

CHARACTERISATION OF EXCAVATED PLASTICS FOR THERMOCHEMICAL UPCYCLING TO PLATFORM CHEMICALS AND LIQUID FUELS

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Introduction

The concept of enhanced landfill mining (ELFM) will be integrated into the EU Landfill Directive in the near future.¹ Landfilled waste will become a potentially valuable resource which is valorised as material (WtM) and energy (WtE).² In Europe, between 1995 and 2015, 5.25 billion tonnes of waste were deposited in landfills³, of which the plastic fraction represents between 5-25 wt. % of the total landfilled waste.^{4,5,6} Changes in physical and chemical properties of plastic waste during its storage in landfill have not been thoroughly studied, and further work is required to properly address this topic. This paper presents an early investigation on the degradation of plastics in landfills, focusing on the characterisation of excavated plastic waste from three different landfills in UK.

Materials and methods

Sample collection

A total of 8 excavated waste samples were collected from 3 different landfills located in the UK, at a depth ranging between 5 to 39 meters (Table 1). The excavated waste has been manually sorted and was divided in 10 fractions (Table 2).^{5,8}

Table 1: Overview of excavated waste samples.

Sample no.	1	2	3	4	5	6	7	8
Depth (m)	39.0	5.0	6.5	18.5	8.0	18.0	6.0	18.0
Quantity (g)	8,44	5,83	553	870	390	603	595	876
	8	8						

Plastic characterisation

The excavated plastic samples were washed with cold water, air dried at room temperature and then weighed to calculate the percentage of impurities, such as soil and semi-degraded paper. The excavated plastic samples of approximately 4 x 4 cm were analysed by a visual-NIR spectrometer (ASD Inc Releases LabSpec 2500) with a spectral range of 350-2500 nm and compared with fresh plastic spectra. The percentages for each plastic type identified were calculated. Similar plastic types were grouped based on their origin and depth. Samples 3, 5 and 7 were collected from the same landfill and depths between 6.0 and 8.0 m, and grouped by plastic type as Sample A. Similarly, samples 4, 6 and 8 were collected from the same landfill and depths between 18.0 and 18.5 m, and group by plastic type as Sample B. SEM-EDS (Environmental Scanning Electron Microscope Philips XL30 ESEM and Energy Dispersive Spectroscopy) was used to characterise the surface morphology and the chemical elements present in the surface of a representative plastic sample for each plastic type and to evaluate degradation and contamination levels.

The ash C, H, N and metal content were determined following the British Standard method.^{9,10,11}

Results and discussion

Excavated waste sample composition

Table 2 shows the percentage of each waste fraction found in the excavated waste samples. The largest fraction is represented by the soil with a range between 53 and 81 wt. % followed by plastic fraction ranging 5-26 wt. %. The fraction 'Other' comprises mostly stones and unidentified materials. This distribution is consistent with previous studies which identified the fines fraction, which includes soil-type material, as the major fraction in excavated waste followed by the plastic fraction.^{4,5}

Table 2: Classification and quantification (in wt. % as received) of waste fractions present in the excavated waste samples from landfill

Waste Fraction Sample no.	PI	P/C	M	G/C	T	W	S/F	B	WE	O
1	26	1	1	0	1	9	53	0	0	8
2	11	1	0	1	2	2	62	0	0	21
3	16	0	0	7	0	1	65	0	0	10
4	8	0	0	4	2	1	81	0	0	5
5	20	1	0	5	1	1	55	0	0	18
6	5	6	0	0	1	2	75	0	0	11
7	24	1	0	1	7	1	63	0	0	4
8	6	0	0	4	0	5	77	0	0	8

PI =plastic; P/C = Paper/cardboard; M = Metal; G/C = Glass/ceramic; T = Textile; W = Wood; S/F = Soil/fine fraction; B = Batteries; WE = WEEE; O = Other.

Excavated plastic waste characterisation

The percentage of impurities in excavated plastic ranges between 62 and 87 wt. % mainly including soil, semi-degraded paper and moisture. Zhou et al.⁷ observed similar results, with impurities ranging from 61.8 and 84.4 wt. %. The results from NIR spectroscopy (Table 3) highlights that the main fraction of the municipal waste plastic is composed of thermoplastics (including PE, PET, PP, PVC, and PS), which is to be expected as thermoplastics represent the 80 wt. % of the plastic consumed worldwide.^{12,13,14} PE is found as the predominant plastic type in all excavated waste samples (Table 3).

Table 3: Plastic types found in the excavated plastic waste, with wt. % of total plastics shown.

Sample no.	PE		PET		PP		PVC		PS		Rest	
	g	%	g	%	g	%	g	%	g	%	g	%
1	184.0	50.1	143.0	38.9	11.5	3.1	3.5	1.0	2.0	0.5	23.5	6.4
2	121.5	60.9	1.5	0.8	23.0	11.5	5.5	2.8	5.0	2.5	43.0	21.6
3	7.0	32.1	-	-	7.0	32.1	-	-	-	-	7.8	35.8
4	5.5	56.1	-	-	1.5	15.3	0.5	5.1	0.5	5.1	1.8	18.4
5	9.5	70.4	-	-	1.5	11.1	-	-	-	-	2.5	18.5
6	3.5	43.8	0.5	6.3	0.5	6.3	-	-	-	-	3.5	43.8
7	16.0	47.1	-	-	0.5	1.5	-	-	2.0	5.9	15.5	45.6
8	4.0	37.0	0.5	4.6	1.5	13.9	0.5	4.6	-	-	4.3	39.8

PE = polyethylene; PET = polyethylene terephthalate; PP = polypropylene; PVC = polyvinyl chloride; PS = polystyrene; Rest = other plastic types.

Figure 1 compares the surface of excavated plastic samples and the surface of fresh plastic waste of the same plastic type established by SEM-EDS. In general, the surfaces of fresh plastic waste (Figures 1A, 1B, 1D and 1I) appear more homogeneous than the surfaces of excavated plastic, which seem altered. Table 4 presents a description of the surface characteristics and level of imperfection which can be associated with the first visual effect of degradation.²⁰

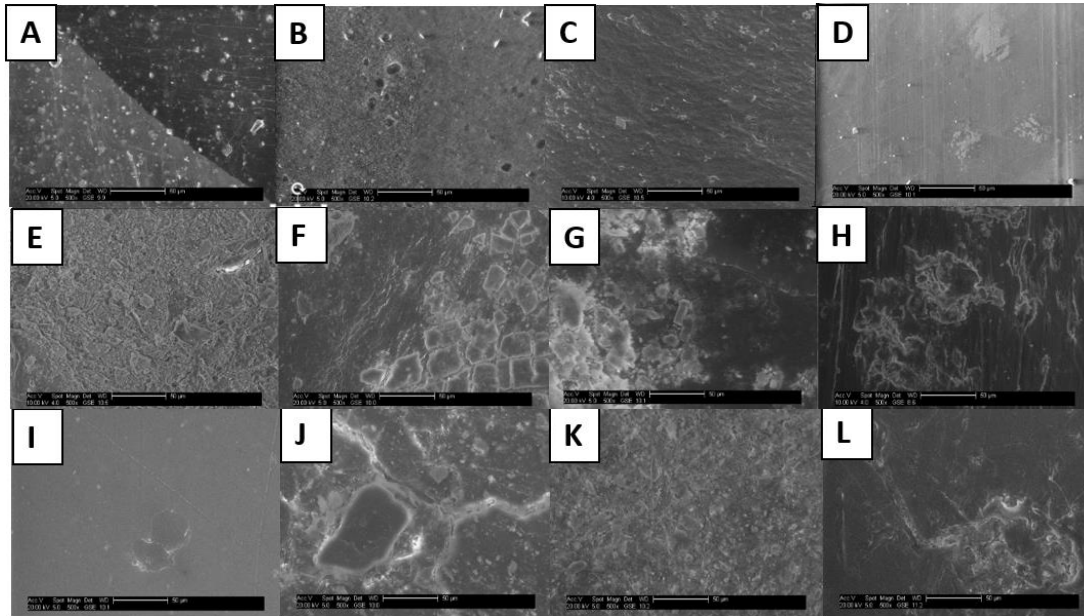


Figure 1: Surface images of fresh plastic waste (A, B, D, I) and excavated plastics (C, E, F, G, H, L, M, N) under 500x magnification. A: HDPE white carry bag; B: LDPE coloured packaging; C: Excavated PE (sample 1); D: PET; E: Excavated PE (sample 2); F: Excavated PE (sample B); G: Excavated PE (sample A); H: Excavated PET (sample 1); I: PP; J: Excavated PP (sample 1); K: Excavated PP (sample 2); L: Excavated PP (sample A).

Table 4: Surface characteristics and chemical elements detected by SEM-EDS (minimum concentration detected 0.08 wt. %) of fresh and excavated samples.

Sample	Figure	Surface texture	Surface degradation level	Main elements	Minor elements (< 5 wt. %)	Trace elements (< 0.5 wt. %)
HDPE	1A	F, AP	Medium	C, O, Ca		S, Cl
LDPE	1B	P	Medium	C, O, Ti	Al, Cl, Ba	Si, P, S, Cu
1 PE	1C	Fl, AP	Medium	C, O, Ca	Al, Si, Cl, K, Ti, Fe	Na, Mg, P, S, Cu, Zn
2 PE	1E	Fl, AP, Gr	High	C, O, Si, Ca	Al, K, Fe	Mg, P, S, Ti, Mn
A PE	1G	AP, Gr	High	C, O	Al, Si, Ca, Fe	Mg, P, S, K, Ti
B PE	1F	F, AP, Gr	High	C, O	Mg, Si, Ca	Al, P, S, Cl, Ti, Fe, Cu, Mo
PET	1D	S	Low	C, O		Al
1 PET	1H	G, AP, Gr	High	C, O	Al, Si, Ca, Fe	Mg, P, S, K, Ti
PP	1I	S	Low	C,	Ca, Ti, Fe	Mg, Al, Si, Cl
1 PP	1J	F, AP, Gr	High	C, O	Si, Ca, Ti, Fe	Mg, Al, S, Cl, K, Zn
2 PP	1K	Fl, AP, Gr	High	C, O, Si, Ba	Al, S, K, Ca, Fe, Zn	Mg, P
A PP	1L	F, AP, Gr	Medium	C, O	Al, Si, Ca, Fe	Cl, K, Zr

F = fractures; AP = adhering parts; P = pits; Fl = flakes; G = grooves; Gr = granulates; S = smooth.

Calcium, which can be linked with the commonly used filler calcium carbonate (CaCO_3)^{15, 16}, is present in fresh HDPE and all the excavated plastic samples. Other identified elements can be related to the use of additives in plastics, such as quartz (SiO_2), wollastonite (CaSiO_3), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), fire retardant $\text{Mg}(\text{OH})_2$, magnetite (Fe_3O_4), titanium carbide (TiC), and pigment (TiO_2).^{16, 17} Ti and Al are Ziegler-Natta catalysts used to produce PP and PE.¹⁸ The presence of Si and Al may be associated to impurities of soil which major constituents are SiO_2 and Al_2O_3 . Indeed, these elements are detected in larger quantities in excavated plastics than in fresh plastic waste. This result agrees with Zhou et al. study.⁷ The roughness of excavated plastic

surface could be explained by the presence of these impurities in the excavated plastics even after washing.

The ash content of excavated waste is found to be higher than fresh waste for PP and PET, while PE is found to generally follow an opposite trend (Table 5; the ash content of 1 PP, A PP and 2 PP are 18.9 wt. %, 1.3 wt. % and 13.3 wt. % respectively, not shown in the table). The higher level of ash in fresh PE might be related to the high level of titanium present in the sample compared to the excavated PE waste.¹⁹ The excavated plastic samples present a lower level of Ni, Pb, Cu, Cr, As compared to other studies.^{5,21}

Table 5: Characteristics of excavated plastic waste and fresh plastic waste.

	39 m		18 m	6-8 m	5 m	Fresh plastic waste		
	1 PE	1 PET	B PE	A PE	2 PE	PE	PP	PET
C (wt .% db)	79.6	62.6	80.8	83.2	83.8	72.9	84.2	62.3
N (wt .% db)	0.5	0.3	0.4	0.3	0.3	0.3	0.2	0.3
H (wt .% db)	13.1	5.0	13.3	13.7	13.9	11.9	13.6	4.9
Ash (wt .% db)	4.5	1.2	11.8	6.2	3.1	7.6	2.2	0.2
Hg (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cd (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Tl (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Sb (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
As (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cr (mg/kg)	2.2	7.9	1.4	2.0	<1	<1	1.6	4.4
Co (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cu (mg/kg)	5.9	13	6.8	7.4	10	11	4.8	12
Pb (mg/kg)	6.7	<1	2.0	1.9	5.8	1.1	5.1	3.7
Mn (mg/kg)	1.3	3.2	1.8	6.2	<1	4.9	2.7	1.1
Ni (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Sn (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
V (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1

db = dry basis.

Conclusion

The analyses of excavated plastic waste highlight the presence of a larger quantity of impurities than those in fresh plastic waste probably due to soil impurities. The surface analysis indicates that the excavated PP and PET have degraded more than excavated PE. Excavated PP and PET show higher ash content than fresh PP and PET waste. Furthermore, the ash content of excavated PP reaches the maximum level in the sample from greater depth (39 m) compared to the shallow depth (6-8 m and 5

m). However, the ash content of excavated PE did not exhibit a clear trend which can be related to the difference in depth.

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