Comparison of pressurised fluid extraction and microwave assisted extraction with atmospheric pressure methods for extraction of additives from polypropylene

The Analyst

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Extraction of Irganox 1010 from freeze-ground polypropylene using several methods has been compared. Pressurised fluid extraction (PFE) (of which accelerated solvent extraction is an example) using a modified supercritical fluid extractor (SFE) and microwave assisted extraction (MAE) both gave faster extraction than any conventional method, and recoveries were not significantly different. The times taken to reach 90% extraction for PFE using propan-2-ol at 150 °C and acetone at 140 °C were 5 and 6 min, respectively. Reflux with chloroform was found to be the fastest atmospheric pressure method with 90% extraction in 24 min. Reflux with cyclohexane–propan-2-ol (1 + 1) required 38 min; ultrasonic, shake-flask and Soxhlet extraction required about 80 min (90% extraction). For effectively complete extraction, from loaded extraction vessel to extract ready for analysis, PFE required 15 min, MAE 28 min and reflux with chloroform 45 min.

Introduction

Extraction methods can be divided into 'traditional' and 'new'. Traditional methods include Soxhlet extraction, boiling under reflux, shake-flask method and sonication. The newer methods of extraction are supercritical fluid extraction (SFE), microwave assisted extraction (MAE) and pressurised fluid extraction (PFE). Accelerated solvent extraction (ASE) is a form of PFE, and is a registered trademark of the Dionex Corporation (Sunnyvale, CA, USA). The new methods can all employ elevated temperatures and pressures, although microwave extraction at atmospheric pressure is also used (*e.g.*, 'Soxwave' extraction). The traditional methods are performed at atmospheric pressure.

A recent review describes developments in extraction from polymers using SFE, MAE and ASE.[1] There are many papers on SFE from polymers, and the processes occurring are fairly well understood where only CO_2 is used as an extractant. Some work using modifiers has been published, but there is no systematic study using different modifiers. SFE can reduce significantly the time needed to extract materials compared to conventional methods. There is little reported work on liquid–solid extractions of polymers at high pressure. MAE has been used successfully to extract oligomers from poly(ethylene terephthalate) (PET)[2] and additives from polyolefins;[3, 4] extraction times are much shorter than using conventional methods. Lou *et al.*[5] extracted monomers and oligomers from nylon and poly(1,4-butylene terephthalate) (PBT) using hexane as extraction solvent in a laboratory-made ASE system. Extraction efficiencies increased in all cases as temperature was raised from 50–170 °C, which was attributed to faster diffusion rates. The authors observed that solvents which are good swelling agents, and hence give fastest extractions during Soxhlet extraction, tend to dissolve the polymer at the high temperatures used during ASE. Melting or softening of the polymer causes the particles to coalesce and reduces the surface area, hence slowing down the extraction. Dissolved polymer reprecipitates on cooling and can block transfer lines in the instrument. Solvents therefore cannot be selected on the basis of those used for atmospheric pressure extractions. They point out that selection of a suitable extraction solvent is probably the most difficult step in optimising ASE, as there is little data on the solubility of polymers in solvents at high temperatures.

Vandenburg *et al.*[6] described the kinetics of ASE extraction using the 'hot ball' model[7] derived for SFE extractions. The fit to the model is generally good, indicating that solubility was not a limiting factor in the system studied (polypropylene (PP)–propan-2-ol) and the extraction is controlled by the rate of diffusion of the additive through the polymer. The diffusion rate can be increased by both increasing the temperature and swelling the polymer by using a stronger solvent. A stronger solvent in this context is one which causes more swelling, ultimately leading to dissolution of the polymer. The use of Hildebrand solubility parameters to aid solvent selection has been described.[6,8] A stronger solvent has a solubility parameter closer to the polymer than a weaker solvent. Hildebrand solubility parameters are widely available for solvents and polymers from published sources.[9,10] The use of a 'strong' solvent for PP (cyclohexane) during PFE resulted in melting or dissolving at moderate temperatures and low extraction rates. The best solvent found for extraction from PP using PFE was propan-2-ol at 150 °C although acetone at 140 °C gave only slightly slower extractions.[6] Addition of 2.5% cyclohexane to the propan-2-ol was reported to give slightly faster extractions with ASE than using pure propan-2-ol.[8]

There is no systematic comparison of new and conventional techniques for extraction from polymers. In this paper we will compare the new methods with each other and the traditional techniques for the extraction of Irganox 1010 from PP.

Experimental

Apparatus

A schematic diagram of the laboratory-made PFE apparatus used is shown in Fig. 1. The pump used was an Isco 100D (Jones Chromatography, Hengoed, UK). Extraction cells were supplied by Keystone Scientific (Bellefonte, PA, USA). Microwave extraction used a MES 1000 Microwave Extraction System (CEM, Buckingham, UK). The ultrasonic bath was a U400 from Ultrawave Ltd. (Cardiff, UK). HPLC analysis was performed using a Merck-Hitachi (Poole, Dorset, UK) pump with a Jasco (Great Dunmow, Essex, UK) 875-UV and a Merck-Hitachi D2500 integrator. Separation was on an ODS2 column (25 × 4.6 mm) (Phase Separations Ltd, Deeside, UK).

Materials and reagents

Polypropylene was commercially obtained as pellets (approximately 3 mm diameter) with a nominal Irganox 1010 content of 0.15% w/w. Irganox 1010 and Irganox 1330 (1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene) were supplied by Ciba Speciality Chemicals (Basel, Switzerland). Solvents were analytical grade or HPLC grade. The internal standard solution was prepared by dissolving Irganox 1330 (0.050 g) in methanol (50.0 ml).

Sample preparation

The polymer was freeze-ground under liquid nitrogen. The freeze-ground particles were classified by sieving, and the particle size distribution is shown in Table 1. Samples were analysed as either pellets, freeze-ground polymer or one of the sieved fractions.

HPLC analysis

Extracted Irganox 1010 was analysed using HPLC. Methanol was the mobile phase with a flow-rate of 1 ml min^{-1} with UV detection at 254 nm. Irganox 1330 was used as internal standard (IS). A calibration curve was constructed by adding known amounts of Irganox 1010 and Irganox 1330 to methanol, in order to cover the concentration range found in the extraction samples, and analysing by HPLC. A plot of the peak area ratio against the weight ratio of Irganox 1010 to Irganox 1330 was constructed, which was linear, with a correlation coefficient of 0.999.

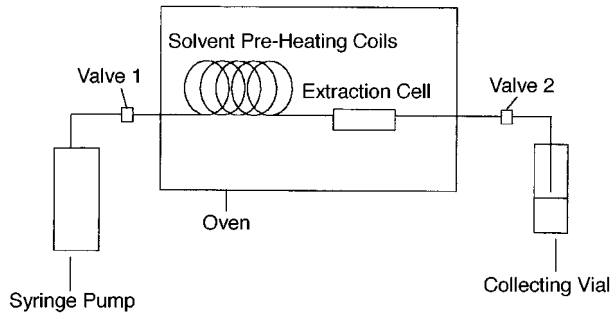

Fig. 1 Schematic diagram of laboratory-made ASE apparatus.

Table 1 Particle size distribution of freeze-ground polymer

Size/greater than μm	Polymer (%)
1000	29.2
500	47.3
250	16.7
125	6.2
63	0.6
38	0.0

Analysis of Irganox 1010 in extracts

Small samples of chloroform, propan-2-ol and cyclohexane containing Irganox 1010 and IS were evaporated to dryness under a stream of nitrogen, re-dissolved in methanol and analysed by HPLC. Cloudy solutions were centrifuged before the evaporation step. Solutions in methanol and acetonitrile were injected directly onto the HPLC column. The quantity of Irganox 1010 present was determined from the peak area ratio and the calibration graph.

Reflux extraction with chloroform and propan-2-ol–cyclohexane (1 + 1)

To determine the extraction curve, freeze-ground PP (0.30 g) and IS were added to solvent (30 ml) in a round bottomed flask and boiled under reflux for 2 h. Samples (100 μl) were removed at intervals and analysed to determine the amount of Irganox 1010 extracted. Once the time for complete extraction had been determined for chloroform, six replicate analyses were performed using sieved freeze-ground PP for 1 h. In this case the internal standard was added after the completion of the reflux time.

Soxhlet extraction

PP (1 g, freeze-ground) was weighed into extraction thimbles and extracted with solvent (50 ml) to which IS had been added. Samples (100 μl) were removed from the solvent at intervals and analysed for Irganox 1010.

Ultrasonic extraction

PP (0.2 g, freeze-ground) was weighed into 21 ml glass vials and chloroform (10 ml) (warmed to 40 °C) and IS added. The vials were immersed above the level of solvent in water in an ultrasonic bath. The temperature of the water was maintained at 40–44 °C by intermittent use of the internal bath heater. Samples (50 μl) were removed at intervals and analysed for Irganox 1010.

Shake-flask extraction

This was carried out in the same way as the ultrasonic extraction at 40–44 °C, but with the ultrasonic bath switched off. The vials were regularly shaken by hand.

Pressurised fluid extraction (PFE)

Cells (3.75 ml) were packed by placing the weighed ground polymer (0.20 g) between glass wool plugs, sometimes mixing with sand before packing. In the latter case it was important to fill the cell completely to prevent the polymer from separating from the sand during extractions. The cells were connected to the pump with Valco 1/16 in stainless steel nuts and ferrules. Solvent was pumped into the cell until the pressure reached 2000 psi, and was allowed to warm up for 3 min. The timing was then started and valve 2 (Fig. 1) opened to allow solvent to pass

into the collecting vessel at a flow-rate of 1.5–2.5 ml min^{-1}. IS was added to each vessel before HPLC analysis. Recovery from the cell was determined by spiking 60 μl of a solution of Irganox 1010 (0.050 g in 50.0 ml methanol) onto sand in the cell with a microsyringe and extracting for 5 min with propan-2-ol at 150 °C.

Microwave assisted extraction (MAE)

Sieved, freeze-ground PP (0.30 g) was weighed into the extraction cells of the MAE. A small amount of glass wool was placed at the bottom of the cells before adding the polymer to help prevent the particles agglomerating. Solvent (30 ml) was added and heated in the microwave oven for the required time. Six samples were simultaneously extracted. After cooling, IS was added and the extract analysed by HPLC. Recoveries were checked by adding Irganox 1010 instead of sample to the solvent, to determine analyte loss during microwaving.

Results and discussion

Atmospheric pressure extraction curves

Irganox 1010 and Irganox 1330 were found to be stable under reflux conditions for 3 h. Graphs of amount of Irganox 1010 extracted from freeze-ground PP against time are shown in Fig. 2. The 100% figure (0.1395%) is taken as that produced from six replicate 1 h reflux extractions with chloroform. This is slightly lower than the nominal figure of 0.15%. Chloroform reflux and ultrasonic extraction are means of triplicate results. Soxhlet extraction and shake-flask extraction are means of duplicate results and cyclohexane–propan-2-ol reflux is the result of a single experiment. The chloroform reflux method is the fastest, with extraction 'complete' after about 40 min. The time taken to reach 90% extraction is given in Table 2.

There is no significant difference between the ultrasonic and shake-flask extraction. The Soxhlet extraction starts slow, but soon catches up with the shake-flask extraction. This is presumably due to the two-step, cycling nature of the Soxhlet extraction. The Irganox 1010 has to be extracted from the polymer into the solvent in the thimble, and then transferred from the thimble to the flask as the condensed solvent fills the extractor.

As the chloroform reflux method is the fastest, the quantity extracted from sieved material was determined using this method for comparison with the new extraction techniques.

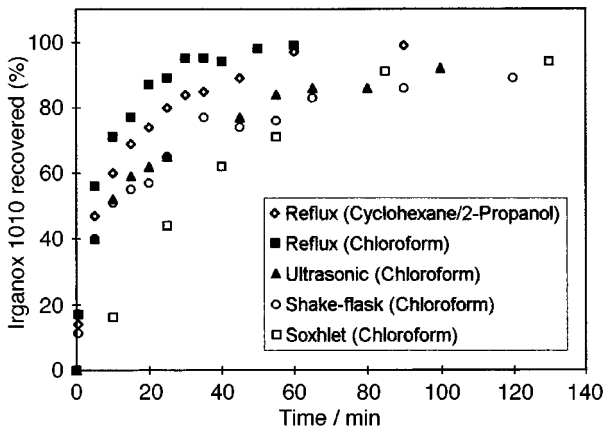

Fig. 2 Extraction curves for atmospheric pressure extractions.

Table 2 Approximate time for 90% extraction from freeze-ground PP (atmospheric pressure extraction)

Extraction technique	Time to reach 90% extraction/min
Reflux (chloroform)	24
Reflux (cyclohexane–propan-2-ol)	38
Ultrasonic (chloroform)	78
Shake-flask (chloroform)	86
Soxhlet (chloroform)	84

Pressurised fluid extraction

Cell packing and recovery. Mixing the ground polymer with sand gave faster extractions at higher temperatures and with stronger solvents (*i.e.*, those with a closer Hildebrand solubility parameter) when the polymer was softened to a greater degree. If no sand was used the particles partially coalesced and extraction rates were reduced. Extraction of spiked sand with propan-2-ol at 150 °C gave recoveries of 98.9% (standard deviation (s) = 7.5%, n = 6).

Solvent selection. Propan-2-ol was found to be the best single solvent for extractions from PP. High temperatures of 150 °C could be used without dissolving the polymer. At these temperatures some dissolution of oligomers occurred, resulting in cloudy extracts. No blockage of the delivery tube occurred. The dissolving of the oligomers indicates that the solvent is interacting with the polymer to a considerable degree, thus swelling the polymer. The polymer can be seen to be swollen when removed from the cell. Therefore with this solvent, the twin benefits of swollen polymer and high temperatures are obtained. Use of propan-2-ol–cyclohexane (97.5 + 2.5) has been reported as offering slight advantages over propan-2-ol alone.[8] In this case, it was considered that variations in reproducibility by using different batches of mixed solvents would offset the slight advantage in extraction times, so 100% propan-2-ol was used. The use of methanol was attempted, but the recovery from the polymer at 150 °C was only 32% after 30 min extraction. Further extraction of the same sample with propan-2-ol at 150 °C fails to recover much more Irganox 1010. Recovery tests with methanol as solvent were performed by adding Irganox 1010 to glass wool in the extraction cell and extracting at 150 °C for 10 min. The recovery was 69% (duplicate extraction), compared with 98.9% using propan-2-ol under similar conditions. Irganox 1010 is soluble in methanol, so the likely explanation for the low recovery is breakdown of the Irganox 1010. Methanol is therefore not a suitable solvent for this extraction. Extractions were performed with chloroform as this was the best solvent at atmospheric pressure. At 80 °C the extracts were very cloudy. On removing the polymer from the cell, the particles were swollen and partly agglomerated, which would slow down extraction. At 90 °C there was significant dissolution of polymer, almost complete agglomeration and some polymer was extruded from the cell. This would result in slow extractions and problems with instrument blockage. Therefore chloroform cannot be used at much above its boiling point (62 °C) without dissolving the polymer, and little benefit from high temperature–high pressure extractions is possible.

Microwave assisted extraction

Selection of conditions. Conditions during the MAE were similar to those during PFE, in that the solvents were kept liquid above their normal boiling points by application of pressure (although MAE at atmospheric pressure is also possible). Therefore, conditions which are successful in PFE are likely to be successful in MAE. Based on the PFE results, the solvents most likely to give successful extractions were propan-2-ol at

Table 3 Comparison of extraction techniques

Extraction method	Extraction temperature/°C	Nominal extraction time/min	Total extraction time/min	Mean Irganox 1010 extracted (%)	Standard deviation (n = 6)	Percentage of 1 h reflux	Significantly different from reflux (1 h) (95% significance)
Reflux in chloroform	63	60	65	0.1395	0.0039	100	—
MAE, propan-2-ol	140	20	43	0.1337	0.0038	95.8	No
MAE, propan-2-ol	140	10	33	0.1359	0.0069	97.4	No
MAE, propan-2-ol	140	5	28	0.1262	0.0067	90.5	Yes
MAE, propan-2-ol	150	5	28	0.1368	0.0030	98.1	No
PFE, propan-2-ol	150	5	8	0.1245	Duplicate	89.2	Yes
PFE, propan-2-ol	150	10	13	0.1396	0.0047	100.1	No

150 °C and acetone at 140 °C. Initial studies using both acetone and propan-2-ol were performed.

Stability of Irganox 1010 under MAE conditions. Using acetone at 140 °C, the recovery had dropped to 57% after just 7 min, indicating rapid degradation of the compound. Therefore even during very short extractions some degradation of the analyte is likely. With propan-2-ol, recovery was 98.2% (s = 3.5%, n = 6) after heating for 30 min at 140 °C, so extraction can be performed under these conditions. However, at 150 °C with propan-2-ol there was some degradation after 30 min and significant degradation after 70 min.

Comparison of extraction methods

Results for the different extraction methods have been compared to refluxing with chloroform for 1 h using sieved, freeze-ground PP (0.5–1 mm particle size). Each result is the mean of six replicate analyses, and the means have been compared using the Student t-test at 95% significance level. Table 3 shows the results for MAE at 140 °C for 20, 10 and 5 min and at 150 °C for 5 min. Where there is no significant difference between the result and that for the reflux extraction, the extraction is effectively complete. All the MAE and PFE were slightly cloudy, and required centrifugation (or filtration) before analysis. The MAE extractions with propan-2-ol for 5 min at 150 °C and 10 min at 140 °C give effectively complete extraction. At 140 °C for 5 min extraction is not complete. To calculate the total analysis time, the warming up time (approximately 3 min for six samples, longer for more samples), analysis time and the cooling down time (approximately 20 min if left in the microwave oven) must be summed. Therefore 23 min is the minimum extraction time possible with this equipment at 150 °C. Faster cooling times are possible if the extraction cells are partially immersed in water to cool. The entire carousel of 12 extraction vessels can also be removed and a new carousel of samples extracted whilst the first is cooling down.

PFE data at 150 °C are also shown in Table 3. The extraction time included a 3 min warm up period. This time was somewhat arbitrary, as the real time required to reach the extraction temperature is not known. Five minutes extraction at 150 °C gives only 89.2% recovery compared to the 1 h reflux. Increasing the extraction time to 10 min (+3 min warm up) gives complete recovery. There is no cool down time for each analysis with this method as the extract is cool when it reaches the collecting vial. In our system, blockages did not occur if the solvent was selected such that it swelled, but did not significantly dissolve the polymer.

Conclusions

Boiling under refluxing chloroform was the fastest atmospheric pressure extraction method used. There was no measurable difference between ultrasonic extraction and shake-flask extraction under the conditions used. PFE and MAE can result in significantly faster extractions with the same recoveries as refluxing at atmospheric pressure. Using these methods, sample preparation time can be reduced to be comparable with analysis time. The best conditions for both techniques determined to date for extraction from PP are propan-2-ol as solvent at 150 °C. The solvent swells the polymer without causing extensive dissolution. This maximises the extraction rate by allowing the highest temperature to be used, without the particles agglomerating or the connecting tubes in PFE blocking. Microwave extraction offers faster sample analysis for large numbers of identical analyses, largely because multiple samples can be extracted simultaneously and the warm up time is shorter. Solvent choice is limited to those absorbing microwaves strongly, but there is no risk of blockages in the equipment. For PFE (including ASE), analysis for a single sample is faster than for MAE, as the sample can be analysed without waiting for it to cool down. There is no restriction on solvents which can be used, but they must be carefully selected so as not to dissolve the polymer and thus cause blockages.

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