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Development of a modified analytical methodology for the identification of low molecular weight compounds in recycled plastics

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Abstract : Recycling of plastics is a grown market in the plastics industries over the last years, since it consists of an easy and low cost application to reduce the impact of the increasing usage of plastics and the drawbacks that follow it, like large quantities of waste. The most important problem that rises is the safety of using recycled plastics in several applications due to the decomposition products or oligomers that might be present after recycling. Present work is focused on developing a method to determine these compounds in recycled polyethylene (PE) using an automated Soxhlet extraction system (Soxtec) combined with gas chromatography-mass spectrometry (GC-MS) analysis. Virgin PE samples were used for method development. Several types of compounds such as n-alkanes, branched alkanes, alkenes and phthalates were detected, indicating that the proposed methodology can be successfully applied for the determination of low molecular weight compounds in various types of recycled plastics packaging materials. A greater number of compounds and mostly at higher concentrations were found in recycled PE samples.

Keywords : Recycled plastics; Recycled polyethylene; Soxtec extraction system; Gas chromatography-mass spectrometry; Decomposition products.

INTRODUCTION

Plastics are typically polymers and may contain other components such as additives and fillers. They are the most efficient, functional, and cost-effective choice for many applications. As a result, consumption of plastic products has increased over the past few decades, and recycling technologies are promoted in order to absorb large amounts of plastic waste to avoid environmental damage[1-4]. Recycled plastics may contain degradation products of the polymers which can be very hazardous especially if the product is intended to be used in contact with foodstuffs. These degradation products include a variety of low molecular weight compounds, such as monomer residues, oligomers, solvent residues

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and additives[5, 6].

Several extraction techniques, especially heat extraction techniques such as headspace solid-phase microextraction (HS-SPME)[6-8], liquid phase microextraction[9], microwave assisted extraction (MAE)[10-12], ultrasound assisted extaction (UAE)[13], supercritical fluid extraction[14, 15] are available for the determination of low molecular weight compounds in polymers.

Soxhlet extraction is widely used due to the advantages it shows: it requires inexpensive basic equipment, the sample is repeatedly brought into contact with the fresh portions of the solvent, the temperature of the system remains relatively high and it can be applied to most sample matrixes. The most significant drawbacks of Soxhlet extraction compared to other conventional techniques for solid sample preparation are, the long time required for the extraction and the large amount of solvent wasted[16-18]. Over the last decades, automated Soxhlet extraction equipment called Soxtec System was developed to overcome these drawbacks. In this system there are two extraction steps: a boiling and a rinsing step, followed by a step for the recovery of the solvent. Despite the fact that Soxtec is mainly used as a way of shortening the leaching time, its extraction efficiency is at least, if not improved, equivalent to that obtained with conventional Soxhlet[16].

Our work is focused on developing a method for the determination of low molecular weight compounds in recycled polyethylene (PE) using an automated Soxhlet extraction system (Soxtec) combined with gas chromatography- mass spectrometry (GC-MS) analysis using a low polarity column. Virgin PE samples were used for method development.

MATERIALS AND METHODS

Plastic materials

The samples used were industrially recycled materials (polyethylene) and virgin plastics in pellets. Virgin PE samples were also used for comparison purposes and for the development of the method that was afterwards applied to the recycled plastics.

Chemicals

Extraction solvents (cyclohexane and isopropanol), p-xylene (internal standard) as well as the standard solution of C_8-C_{20} alkanes mixture used for the determination of Kovats indices, were purchased from Merck (Darmstadt, Germany).

Automated soxhlet (soxtec) extraction

Sample preparation conditions were the subject of investigation, and the optimized procedure is described here. Approximately 4 g from each of the polymer was weighed into a cellulose thimble and placed in a Soxtec apparatus (Velp, SER148 Solvent Extraction Unit) where 40 ml of solvent cyclohexane/isopropanol (75:25) were added. Temperature of heating plate was set at 140°C and immersion time was 60 min, followed by 20 min washing time and 10 min recovery time. The solution was evaporated to dryness and the solid residue redissolved in 5 ml of the solvent mixture.

GC-MS analysis

The analysis was carried out with a Hewlett Packard HP-6890 series gas chromatograph linked with a Hewlett Packard HP-5973 mass selective detector (Wilmington DE, USA). A low polarity capillary GC column HP5-MS 30 m × 250 μm, 0.25 μm film thickness was used. Helium was the carrier gas at a flow rate of 1.1 ml/min. The injector was operated in a splitless mode at 270°C. The initial temperature of column was 50°C hold for 1 min, raised to 150°C at a rate of 8°C/ min, to 270°C at a rate of 5°C/ min and hold at this temperature for 20 min. MS conditions were as follows: MS conditions were as follows: acquisition was performed in electron impact (EI) mode (200eV) by 2.92 scans s^{-1} and the mass range used was mass/charge (m/z): 29–550. The temperature of the transfer line was held constant at 270°C.

Identification of low molecular weight compounds

The identification of low molecular weight compounds was performed by calculating linear retention (Kovats) indices (KI) using n- alkanes (C_8-C_{20}) standards as external references[19]. Peak identification was completed by comparing the mass spectra

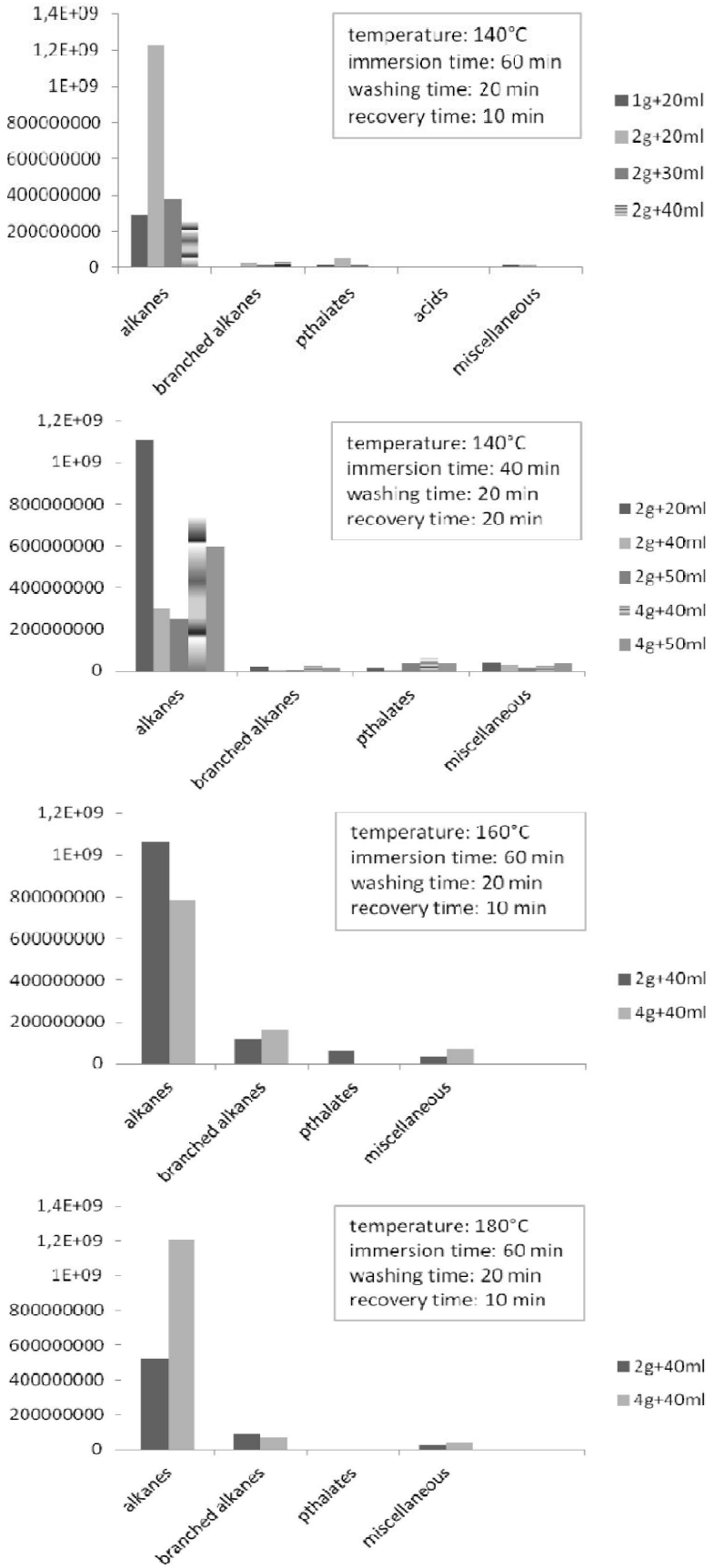

Figure 1 : Method optimization

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of the eluted compounds with those of the Wiley 275L library and NIST98 MS library.

Semi quantitative determination of low molecular weight compounds

The semi quantitative determination of low molecular weight compounds was achieved using the internal standard method. P-xylene was used as internal standard. Each analysis was carried out in triplicate.

RESULTS AND DISCUSSION

A binary solvent system was used, that it provides better extraction results[17]. The choice of the solvents (mixture of cyclohexane and isopropanoal) was based on health and environmental issues, so non chlorinated solvents were preferred. Furthermore cyclohexane and isopropanol have similar boiling points (80.7°C and 82.4°C, respectively), which is ideal for the technique used. For method optimization different temperatures and extraction times were tested, as well as different virgin PE samples and solvent amounts. Specifically, 1, 2 and 4 g of plastic samples and 20, 30, 40 and 50 ml of solvent (cyclohexane/ isopropanol mixture at a ratio of 75 to 25) were used. Three extraction temperatures were tested (140, 160 and 180 °C) combined with different extraction times for the three steps of Soxtec extraction (immersion, washing and recovery). Results are shown in Figure 1.

Typical chromatograms obtained with GC-MS for the virgin and recycled PE are shown in Figure 2 and Figure 3, respectively.

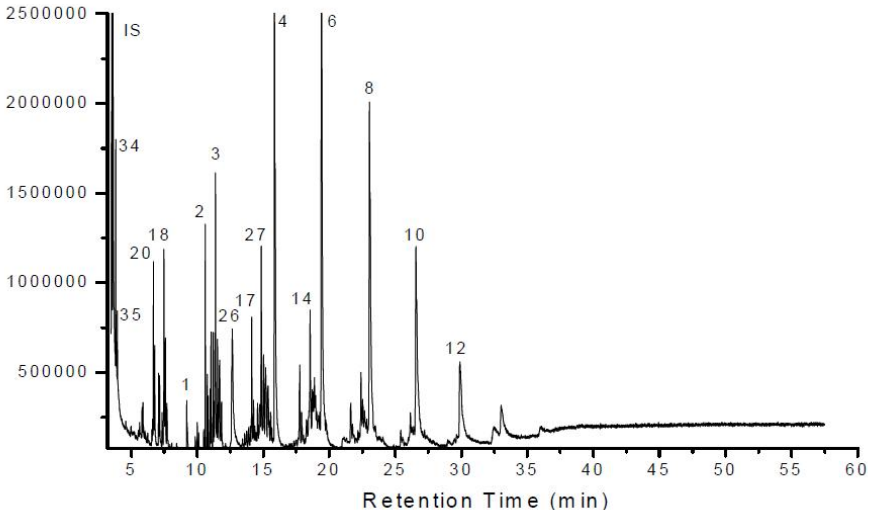

Figure 2 : Typical chromatogram of virgin PE. peak numbers found in TABLE 1

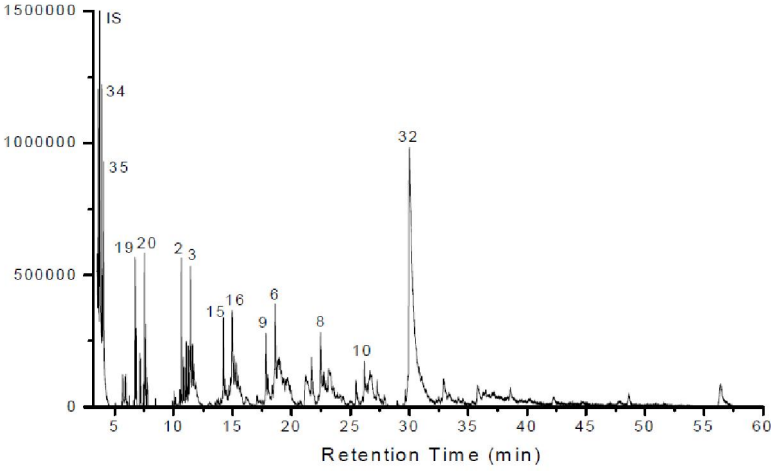

Figure 3 : Typical chromatogram of recycled PE. peak numbers found in TABLE 1

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TABLE 1 : Low molecular weight compounds extracted from virgin and recycled PE

Peak No	Compounds	Virgin PE (mg/Kg)	Recycled PE (mg/Kg)	KIexp[a]	KIlit [b]
	Alkanes				
1	dodecane	4.05	-	1183	1200
2	tetradecane	34.63	41.02	1359	1400
3	pentadecane	47.64	18.89	1461	1500
4	hexadecane	83.52	6.29	1606	1600
5	heptadecane	3.12	2.47	1679	1700
6	octadecane	126.65	56.33	1827	1800
7	nonadecane	6.02	18.13	1954	1900
8	eicosane	91.99	63.23	2082	2000
9	heneicosane	4.65	41.81	2071	2100
10	docosane	81.93	44.12	2223	2200
11	tricosane	-	9.69	-	2300
12	tetracosane	28.85	10.32	-	2400
13	pentacosane	8.34	19.58	-	2500
14	hexacosane	17.87	18.56	-	2600
15	heptacosane	-	20.78	-	2700
16	triacontane	-	20.37	-	3000
	Branched alkanes				
17	3-methyl-decane	19.58	5.31	1071	1069
18	5-methyl-undecane	15.70	1.41	1161	1154
19	4-methyl-undecane	-	15.63	1168	1158
20	3,6-dimethyldecane	17.37	25.99	1122	1129
21	4,7-dimethyl-undecane	2.64	11.81	1244	1207
22	4,6-dimethyl-undecane	1.80	3.15	1208	1193
23	4,6-dimethyl-dodecane	-	12.71	1250	1285
24	5-methyl-pentadecane	-	4.76	1564	1551
25	2,6,11-trimethyl-dodecane	-	2.56	1361	1320
26	2,6,10,14-tetramethyl-pentadecane	12.36	6.61	1628	1682
27	2,6,10,14-tetramethyl-hexadecane	14.33	45.42	1831	1811
28	3-methyl-heptadecane	4.24	-	1753	1770
29	5-butyl-nonane	-	11.01	1272	1204
	Esters				
30	Isobutyl phthalate	-	4.24	-	1853
31	Butyl phthalate	-	6.10	-	1990
32	Bis(2-ethylhexyl)phthalate	-	224.40	-	2385
	Acids				
33	Nonahexacontanoic acid	-	1.09	-	7236
	Miscellaneous				
34	cyclohexanol	22.73	30.56	856	881
35	cyclohexanone	15.38	25.41	896	897

[a]Kovats indices determined experimentally; [b]Kovats indices from literature data

The identified low molecular weight compounds that were extracted from virgin and recycled PE are

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shown in TABLE 1.

Several types of compounds such as n-alkanes, branched alkanes, acids and phthalates were detected, indicating that the proposed methodology can be successfully applied for the determination of low molecular weight compounds in various types of recycled plastics packaging materials. A greater number of compounds were detected in recycled PE samples and as it can be seen, in most cases, the concentration of the detected compounds is higher in the recycled plastic samples compared to virgin materials. Especially, the three phthalate esters were only detected in recycled materials and in large amounts. Isobutyl phthalate or diisobutyl phthalate (DIBP) is a plasticizer with excellent heat and light stability, and it has similar properties as butyl phthalate (or dibutyl phthalate, DBP). Butyl phthalate has been recently banned from children's toys, since it was added to the "California Proposition 65" list of suspected teratogenic compounds[20]. Bis(2-ethylhexyl)phthalate (DEHP) is another plasticizer very commonly used in plastics. It can easily migrate to the foodstuff which is in contact to the plastic, so the Food and Drug Administration (FDA) allows the use of plastics containing DEHP only for foods that primarily contain water. EU banned the use of DEHP along with several other phthalates in toys for young children[21, 22]. It is rather surprising but a number of plasticizers including DEHP are used in small amounts for various purposes in PE technologies such as low density PE and microporous film production[23]. However, as plasticizers are not typically associated with PE other than through the printing inks used in food packaging[24, 25], their presence in recycled PE is probably due to contamination with inks or other plastics containing plasticizers.

In conclusion, automated Soxhlet (Soxtec) extraction combined with GC-MS has been proven as a rapid and effective technique for the analysis of low molecular weight compounds in plastic materials and it can be applied in other types of plastics.

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