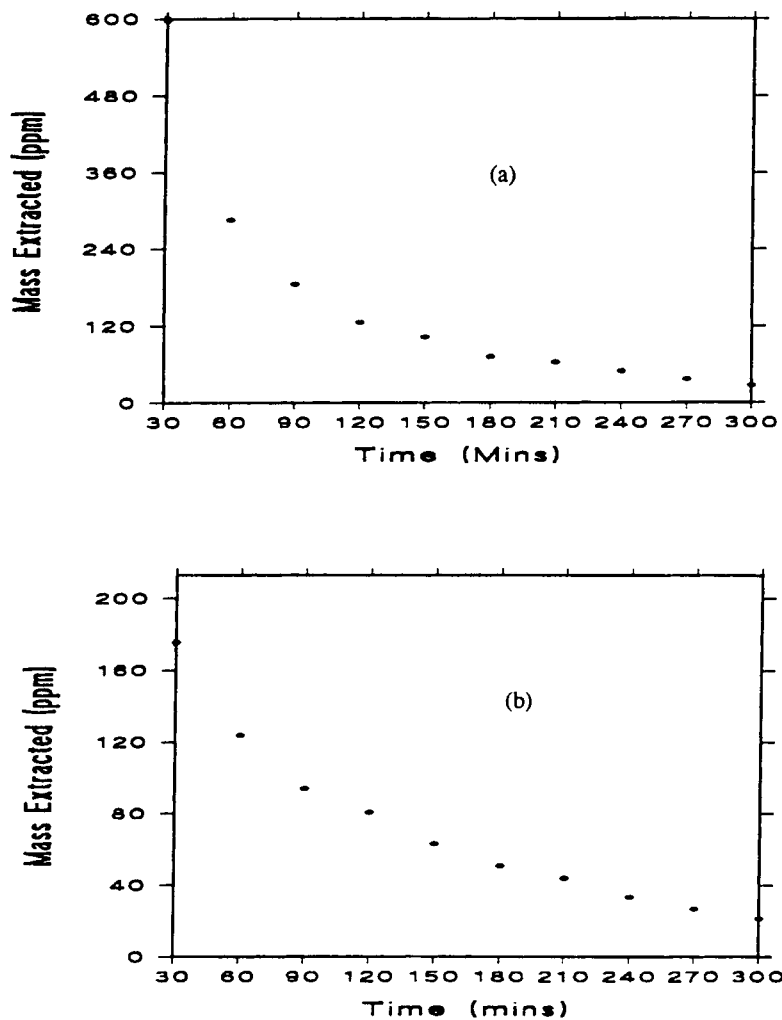
Figure 4   Mass extracted during each 30 min period of SFE of (a) Irgafos 168 and (b) Irganox 1010 at 50°C.

A plot of t_r vs. $\ln(m/m_0)$ for two different particle sizes, one with a 1 mm radius and the other with a 2 mm radius, is shown in Figure 6. The rate of fall of extraction at longer times is four times greater for the 1 mm radius particle than for the 2 mm radius particles, in agreement with eq. (10). For larger particle sizes, the graph takes longer to become a straight line, i.e., the last term in eq. (10) contributes to the value of $\ln(m/m_0)$ for a longer period. This has implications for the extrapolation procedure proposed[21] to obtain quantitative results in a shorter time than needed for exhaustive extraction. If extraction is carried out at least as long as the initial nonexponential period to obtain an extracted mass m_1, followed by extraction over two subsequent equal time periods to obtain masses m_2 and m_3, then it can be shown[21] that m_0, the total mass in the sample, is given by

$$m_0 = m_1 + \frac{m_2^2}{m_2 - m_3} \qquad (11)$$

The length of the initial nonexponential period depends on the ratio between the diffusion coefficient, D, and, as previously mentioned, the radius squared, D/r^2.

Use of the extrapolation procedure for the ground polypropylene gave results that confirmed the validity of this approach (Table I): 1625 ± 16 ppm for Irgafos 168 and 802 ± 1 ppm for Irganox 1010 compared with the actual values of, respectively, 1600 and 800 ppm. Plots of $\ln(m/m_0)$ vs. time for the extraction for two additives from ground polypropylene and from polypropylene pellets are shown in Figure 7. For the pellets, the extrapolation gave low values for m_0 due to the larger radii causing the initial nonexponential period to be extended. In effect,
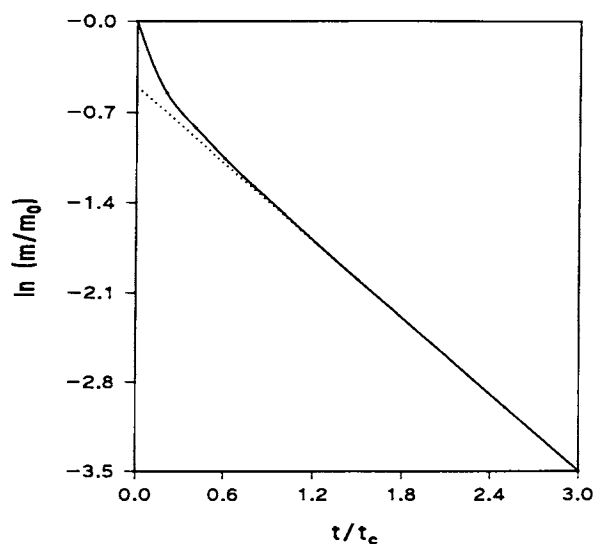
Figure 5 Theoretical curve of $\ln(m/m_0)$ vs. time for SFE of spherical particles with a uniform initial concentration distribution.

Figure 6 Theoretical curves of $\ln(m/m_0)$ vs. time for SFE of spherical particles with the effect of different diameters.

extrapolation is from this portion of the curve, and so very low values for m_0 are deduced. Therefore, the m_0 quoted was used. Compared to the model, the ground polypropylene extractions fitted well although intercepts greater than -0.5 were obtained, implying a solubility effect. This is more pronounced for Irganox 1010, as is to be expected since this compound is probably less soluble in supercritical CO_2 than is Irgafos 168, due to its larger molecular weight; this is indicated by the greater retention time in SFC (Fig. 2), and this is investigated and explained in the next section. The other possibility is that the polypropylene has lost the additives from the surface, resulting in a concentration gradient within the particles. The loss can be explained by the consumption of the additive during normal chemical stabilization processes that would occur
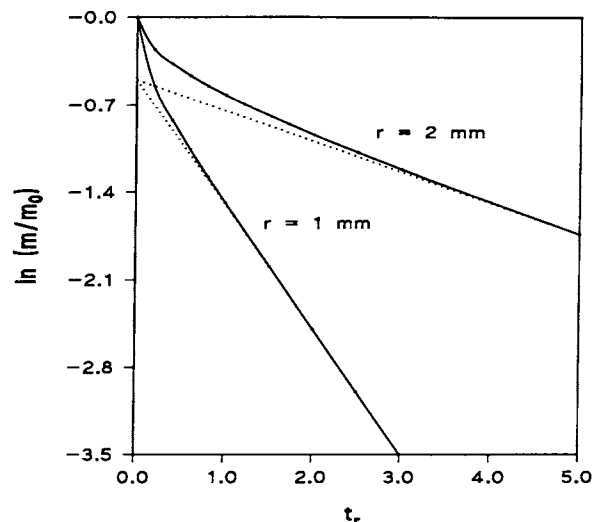
more readily near the surface. The gradient of the straight portion of the curve can be used to calculate the diffusion coefficient, for Irgafos 168 and Irganox 1010 in ground polypropylene at 50°C, as (1 ± 0.5) $\times 10^{-7}$ cm^2 s^{-1} and $(8 \pm 4) \times 10^{-8}$ cm^2 s^{-1}, respectively. A large part of the error is due to the range of particle sizes, between 0.6 and 1 mm.

A range of methods has been used to determine diffusion coefficients for a variety of additives in polypropylene, a selection of which are shown in Table II. As can be seen, most of the reported coefficients are at least two orders of magnitude smaller than are indicated in this work. This is probably due to the sorption of the CO_2 by the polymer, which may cause a decrease in the effective diffusion path.

The solubility of CO_2 in many commercial polymers at moderate temperatures and pressures has

Table I Extrapolation of Extraction Data for Two Additives from Polypropylene

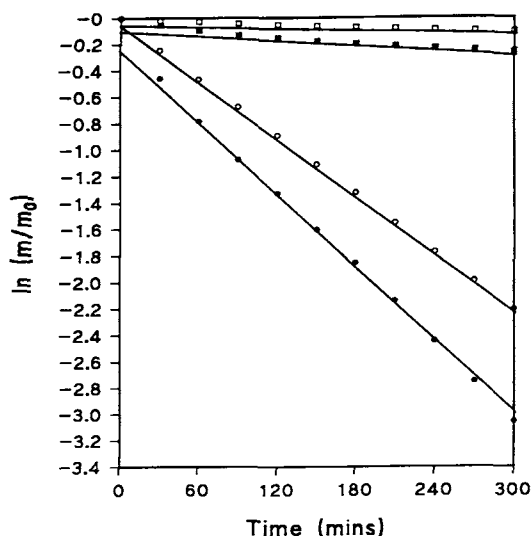| Extraction Periods (min)	Irgafos 168		Irganox 1010	
	Amount Extracted (ppm)	Results Predicted from eq (11)	Amount Extracted (ppm)	Results Predicted from eq. (11)
0–60	884.0		299.5	
60–120	311.3		175.0	
120–180	175.4	1597.1	114.2	803.2
0–120	1195.3		474.4	
120–210	239.1		158.2	
210–300	114.3	1653.4	81.8	801.9

Figure 7 $\ln(m/m_0)$ plots for Irgafos 168 (●) from ground polypropylene and (■) from pellets and for Irganox 1010 (○) from ground polypropylene and (□) from pellets.

been well documented, especially in the measurement and interpretation of the sorption isotherms, depending on the morphology of the polymer. As a simple approximation, the dissolution of a sparingly soluble gas in a rubbery polymer will obey Henry's law:

$$C = K_D P \qquad (12)$$

where C is the concentration of the sorbed gas in the polymer at equilibrium, at pressure P in the gas phase, and K_D is the solubility coefficient. This relationship has been confirmed by Chiou and Paul[27]

for CO_2 sorption in a 80% PVF_3, 20% PMMA blend. Sorption of CO_2 in low-density polyethylene was investigated gravimetrically by Kamiya et al.,[28] who found that the sorption is described by Henry's law for gas pressures up to 50 atm at temperatures from 25 to 55°C.

For systems that absorb to a larger extent, deviations from Henry's law will be observed in the form of sorption isotherms that are convex with respect to the pressure axis. This behavior is described by the Flory–Huggins theory represented by

$$\ln\left(\frac{P}{P^0}\right) = \ln(1 - Vp) + Vp + \chi Vp^2 \qquad (13)$$

where P is the pressure of the gas; P^0, the standard vapor pressure of the gas; V_p, the volume fraction of the polymer; and χ, the Flory–Huggins parameter. The Flory–Huggins equation provides a good description of sorption isotherms providing there are no interactions between the sorbing gas and the polymer. The convex curvature in the isotherm is explained by the swelling of the polymer, due to a high concentration of the gas. Further sorption is therefore made less difficult. Fleming and Koros[29] measured sorption of CO_2 in silicone rubber. They found for pressures up to 300 psi that sorption followed Henry's law. However, the sorption isotherm at pressures exceeding 300 psi show a convex form that they fitted successfully to the Flory–Huggins equation. Chiou et al.[30] predicted this kind of behavior for sorption of CO_2 in cross-linked butyl rubber.

It can be argued that all of this work deals with amorphous polymers while polypropylene is a semi-

Table II   Reported Diffusion Coefficients for Additives in Polypropylene

Additive	Temperature (°C)	Diffusion Coefficient (cm² s⁻¹)	Reference
2,4-Dihydroxybenzophenone	75	1.9×10^{-9}	23
2-Hydroxy-4-octoxybenzophenone	44	1.7×10^{-10}	24
	75	4.7×10^{-9}	
Didodecyl, 3,3-thiodipropionate (DLTB)	56	$(5.4 \pm 0.4) \times 10^{-10}$	25
	78	$(4.1 \pm 0.2) \times 10^{-9}$	
	96	$(1.9 \pm 0.2) \times 10^{-8}$	
	100	$(2.1 \pm 0.2) \times 10^{-8}$	
	135	$(1.89 \pm 0.15) \times 10^{-7}$	
1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) mesitylene (Irganox 1330)	80	1.4×10^{-10}	26
	100	7.7×10^{-10}	
	110	2.8×10^{-9}	
	120	8.4×10^{-9}	

crystalline material; Micheals and Bixler[31] discussed this point with respect to semicrystalline polyethylene and cited evidence that at 25°C the solubility of CO_2 is dependent on the volume fraction of amorphous polymer, indicating that the gas is insoluble in the crystalline fraction of the polymer. Lambert and Paulaitis[32] agreed, stating that the extent of crystallization will affect gas sorption by reducing the equilibrium solubility of the diffusivity of the gas in the polymer. It is therefore assumed that CO_2 sorption by polypropylene will be similar to sorption of CO_2 in silicone rubber.[29]

Solubility Limited Extractions

The spherical model may be extended to include the effects of solubility to predict extraction profiles. If t_c is substituted into eq. (2) where t_c is given by eq. (5), then graphs of $\ln(m/m_0)$ vs. t_c for different values of hr can be calculated (Fig. 8). For very large values of hr, the $\ln(m/m_0)$ plot will tend toward the diffusion-limited plots described in the previous section. It can be seen that the effect of solubility limitation is to reduce the rate at the beginning of the extraction, to decrease the slope, and to move the curve upward on the graph.

Extraction profiles were obtained from the results of extraction from ground polypropylene at different pressures and at a constant flow rate. Plots of $\ln(m/m_0)$ vs. time (Fig. 9) give curves of the type predicted by the model. It would be reasonable to assume that curves of this type could also be generated by de-

creasing the flow rate rather than pressure since this decreases the effective volume of the solvating SCF passing over the sample.

Figure 10 shows the effect of flow rate on extraction at different pressures. A plateau should be observed for the higher pressures when the flow rate is increased as the extraction becomes totally diffusion-limited. Even at low pressures, the plateau should be reached but the required flow rates could not be obtained by the pumping equipment used in these experiments. The plateau can be observed for Irgafos 168 at 400 atm, but is not clear for Irganox 1010. There is also a point for the higher pressures when the solubility becomes critical and the amount extracted drops off rapidly, suggesting a purely solubility limited extraction. For analytical purposes, it is important to be well above this point. A problem may occur at high flow rates as the collection technique of the extract becomes difficult. In this experiment, the extract is collected by depositing into a vial containing approximately 5 mL of solvent. As the flow rate increases, so does the volume of CO_2 depressurizing into the solvent. At large flow rates, some of the extract, especially for volatile components, may escape with the CO_2. A decrease in trapping efficiency with increasing flow rates is also observed for solid traps.

Effect of Temperature

An increase in extraction temperature may result in (a) a decrease in the density of the CO_2, therefore
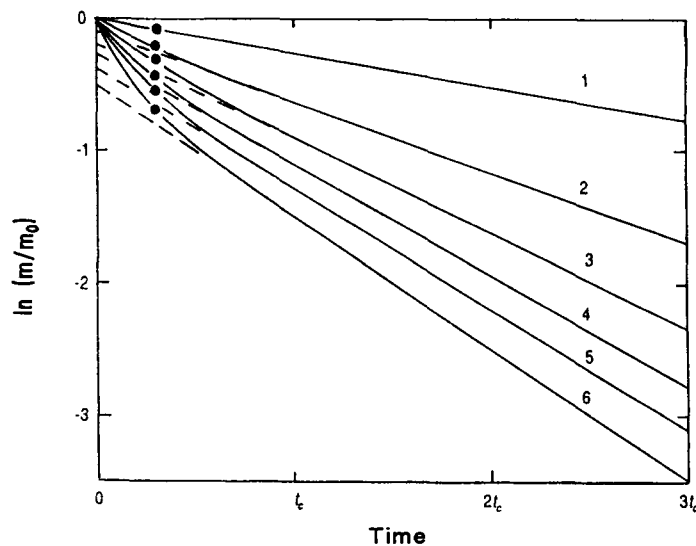

Figure 8 Plots of $\ln(m/m_0)$ calculated using eq. (2) vs. time in units of t_c. Curves 1–5 are calculated using values for hr of 1, 3, 6, 11, and 21, respectively, and curve 6 with the value hr tending to intinity.
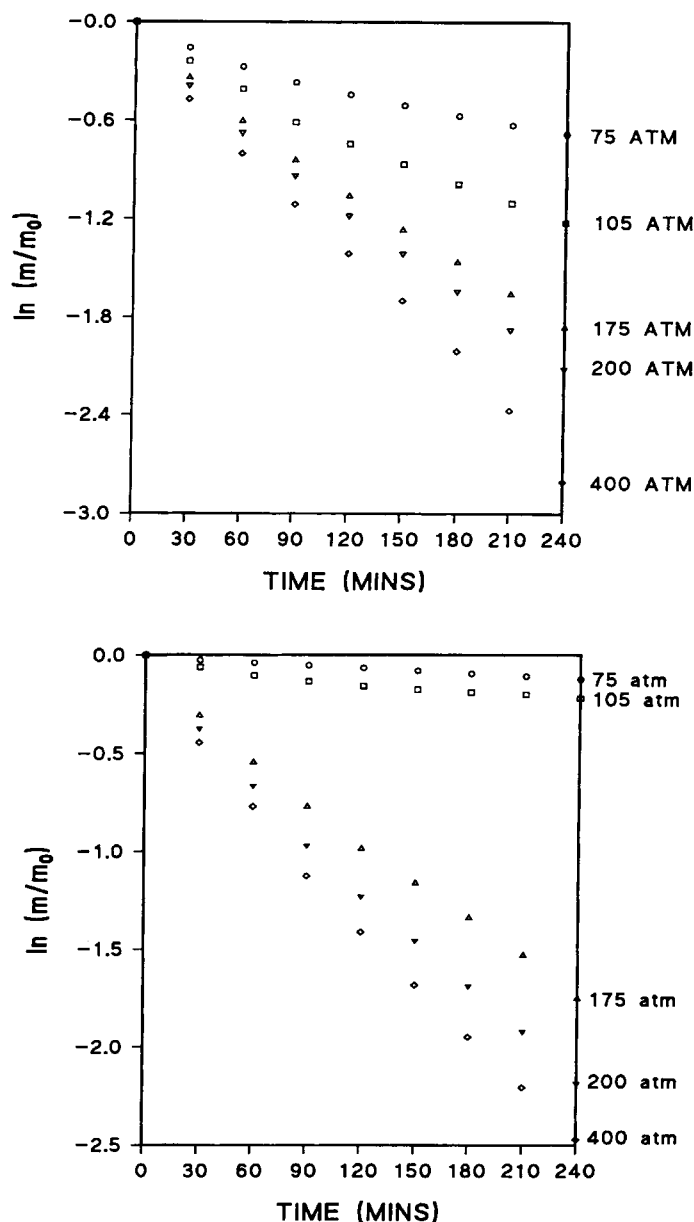
Figure 9 (a) Plots of $\ln(m/m_0)$ against time for Irgafos 168 at 50°C and a flow rate of 7 cm/s. (b) Plots of $\ln(m/m_0)$ against time for Irganox 1010 at 50°C and a flow rate of 7 cm/s.

decreasing its solvation powers; (b) an increase in the diffusion coefficient for the additives in the polymer, so increasing mass transfer into the extracting solvent; and (c) polymer melting or softening. The decrease in density with increasing temperature is almost linear, as shown in Figure 11. This will be of most importance where the solubility of the extract in the SCF completely limits the extraction. The variation of diffusion coefficient with temperature is given by the Arrhenius type equation:

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \qquad (14)$$

where E is the activation energy and D_0 is a constant related to the entropy of activation. An increase in temperature will also affect the physical state of the polymer. There should be an increase in rate of extraction when a semicrystalline polymer is in its rubbery state rather than in its glassy state. This has been confirmed by Kuppers[33] who found an in-
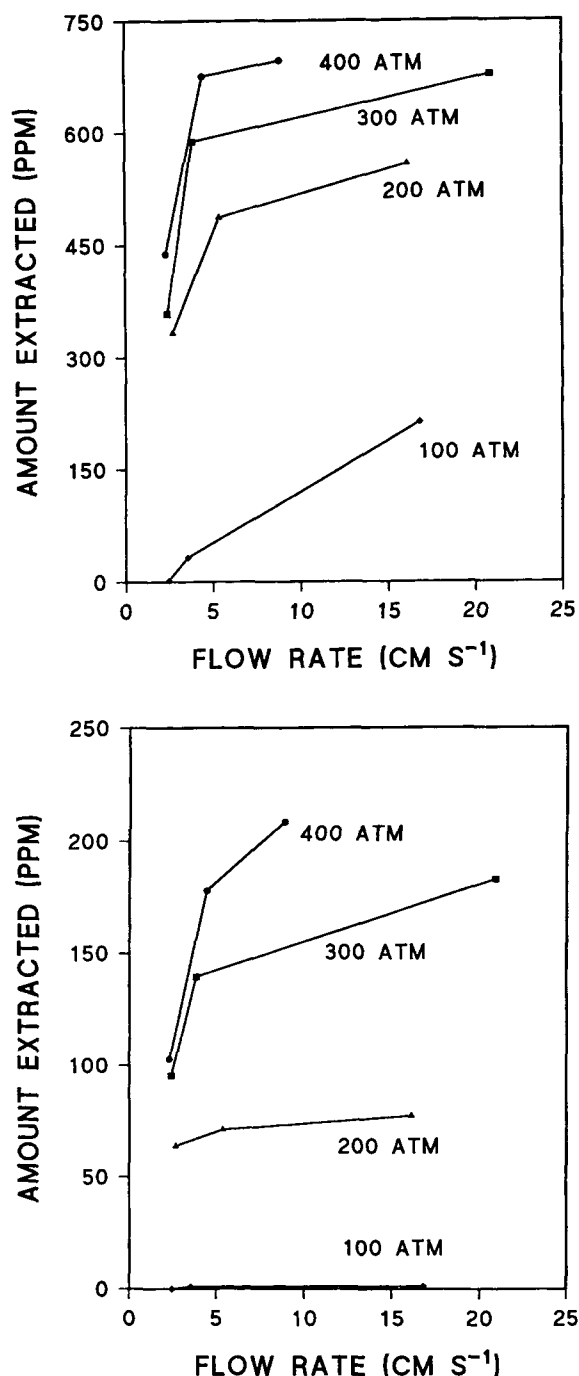
Figure 10   (a) Mass extracted of Irgafos 168 at a variety of different pressures and flow rates from polypropylene at 50°C for 30 min. (b) Mass extracted of Irganox 1010 at a variety of different pressures and flow rates from polypropylene at 50°C for 30 min.

crease in extraction of oligomers from PET when the extraction temperature was raised above its T_g. This is not important for polypropylene, as T_g is well below any realistic extraction temperature.

However, an increase in temperature below T_m under atmospheric pressure will increase the volume. The expansion would occur mainly in the amorphous part of the polymer, allowing faster diffusion of the additives. Expansion of the polypropylene was observed, after decompression of the SCF, for extraction temperatures over 120°C. At temperatures above T_m, the expansion was so pronounced that the sample had to be drilled out of the cell after the extraction. Melting had occurred, followed by recrystallization when the pressure and the temperature were reduced. The structure is foamlike, indicating the desorption of CO_2.

Measuring the extent of swelling in polymers caused by sorption of gases, or SCF, has been considered by a few workers. The most extensive study, carried out by Liau and McHugh,[34] determined the swelling of PMMA by sorption of CO_2 at 41.8, 58.1, and 68.0°C and pressures up to 4000 psia. Swelling was found to increase linearly with pressure for pressures up to about 800 psia, after which a limiting value is reached. This situation is removed from that investigated here as the PMMA is below its T_g of 105°C, but the results, nonetheless, give an indication of how swelling increases with pressure. Vittoria and Riva[35] investigated solvent-induced crys-
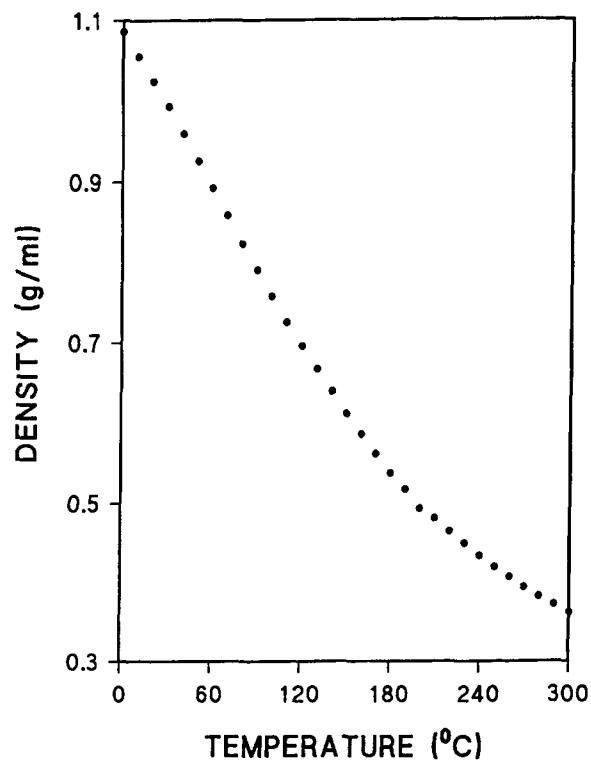

Figure 11   Variation of CO_2 density with temperature at a constant pressure of 400 atm.

tallization of quenched isotactic polypropylene and found that upon exposure to a variety of solvents the polymer initially swelled rapidly and then reached a constant volume. Another consideration is that sorption of the CO_2 will cause plasticization of the polymer. As Chiou et al.[30] observed, plasticization can lower the T_g so that the polymer will become a rubber for glassy systems whose T_g are not much higher than the temperature of sorption. The T_g of the amorphous blend containing 65% PMMA and 35% PVF_2 was lowered by sorption of CO_2 from 62°C to below 35°C when exposed to 16 atm of CO_2. In another study, Chiou et al.[36] found the T_g of PET to be depressed by 52°C when CO_2 was sorbed as 20 atm. Whether the T_m is lowered by the plasticization in a semicrystalline polymer is debatable, but the phenomenon may occur during the extraction at temperatures slightly below the true T_m.

As shown in Figure 12 for a 30 min extraction, the amount of additive obtained increased with increasing temperature until it rapidly fell away at about 140°C. The fall may be due to the decrease in density of the SCF, which may cause the solubility to become critical at this point. The more likely explanation is the interfering effects caused by the melting of the polymer. Calvert and Ryan[37] observed the distribution of additives in polypropylene by UV and fluorescent microscopy and by scanning electron microscopy, showing them to be present only in the amorphous polymer. This distribution was found to
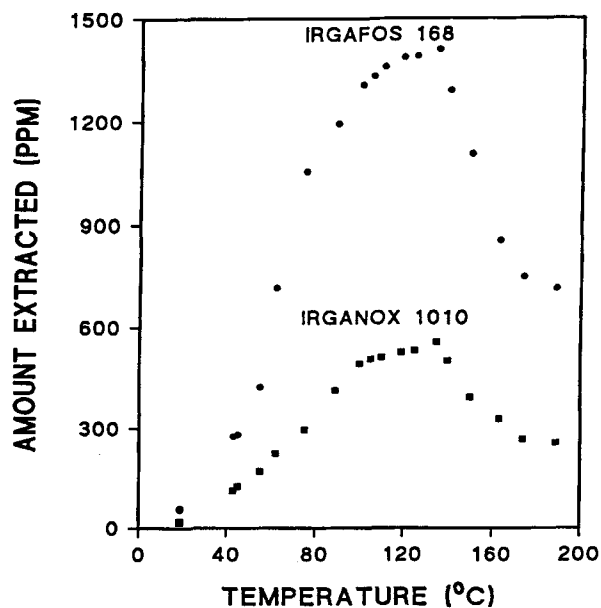
be uniform, providing enough time was given after the formation of the spherulites during crystallization for the rejection of the additives to the spherulite boundaries. The distribution of the amorphous material is not uniform within the polymer with an increase from the highly crystalline spherulite centers to the boundaries, where the highest concentration of amorphous material is found. Frank and Lehner[38] and Billingham and Calvert[39] also used UV microscopy to observe this type of additive distribution in polypropylene. It follows that during an extraction the melting of the crystalline material could hinder diffusion of the additives as the volume from which extraction is taken place is increasing with no additional increase in the amount of additive. This hypothesis would be consistent with the decrease in rate of increase of extracted additive with temperature as the melting process begins at approximately 100°C. The plateau observed as the temperature approaches 200°C indicates completion of the melting process. However, extraction should not be carried out at these temperatures since decomposition of polymer with free-radical formation may occur, thus depleting the concentration of additives and giving erroneous results. From an analytical point of view, the optimum extraction temperature would be near 120°C, before excessive melting has taken place. The thermal stability of the additives must also be considered when choosing an extraction temperature.

The rapid increase in the rate of extraction of the additives between 20 and 140°C can be explained by the increase in diffusion coefficient with increasing temperature. Several workers have demonstrated this relationship and a selection of literature results is shown in Table II. If the results of Jackson et al.[25] are used, an at least twofold increase in the diffusion coefficient between 56 and 135°C may be conservatively assumed. With the extraction diffusion coefficient for Irgafos 168 at 50°C calculated previously as 1×10^{-7} cm^2 s^{-1}, eq. (1) indicates a 99% recovery in 4.5 min when the diffusion coefficient is increased by two orders of magnitude. Such an increase was not observed since the solubility limits the extraction; the density of the SCF decreases with increasing temperature. Ideally, the pressure could be increased to keep the density constant, but our apparatus was limited to 400 atm. Flow-rate increases are also limited since a syringe pump was used with a capacity of only 137 mL of liquid CO_2, which is consumed quickly at large flow rates. However, with the use of pneumatic booster pumps and careful consideration of the collection and restriction procedure, quantitative extraction of low molecular

Figure 12 Mass extracted of additive at different temperatures from polypropylene for 30 min at 400 atm and a flow rate of 7 cm/s.

compounds in polymeric material can be achieved very rapidly.

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