



Degradation of excavated polyethylene and polypropylene waste from landfill



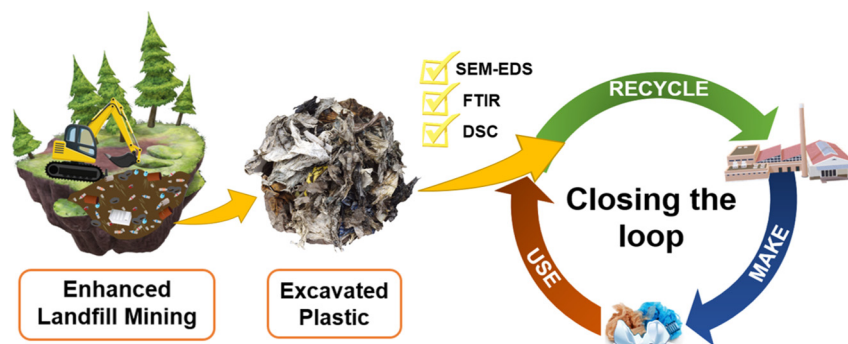
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HIGHLIGHTS

- Cl excavated PP samples >10 years was almost 2 times higher than newer PP.
- CH₂ and CH₃ of samples >10 years were statistically lower than the newer samples.
- Crystallinity of PP and PE >10 years was 1.3 times higher than fresh materials.
- Production of chemical base compounds through excavated plastics pyrolysis
- Chemical base compounds potential revenue is \$402–805 million.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 June 2019

Received in revised form 25 August 2019

Accepted 25 August 2019

Available online 26 August 2019

Editor: Damia Barcelo

Keywords:

Enhanced landfill mining

Plastic recovery

Excavated plastic

Plastic degradation

ABSTRACT

In 2016, it was estimated that 7.4 million tonnes of plastic waste have been disposed in landfill in Europe. This waste represents an important opportunity for resource recovery through enhanced landfill mining consistent with recent Circular Economy initiatives. However, a recent review found a lack of data describing the degradation of excavated plastic waste and the potential impact on recycling products such as pyrolysis oil. In this study, the physicochemical characteristics of the main plastic types found in landfills and their implications for recovery and recycling were investigated using a combination of scanning electron microscopy energy dispersive spectroscopy (SEM-EDS), attenuated total reflectance Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Loss of gloss was visually detected for the buried plastic waste samples (polyethylene (PE) and polypropylene (PP)) compared to fresh plastic samples. The SEM-EDS analysis further showed that oxygen was the main element related to the plastic surface alteration. The carbonyl index (CI) of plastic samples buried for >10 years was between 1.5 and 2 times higher than <10 years and fresh materials. Similarly, the degree of crystallinity of the old samples (>10 years) was 2 times higher than the fresh and < 10 years samples. Based on these findings, tertiary recycling, such as pyrolysis, seems to be a convenient route for upcycling of recovered plastics from municipal solid waste landfills.

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1. Introduction

In 2017 the MSW generated in Europe (EU-28) was 487 kg per capita (Eurostat, 2018). 23% of this waste has been disposed in landfill for a total of 58 million tonnes (Eurostat, 2018). The growing awareness

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about conscious waste management led to an absolute reduction of about 60% (63% per capita) from 1995 to 2017 of landfill waste in Europe (Eurostat, 2018). Europe is moving towards the concept of Circular Economy which promotes to “closing the loop” of product lifecycles (European Commission, 2018a). The EU targets include the recycling of 65% of municipal waste and 75% of packaging waste by 2030 (European Commission, 2018a). Plastic waste represents a large part of MSW. In 2016, plastic waste amounted to 27.1 million tonnes in Europe (EU-28) and 27.3% was landfilled for a total of 7.4 million tonnes (Eurostat, 2018; Plastics Europe, 2017). For this reason, the European Commission has included a strategy for plastics in the Circular Economy, which aims to reduce single use of plastic products and increases its reuse and recycling (European Commission, 2018b). In conjunction with the reduction of new waste, there is still a need to manage waste legacy contained in landfill. It has been estimated there are between 125,000 and 500,000 landfills in Europe (EURELCO, 2017), which contain potential secondary raw materials that can become part of the Circular Economy (Wagland et al., 2019). Although some concerns exist about the recovery of waste in landfill, in some cases landfill mining is an urgent necessity. Coastal landfills can be sources of marine and terrestrial plastic pollution affecting the ecosystems (Malizia and Monmany-Garzia, 2019). According to Brand et al. (2018) in only 6 years a great amount of waste from 79 UK coastal landfills will potentially increase sea pollution due to erosion. In order to avoid further environmental damage, it is important to investigate the most appropriate way to recover this waste. Besides the circular economy paradigm, the vision of dynamic landfill management (DLM) has been introduced during the Second enhanced landfill mining (ELFM) Seminar in the European Parliament in 2018. It involves a multidisciplinary approach for landfill management, pollution control, recovery of materials, energy and land in respect of European Policy and legislation (Jones et al., 2018). The ELFM concept focuses on maximising the valorisation of waste as material (WtM) and energy (WtE). The viability of ELFM is strictly related to the quality and quantity of buried waste material in the landfill (Bosmans et al., 2013). Plastic waste in landfill represents one of the major waste fractions that can potentially be recycled. However, due to contamination, such as trace heavy metals or corrosive compounds, and structural changes derived from the landfilling process, it might not meet the requirements for conventional recycling (Canopoli et al., 2018a). Polyethylene (PE) and polypropylene (PP) are the most demanded thermoplastics in Europe (Plastics Europe, 2018) and the most common types in the MSW.

Photodegradation and thermo-oxidative degradation are the most common causes of degradation for PE and PP in an aerobic and anaerobic environment (Webb et al., 2013; Andradý, 2011; Gijsmán et al., 1999). In the case of photodegradation, the chromophores present in the plastic polymer absorb the sunlight initiating the process of auto-oxidation which the formation of polymer fragments (Andradý, 2011). In thermo-oxidative degradation, the auto-oxidation process can be thermally initiated in a combination of mechanical stress (Gijsmán, 2008).

Photo and thermal oxidation of PE and PP can be described in three steps, initiation, propagation and termination. The initiation step involves the formation of free radicals in the polymer chain caused by chromophoric or thermolabile group (Gardette et al., 2013). During propagation, the free radicals react with oxygen forming hydroperoxides which further decompose in alkoxy and hydroxyl radical. Then, the following reactions between alkoxy and hydroxyl radical, lead to the formation of different products through β scission, abstraction of hydrogen, or cage reaction (Gardette et al., 2013). The Norrish reactions I and II are only present during photodegradation (Gardette et al., 2013). The reaction terminates when the radicals recombine in a stable form.

Some of the degradation effects are visible such as discolouration and brittleness while other chemical changes, such as bond scission and the formation of new functional groups can be detected only

with specific analyses. Indeed, in order to identify the best approach for the recycling of excavated plastics, it is important to evaluate the condition of these plastics, such as the degradation level. Although several studies have investigated the degradation of plastics in soil and water under different experimental conditions, to the best of the knowledge of the authors none of them has specifically investigated plastic degradation under genuine conditions in landfill (Canopoli et al., 2018a). The landfill environment is characterised by different stages and the waste is subject to mechanical stress, presence of leachate, decomposition of organic material, chemical reaction mostly in anaerobic condition (Kjeldsen et al., 2010). For these peculiarities, degradation of excavated plastics can easily be affected and need further investigation. Gaining such information is key to assess recycling and upcycling options of recovered plastics. Current recycling methods for fresh waste are reuse (primary), mechanical recycling (secondary), chemical and thermochemical recycling (tertiary) and energy recovery via incineration (quaternary) (Al-Salem et al., 2009). Recent studies on excavated plastics have identified tertiary and quaternary recycling as possible routes for this type of feedstock (Zhou et al., 2014; Breyer et al., 2017; Santaweek and Janyalertadun, 2017) but the information is still scarce. In the present study, the physicochemical characterisation of excavated PE and PP, from various waste layer depths and ages, from four landfill sites was carried out to shed light on the extent of degradation of buried plastic samples and its potential implications for recycling opportunities.

2. Materials and methods

2.1. Plastic samples collection and preparation

A total of 30 waste samples from 4 MSW landfills located in the UK were collected at depths between 5 and 55 m following the method used in previous studies (Frank et al., 2017; García et al., 2016; Gutiérrez-Gutiérrez et al., 2015). The cores were drilled at different depths and years of waste storage were given by the landfill site operators (Table 1, details in supplementary data Table S1). The samples were grouped according to the age of the buried MSW as follows: <10 years (7 waste samples) and >10 years (23 waste samples). The plastic fraction was extracted by manual sorting of the waste samples. The sample used in the SEM were washed and left to dry at ambient temperature. The rest of the samples have been dried at 60 °C for 2 h. Before the DSC analysis, the samples were ground in small particles ≤ 1 mm.

Table 1
Landfill samples information. Details are available in the supplementary data.

	Samples n.	Years	Depth (m)	Waste sample	Plastic (wet)		Plastic (dry)		Impurities (wet)	
				(g)	(g)	(wt %)	(g)	(g)	(wt %)	
<10	7	<10	5–18	12,335	1407	11	302	1105	79	
Average				1762	201	13	43	158	78	
SD				2953	332	7	70	263	5	
Min				390	31	5	9	22	70	
Max				8448	951	24	200	751	85	
>10	23	>10	3–55	141,603	9276	7	5084	4192	45	
Average				6157	403	7	221	182	45	
SD				2596	351	6	184	230	18	
Min				1891	21	0	12	9	11	
Max				11,586	1510	26	602	1143	76	
TOT	30			153,938	10,683	7	5386	5297	50	
Average				5131	356	9	180	177	52	
SD				3239	352	7	181	233	21	
Min				390	21	0.3	9	9	11	
Max				11,586	1510	26	602	1143	85	

2.2. Surface morphology and chemical characterisation of the excavated plastic fraction

Environmental Scanning Electron Microscopy was used to characterise the surface morphology of the PE and PP fragments at a magnification of x500. Concomitantly the chemical elements present at the surface of a representative plastic sample for each plastic type was determined using Energy Dispersive spectroscopy to evaluate the extent of degradation and contamination levels of the plastic fragments. The surfaces of the excavated samples were compared with the surface of fresh PE and PP waste. The excavated PE and PP analysed were the largest pieces, and for this reason the most representative, from each group (<10 years and >10 years).

2.3. Composition of the excavated plastic fraction

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used for the identification of different plastic polymers and calculation of the carbonyl index (Barbeş et al., 2014). The carbonyl index is often used to evaluate the oxidation level of polymers. It is defined as the ratio of the band area attributed to the carbonyl group $\text{C}=\text{O}$ and the band area attributed to methylene group -CH_2 (ter Halle et al., 2017; Barbeş et al., 2014). The carbonyl band was integrated between 1779 and 1680 cm^{-1} and the methylene between 1490 and 1420 cm^{-1} for PE, 2700 – 2750 cm^{-1} for PP (ter Halle et al., 2017; Moldovan et al., 2012; Longxiang et al., 2005). According to Rouillon et al. (2016) study, the oxidation of PP leads to the formation of volatile products that carry CH_3 moieties such as acetic acid and acetone. Therefore, it is expected that CH_3 decreases during oxidation. Carbonyl index, CH_3 for PP and CH_2 for PE, taken between 1490 and 1420 cm^{-1} have been analysed.

FTIR was applied on the fresh and excavated plastic waste samples using a Bruker vertex 70 instrument equipped with an attenuated total reflection (ATR) device Bruker Platinum ATR. Background and sample spectra were acquired using 16 scans at a spectral resolution of 4 cm^{-1} in the wavenumber range of 4000 to 400 cm^{-1} (ter Halle et al., 2017). A minimum of 3 replicates of infrared spectra were recorded for fresh PE and PP and excavated PE and PP samples.

2.4. Differential scanning calorimetry analysis

To understand the amorphous and crystalline behaviour of the excavated plastic residues, differential scanning calorimetry (DSC) analysis was conducted on 3 replicates of each sample (weight between 4 and 10 mg) using a DSC Q-200 (TA Instruments, UK). The temperature ranges were from 20 to $150\text{ }^\circ\text{C}$ for PE, and from 20 to $180\text{ }^\circ\text{C}$ for PP. A heating rate of $10\text{ }^\circ\text{C}/\text{min}$ was used in a nitrogen atmosphere for first and second cooling and heating cycles. The degree of crystallisation of the samples was calculated from the first heating experiment, which gives information on thermal history, using formula (1):

$$\% \text{Crystallinity} = \frac{\Delta H_m}{\Delta H_m^{\text{ref}}} \times 100 \quad (1)$$

where ΔH_m is the melting enthalpy of the sample and ΔH_m^{ref} is the melting enthalpy of 100% crystalline polymer. The ΔH_m^{ref} was taken as 293 J/g for PE and 207 J/g for PP (Blaine).

The peaks were measured using sigmoidal baseline (ISO 11357-1, 2016).

2.5. Statistics

t-Test is normally applied to compare the means of two groups and check if there is a statistically significant difference between them. Two-tailed t-test has been applied to analyse the results from FTIR, such as carbonyl index, CH_2 and CH_3 , and DSC, crystallinity and melting. The

significant difference was considered $p < 0.05$. It was used to evaluate the difference between excavated (>10 years and <10 years) and fresh samples for each plastic type, PE and PP.

3. Results and discussion

3.1. Percentage of excavated plastics from landfill

The average percentage of excavated plastics with >10 years of disposal is 8 wt%, ranging from 0.3 wt% to 26 wt%. The average percentage of excavated plastics with a disposal period of <10 years is 12 wt% ranging from 5 wt% to 24 wt%. This result is in accordance with other studies where the mean values of plastic percentage were between 10 and 26 wt% (García et al., 2016; Sel et al., 2016; Quaghebeur et al., 2013; Jones et al., 2013; Van Passel et al., 2013).

The excavated plastics were divided into different plastic types with FTIR spectroscopy. Thermoplastic such as PE and PP are the most demanded polymer types; about 36 wt% of the total plastic demand in Europe which amounts to 50 million tons (Plastics Europe, 2018; Plastics Europe, 2017). According to this, the PE and PP represent also the major fractions found after sorting in both groups (Table 2). The percentages of PE and PP in the MSW samples with <10 years were 50 wt% and 13 wt%, respectively. The PE and PP percentages in the MSW samples with >10 years were 48 wt% and 19 wt%, respectively. Rubber properties are different from conventional plastic and need a specific recycling route. For this reason, rubber is not considered in the main plastic types of this study.

3.2. Surface degradation of the excavated plastics

Comparison of fresh and excavated PE and PP surfaces showed a general major surface alteration in the excavated samples (Fig. 1). The first visual sign of surface degradation that can be detected is the loss of gloss which is characteristic of fresh PE and PP (Rouillon et al., 2016; Gijsman, 2008). Table 3 summarises the main characteristics of the analysed surfaces and elements detected from the EDS. Oxygen was in the main elements in all samples except for fresh PP. Presence of oxygen in PE and PP is a sign of degradation. This can be seen also in the surfaces images. In fact, fresh PP has visible smooth surface compared to the other samples (Fig. 1), showing a lower degree of degradation. Cracks are present in PE <10 years (Fig. 1B) and PP >10 years (Fig. 1F) which are signs of ageing (Elanmugilan et al., 2013). General roughness increase can be detected in the surfaces of excavated PE and PP compared to the fresh samples (Fig. 1). The SEM images do not show a clear difference in surface degradation between <10 years and >10 years samples.

Table 2

Percentages of different plastic types. Details are available in the supplementary data.

	Sample n.	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
		(wt%)								
<10	7	55	12	2	2	1	1	0	0	26
Average		50	13	4	5	4	7	1		31
SD		14	10	1	2	3	7			11
Min		32	2	3	3	1	0	1		18
Max		70	32	5	6	6	15	1		43
>10	23	45	19	11	4	3	0	0	14	4
Average		48	19	16	5	20	6	1	34	8
SD		27	21	17	4	26	7		40	11
Min		2	1	0	1	2	1	1	0	0
Max		92	85	50	16	39	11	1	97	41
TOT	30	45	19	10	3	3	0	0	13	6
Average		48	17	14	5	11	6	1	34	14
SD		24	18	16	4	16	6	0	40	15
Min		2	1	0	1	1	0	1	0	0
Max		92	85	50	16	39	15	1	97	43

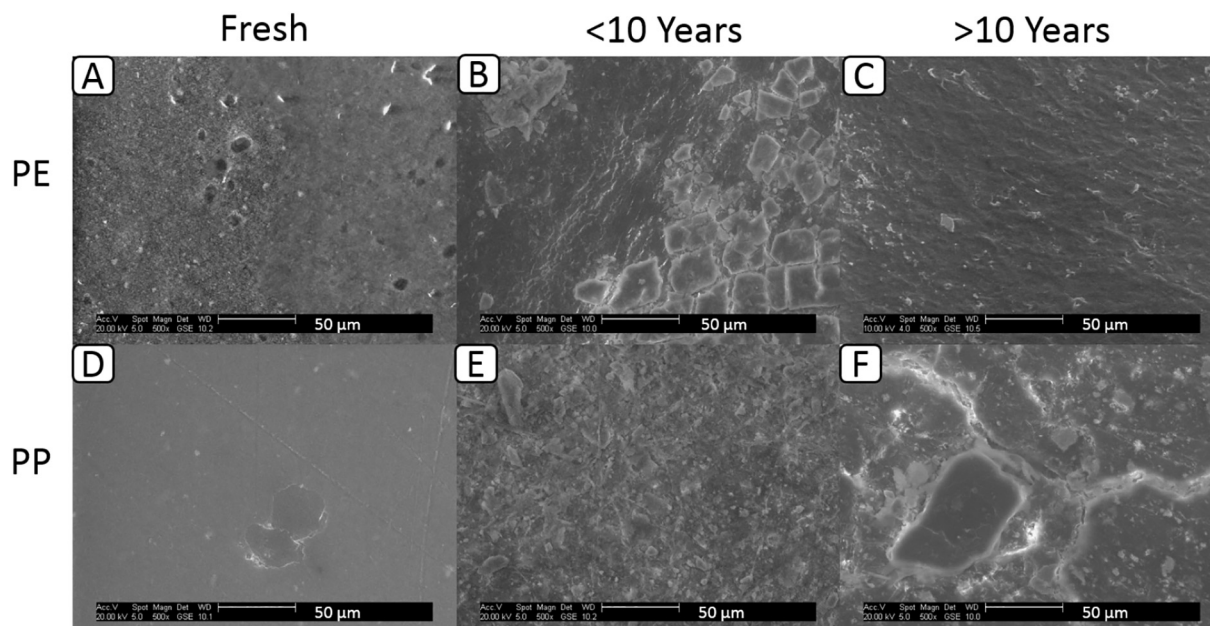


Fig. 1. Scanning electron microscope (SEM) images of fresh plastic waste (A and D) and excavated plastic (B, C, E, F) under 500 \times magnification. Fresh PE coloured packaging; B: Excavated PE <10 years; C: Excavated PE >10 years; D: fresh PP; E: Excavated PE <10 years; F: Excavated PE >10 years. Adapted from Canopoli et al., 2018b.

The elements identified in the majority of the samples are calcium (Ca), Titanium (Ti), Silicon (Si), Magnesium (Mg) and Aluminium (Al) (Table 3). Ca can be linked to the commonly used filler calcium carbonate (CaCO_3) (Tolinski, 2015; Brydson, 1999). Ti and Al are used in Ziegler-Natta catalysts for PP and PE production (Shamiri et al., 2014). Si and Al present in the excavated samples can be related to the SiO_2 and Al_2O_3 contained in the soil. The identified elements can also be associated 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) (Turku et al., 2017; Brydson, 1999).

3.3. Carbonyl index of the excavated plastic materials

The carbonyl index (CI) is presented as the average value of different infrared spectra for each sample. The CI average of fresh PE is 0.53, higher than the excavated PE which seems to decrease over time, 0.46 and 0.41 for PE <10 years and PE >10 years respectively (Fig. 2). However, the CI results of PE do not present a statistically significant difference. The slight decrease of carbonyl index in the PE samples with >10 years disposal could indicate an advanced degradation. Indeed, after initial degradation the samples may proceed the degradation with chain scission, crosslinking and CO release (Moldovan et al., 2012). In this case, the carbonyl group is depleted and the CI decreases consequently. The difference between fresh and excavated PE can be related to the presence of TiO_2 additive. Indeed, Ti is found as a major element only in fresh PE (Table 3).

Conversely, PP presents an opposite trend which suggests that the CI average increases with storage years 0.76, 1.34 and 1.78 for fresh PP, PP

<10 years and PP >10 years respectively. CI results of PP, fresh and excavated, are statistically different (Fig. 2).

The CH_2 absorbance of excavated PE >10 years is significantly lower compared with fresh and <10 years PE (Fig. 3).

PP showed similar results (Fig. 3). In fact, the difference between excavated PP >10 years and the other two samples, fresh and <10 years, is statistically significant. CH_3 band of PP samples >10 years storage is lower than newer samples and this can be related to the loss of volatile products as suggested by Rouillon et al. (2016).

Hydroxyl group ($-\text{OH}$ 3650–3200 cm^{-1}) is another degradation product together with carbonyl group (Moldovan et al., 2012). The degradation products showed in this band are alcohols and hydroperoxides (Gardette et al., 2013). Presence of a broad peak can be distinguished in the excavated samples compared to the fresh samples in both PE and PP (Fig. 4).

3.4. Differential scanning calorimetry (DSC)

The crystallinity in PE increases during ageing (Fig. 5). Higher crystallinity for the older samples can be related to the different degradation rate of the crystalline and amorphous phase of plastic (Andrady, 2017). In fact, the amorphous fraction is the first part that is affected by mechanical stress, biodegradation and weathering (Andrady, 2017; Yang et al., 2014; Shah et al., 2008). The crystallinity average is 39%, 45% and 51% for fresh PE, PE <10 years and PE >10 years, respectively. However, only fresh PE and PE >10 years present a significant difference. Fig. 5 presents the thermograms of fresh and excavated PE. The presence of a double peak, such as in the excavated PE, characterises plastic samples with different lengths of molecular chains and degraded

Table 3
Surface characteristics and chemical elements detected by SEM-EDS (minimum concentration detected 0.08 wt%) of fresh and excavated PE and PP. Adapted from Canopoli et al., 2018b.

Sample	Figure	Surface texture	Main elements	Minor elements (<5 wt%)	Trace elements (<0.5 wt%)
PE	1A	P	C, O, Ti	Al, Cl, Ba	Si, P, S, Cu
PE < 10 years	1B	F, AP, Gr	C, O	Mg, Si, Ca	Al, P, S, Cl, Ti, Fe, Cu, Mo
PE > 10 years	1C	Fl, AP	C, O, Ca	Al, Si, Cl, K, Ti, Fe	Na, Mg, P, S, Cu, Zn
PP	1D	S	C,	Ca, Ti, Fe	Mg, Al, Si, Cl
PP < 10 years	1E	Fl, AP, Gr	C, O, Si, Ba	Al, S, K, Ca, Fe, Zn	Mg, P
PP > 10 years	1F	F, AP, Gr	C, O	Si, Ca, Ti, Fe	Mg, Al, S, Cl, K, Zn

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

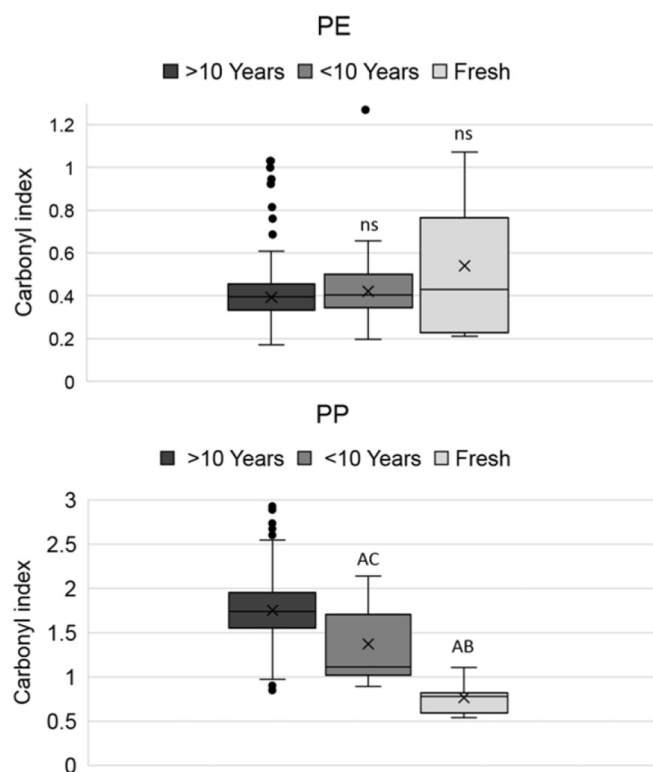


Fig. 2. Carbonyl indices of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). Outliers are plotted individually (points).

samples (Stangenberg et al., 2004). In fact, fresh plastic polymer presents a single peak (Fig. 6). The melting point average of fresh PE, PE <10 years and PE >10 years was 116.6 °C, 130.5 °C and 127.5 °C respectively. These results are not statically different from each other.

The crystallinity percentage average of fresh PP, PP <10 years and > 10 years is 38%, 35% and 41%, respectively (Fig. 5). There is not a clear trend and only PP >10 years and PP <10 years present a statistically significant difference. The melting average is 163.5 °C, 155.4 °C and 164.5 °C for fresh PP, PP <10 years and PP >10 years respectively. These results are not statistically different.

3.5. Recycling implication

These results need to be considered for the evaluation of the introduction of excavated plastics into the circular economy. Not all recycling routes of fresh plastic waste are feasible for excavated plastics. Due to the physico-chemical characteristics of excavated plastics, thermo-chemical recycling might be the best option compared to mechanical recycling and energy recovery via incineration. Mechanical recycling requires higher quality sorting for the identification of polymer types and feedstock material with appropriated physico-chemical properties (Butler et al., 2011). Plastic degradation comprises of contaminants such as oxygenated groups and organic matter which can affect the product quality (Ragaert et al., 2017). Indeed, changes in crystallinity and CI affect the mechanical properties of plastic. Increasing the degree of crystallinity and CI, the plastic material becomes more brittle and more susceptible to future thermo and photo-degradation (Wypych, 2013; Fotopoulou and Karapanagiotti, 2019). Mechanical recycling of plastics is known to decrease the mechanical properties of plastics after a certain number of extrusion cycles (Oblak et al., 2016). Energy recovery via incineration cannot be considered practicable in the circular economy view. In contrast, pyrolysis can process contaminated plastics and heterogeneous feedstock, and represents a valuable opportunity for

the excavated plastics recycling (Fox and Stacey, 2019; Ragaert et al., 2017; Butler et al., 2011). However, the use of plastic polymers such as PVC and PET should be avoided during pyrolysis (Lopez et al., 2017). The presence of carbonyl groups in the feedstock could lead to the production of oxygenated compounds in the pyrolysis oil. Oxygenated compounds are undesirable products that cause corrosion problems and negatively affect the pyrolysis oil quality decreasing the calorific value and stability (Czajczyńska et al., 2017; Lu et al., 2009). These compounds such as hydroxyl groups are present in the pyrolysis of plastic and can be attributed to the additives (Hakeem et al., 2018). To the author's knowledge, the effect of degradation of excavated plastics on pyrolysis products has not been verified. On the other side, limited information is available about the contamination effect from elements such as Al and Fe. Presence of Al_2O_3 and Fe_2O_3 can catalyse the decomposition of plastics during pyrolysis (Bosman et al., 2014; Liu and Meuzelaar, 1996). Chemical compounds such as ethene, propene and benzene, could be recovered through the pyrolysis of excavated plastic waste and reintroduced in the circular economy. A recent study (Fox and Stacey, 2019) has investigated the potential profit of fresh plastic waste pyrolysis and selling of alkene products. The potential value of fresh plastic waste is evaluated between \$80–\$160 per tonne (Fox and Stacey, 2019). Table 4 shows the potential revenue of excavated plastics disposed in landfill in 2016. The plastic types amounts have been calculated from the percentages found in this study. The plastic types considered for the pyrolysis are PE, PP, PS, PE/PP blend. The potential revenue is between \$402 million and \$805 million. Further studies are needed to investigate the production of chemical compounds from the excavated plastics pyrolysis and their marketability.

4. Conclusion

PE and PP are the most common polymer type found in excavated waste from landfill. Fresh PP presents a smooth surface compared to the other samples and no oxygen has been detected from the EDS. The

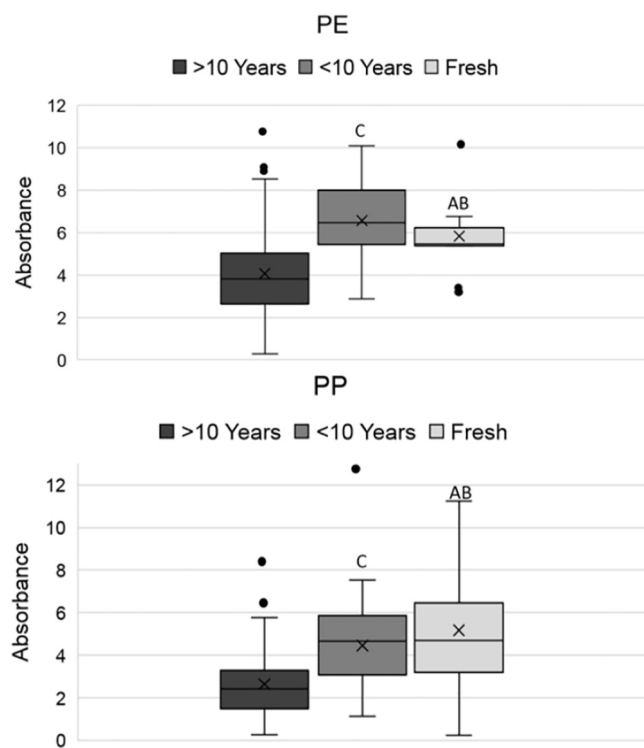


Fig. 3. Absorbance of CH_2 and CH_3 vibration of $\sim 1456\text{ cm}^{-1}$ of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples Outliers are plotted individually (points).

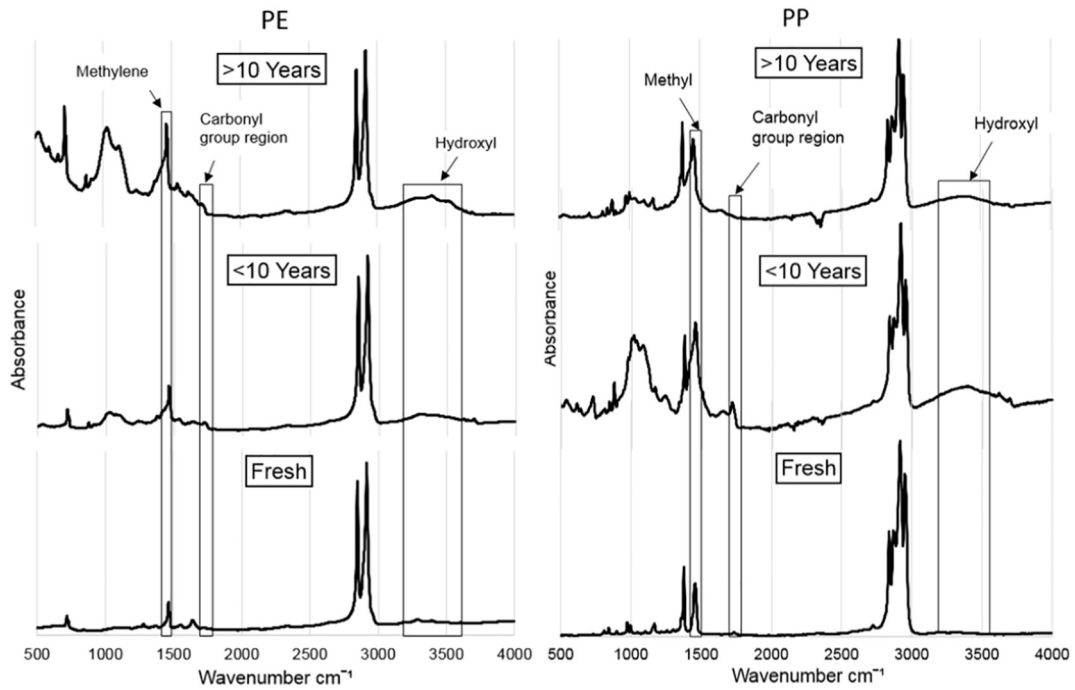


Fig. 4. FTIR spectra of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

CI excavated PP samples >10 years was almost 2 times higher than <10 years and fresh PP, respectively, confirming the increase of degradation over time. CH₂ and CH₃ of excavated PP and PE >10 years were statistically lower (almost twice) than the newer samples. The degree of

crystallinity of PP and PE samples >10 years was also 1.3 times higher than fresh materials. Overall, the PE and PP which have been buried for >10 years had a greater extent of degradation than samples with

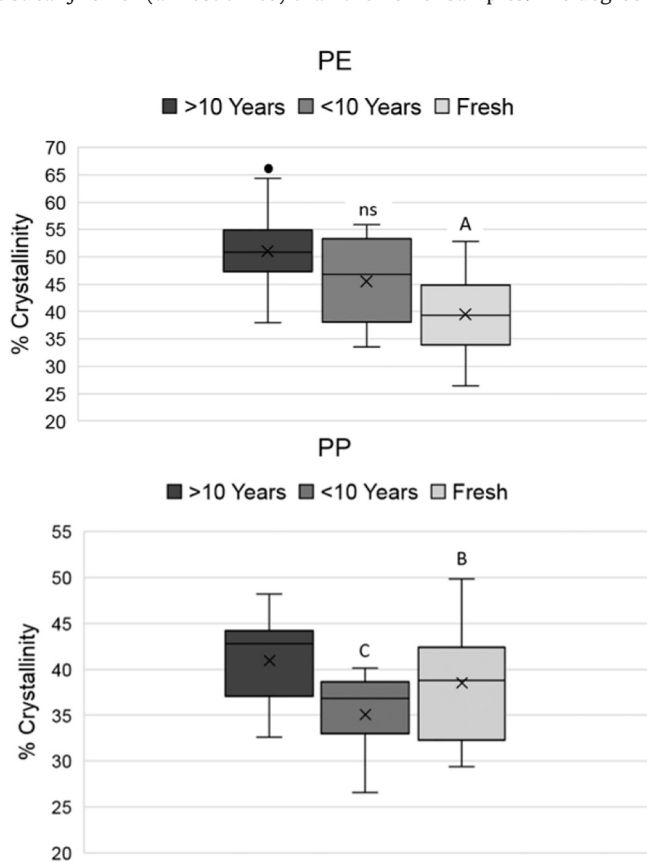


Fig. 5. Crystallinity percentage of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). Outliers are plotted individually (points).

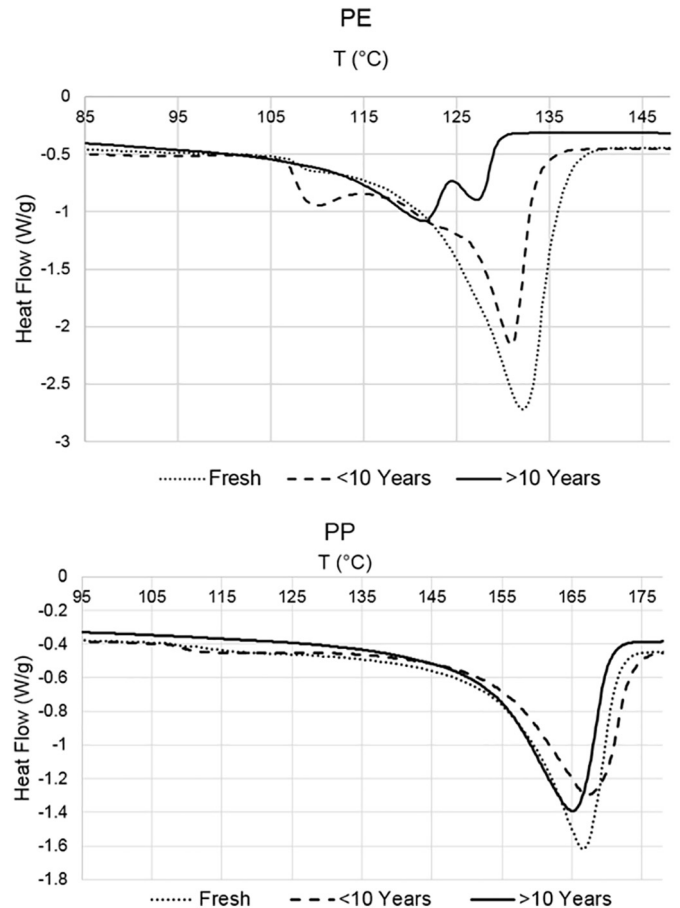


Fig. 6. DSC thermograms of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

Table 4

Potential revenue from plastic waste disposed in landfill in 2016. Price per tonne from Fox and Stacey, 2019.

Landfilled plastic 2016	Weight (%)	Tonnes	Price per ton \$80	Price per ton \$160
PE	45	3,330,000	266,400,000	532,800,000
PP	19	1,406,000	112,480,000	224,960,000
PS	3	2,22,000	17,760,000	35,520,000
PE/PP blend	1	74,000	5,920,000	11,840,000
PVC	10	740,000	–	–
PET	3	222,000	–	–
Rubber	13	962,000	–	–
Rest	6	444,000	–	–
Tot		7,400,000	402,560,000	805,120,000

fewer years of storage, which suggests that chemical and thermochemical recycling such as pyrolysis with the production of chemical base compounds would be the preferred route for excavated plastics. It would also contribute to the circular economy and the development of ELMF projects. Future studies should evaluate if the increase of CI in the feedstock lowers the pyrolysis oil quality due to the presence of a major quantity of oxygenated compounds. The presence of oxygenated compounds is known to lower the heating value which is an important parameter for transportation fuels (Lopez et al., 2017). In addition, the catalyst effect of elements such as Al and Fe should be further investigated. Indeed, these elements found in the excavated plastic samples, are known to act as catalysts during the pyrolysis of plastic waste (Bosmans et al., 2014; Liu and Meuzelaar, 1996).

CRedit authorship contribution statement

Luisa Canopoli: Conceptualization, Investigation, Writing - original draft. **Frederic Coulon:** Supervision, Conceptualization, Writing - review & editing. **Stuart T. Wagland:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) through the Doctoral Training Partnership (DTP) (EP/N509450/1). Data underlying this paper can be accessed at [10.17862/cranfield.rd.9110345](https://doi.org/10.17862/cranfield.rd.9110345).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.134125>.

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