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Study of the degradation profile for virgin linear low-density polyethylene (LLDPE) and polyolefin (PO) plastic waste blends

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Abstract

In this study, the properties of virgin linear low-density polyethylene (LLDPE) and its blends with reclaimed plastic solid waste (PSW) are investigated by thermogravimetry, differential scanning calorimetry (DSC), infrared spectroscopy and scanning electron microscopy (SEM). The PSW constituted polyolefin (PO) polymers recycled mechanically via extrusion/blown-film and exposed to accelerated weathering tests to determine the change in their degradation behaviour. The oxidation products determined using the FTIR analysis and thermal stability studies points toward the blend constituting 25% of waste by weight as the most stable. Changes in crystallinity of the polymers were attributed to the crystal size change as a consequence of the weathering mechanism. The DSC results revealed that both oxidation induction temperature (OIT) and crystallinity were affected by the PO waste content. This points towards the impact of polymers immiscibility and polydispersity within the matrix of the blends due to chain scission reaction and oxidation with the UV exposure.

Keywords

Weathering, FTIR, Waste, Polyolefin, Crystallinity

Introduction

The incorporation of materials as fillers and reinforcing agents to polyolefin (PO) polymers is a practice carried out with the aim of producing more durable products with an acceptable market longevity. Such a practice has been notably conducted in the past with wood fibres, short glass and polyesters, to produce various plastic composite blends [1, 2]. These products perform various functions as commodity plastic products stretching from film applications to more engineered and tailored ones, such as insulators and protection surfaces. Furthermore, PO polymers are derived from non-renewable resources such as refined petroleum products and natural gas. The dependency on them will only increase the depletion potential of such natural resources which are used as a primary source of energy and fuels.

PO polymers have been noted to have an increasing trend in market growth, mainly driven by the Asian market consumption. Mainland China, India and the Middle East (ME) have shown a steady annual consumption rate with an expected growth in consumption of 5.5% per annum [3]. The main contributing factor to this economic growth is the increasing demand of various countries in Asia. This makes the strain greater on producers for having an increased production

capacity with more competing products on the market. Currently, China alone has a per capita consumption of polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) of 38 kg per person. This is considerably less than the European per capita consumption of 50 kg per person and the United States (US) of 68 per person [4]. The ME consumption of PO polymers has reached 25 million tons in the year 2015 from an estimate of around 5 million tons in the year 2000 [3]. This is also reflected in both the ME demand of plastics and basic chemicals which led to the increase in production capacity of PO. Within the ME region, the State of Kuwait is noted to be one of the major petrochemical and plastic producers along with the Emirates and Saudi Arabia. Increase in PO production capacity and overall dependency on plastic articles has led to an alarming generation rate and accumulation of plastic solid waste (PSW).

Globally, PSW constitutes 10% on average of the solid waste generated from various sources (SW) [5]. Developed and industrial countries associated with high income and gross domestic product (GDP) index are noted to have a high rate of SW generation, and in particular PSW [6]. The World Bank databank reports that PSW makes up 12, 22 and 19% of the total SW produced by the US, Germany and the Netherlands, respectively [5]. However, these countries have a well-established infrastructure that drives circular economy towards a more sustainable practice in integrated solid waste management (ISWM) strategies. In a European context, landfilling is the major routes of waste disposal where 38% of SW is typically disposed of in this manner [6]. This is with the expectation of Scandinavian and few West European countries that have approached their zero landfill strategy.

In an environmental context, SW is to be managed in alternative means to landfilling for a better and a safer practice to preserve natural resources. Past research has suggested that landfilling SW including plastics has adverse effects on the surrounding environment due to concern of toxic chemicals migration by leaching, harmful emissions from additives, bacteria growth and greenhouse gas (GHG) evolution. Such concerns have been reported in the Arabian Gulf Council Countries (GCC) [7]. These countries have a considerable proportion of their SW comprising of plastics averaging at 13% of the total municipal solid waste (MSW) [8, 9]. Governments and private-holding entities alike are investing vast amounts nowadays on valorising this particular type of SW. Moreover, recycling of PSW is noted to be a priority due to the fact that it can produce desirable products that can be marketed with ease. Recycling techniques of PSW follow an ascending order of preference within the PSW management hierarchy [10], covering a plethora of methods from reprocessing of plastics to energy recovery via combustion and power generation. However, in countries such as the State of Kuwait where an infrastructure for SW management is still lacking, mechanical (secondary) recycling methods of PSW presents themselves as an optimal solution to the accumulation problem faced by urban communities. PSW comprises 13% of the total household solid waste (HHSW) in Kuwait totalling at some 150 ktpa [11]. On the other hand, PSW makes up over 18% of the MSW sector with a generation rate of 220 ktpa [12, 13]. Therefore, implementing mechanical recycling techniques with the aim of plastic product development from SW origin can be considered an economical and a suitable solution to the problem.

For mechanical recycling to be considered successful, the final product must result from a polymeric blend that can perform to a suitable standard acceptable on the market [14, 15]. The products from mechanical recycling processes can be truly proven to be suitable when the virgin polymer is substituted with a post-consumer recycle that can perform the intended application. Typically, PSW is mixed with virgin polymer to achieve a certain acceptable blend with or without the use of fillers or additives. Past work on blends of PSW with virgin PO polymers has shown that the properties vary considerably with respect to the polymers degradation profile and processing conditions that will alter the molecular structure. Both mechanical properties and thermal stability have been altered in waste high-density polyethylene (HDPE) and polyamide

blends after extrusion [16]. The improvement of properties was attributed to the decrease of size domains in the recycled HDPE. Extrusion also results in a notable change in rheological properties of PO polymers. This is due to the cross-linking reaction that results from the thermal degradation in recycling processes [17]. A notable change in crystallinity was also reported in the past with recycled blends of PE due to the hindering of crystallites formation with the presence of virgin PP.

Weathering tests have been conducted in the past as a means to study the degradation of polymers and blends. Weathering can determine the materials integrity and its suitability for outdoor applications. It is also well established that PO polymers are very susceptible to UV radiation leading to changes in molecular structure and properties [18]. Free radical formation is reported in weathering studies which can lead to peroxides and hydroperoxides evolution after combination with surrounding oxygen [19, 20]. This leads to the formations of various chemicals such as alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acids and keto-acids, which leads to the deterioration of the material and the decrease in its molar mass [21, 22]. Branching, cross-linking and chain scission have also been reported with PO polymers after weathering [23, 24].

Various attempts are reported in technical literature with regards to the determination of the degradation behaviour of PO polymers, typically focusing on virgin resins and grades [25, 26, 27, 28]. However, efforts undertaken to determine the degradation behaviour of blends with high content of PSW are very scant. In this work, the degradation of PSW blends with virgin linear low-density polyethylene (LLDPE) is reported after carrying out an extensive campaign of characterization and properties evaluation executed with the aim of developing recycled products suitable for the market in an effort to reduce SW accumulation. Physical and mechanical properties were characterised and extensively discussed in our previous communications [29, 30, 31]. The materials chosen are commercially available and used for various applications, hence are of interest to study post-use and reclamation as PSW. This study focuses specifically on the alterations caused by accelerated weathering (ageing) on the film samples originating from reclaimed PSW. The work carried out is useful for developing more resistant materials available on the market, as well as, extend the durability of the developed blends. This work also contributes to the scientific literature with a knowhow based methodology for the evaluation of degraded recycled films. Chemical and morphological alterations are reported in this article, in addition to the blends thermal stability post-accelerated weathering. The results in this work lead to the determination of appropriate blends for future upgrading into market products acceptable for consumers indoor and outdoor applications. These products will be the result of a mechanical recycling scheme that is appropriate for plastic film waste. The incorporation of PSW has an additional embedded objective which is the valorisation of a major component of SW and the reduction of environmental stressors associated with it. To the best of the authors' knowledge, no such attempt is reported in scientific literature.

Materials and methods

Sample preparation and compounding

Reclaimed plastic waste in the form of refuse films recovered from both commercial outlets and households from the six governorates of the State of Kuwait were used in this work. The amount of 200 kg was secured from a local waste distributor. The constituents of the PSW used were determined using random sampling following ISO 24153 [32] to determine the constituting polymers melting point (T_m). The total of 150 samples was tested using a TA instrument Q-series model differential scanning calorimeter (DSC). A 9 ± 0.1 mg sample was placed in the DSC crucible (pan), equilibrated at 40 °C for 5 min, after which the sample was heated using a 10 °C

min⁻¹ heating rate to 200 °C. The cooling cycle was achieved by the same heating ramp to 40 °C. The average of two heat flow cycles was used. The PSW used consisted of the following polymers by weight (%): LLDPE (46%), LDPE (51%), HDPE (1%), and PP (2%), respectively. Further details can be found elsewhere [29, 31]. Furthermore, the waste films were milled to 3 mm flakes using a Tecnova Model cutting mill and pelletized to 3 mm pellets using a Tecnova industrial single-screw extruder ($L/D = 30$) at 40 bar pressure with a speed of 70 RPM and cooling temperature maintained between 16 and 17 °C. Commercial grade LLDPE (EFDC-7050) was graciously supplied by EQUATE Petrochemical Company (Kuwait-DOW Chemicals Co.) and used in this work as white translucent pellets with a particle density (ρ) of 0.918 g cm⁻³ and a melt flow index (MFI) of 2 g/10 min. For the purpose of confidentiality, the company did not provide further details of the additives embodied in the material.

Dry blends (i.e. blends with no commercial additives/chemical addition at the blending stage) of both virgin and waste polymers were weighed, extruded, and film blown using a single-screw extruder (Tecnova, $L/D = 30$, 45 bars and 85 RPM) and a film-blowing machine (Kung Hsing monolayer) with a water cooling temperature maintained between 16 and 17 °C. A die head temperature (DHT) of the extrusion assembly was maintained at 175 °C [29]. The adapter and lower die temperatures were consistent among each formulation. The compounding temperatures were chosen to accommodate the virgin LLDPE grade used, and produce sheets with no visible cracks or alternation in thickness. The virgin LLDPE (V) to waste (W) ratios (in weight) considered in this study were: 100/0, 75/25, 50/50 and 25/75, respectively. The extruded sheets of 100 μ m thickness were cut using a standard cutting die (Ray Ran UK cutting press/model RR/PCP) to produce 20 \times 1 cm films for further characterization. The thickness was chosen as it represents an average value of plastic products used on the market between thin film applications (10–50 μ m) and plastic covers (above 120 μ m). The samples appeared consistent with no visual fractures or crazing and were comparable to each other by touch. All samples were stored in laboratory conditions at 23 °C/50% relative humidity (RH) and in the dark between sample formulation and testing.

Accelerated weathering

Accelerated (artificial) indoor weathering (ageing) tests are commonly used for studying materials' integrity. Films of the different formulations were exposed to AW in accordance with ASTM D 4329 [33]. Samples were mounted on the racks facing the UV lamps with no empty spaces in the panels to maintain uniform repeatable test conditions. Cycle A procedure was used for general applications durability testing, i.e. 8 h of UV exposure at 60 °C followed by 4 h of condensation at 50 °C. At the end of each continuous weathering test, the chamber was cooled to room temperature and trays were set to rest on a flat surface for a minimum of 24 h. Samples were laid to rest for a minimum of 72 h before characterization following the methodology of Johnson et al. [34], Al-Salem et al. [31] and Al-Salem [35]. A minimum of four replicates were exposed to the different exposure durations in the QUV machine chamber. UV lamps irradiance was also selected to be 0.68 W m⁻² [33] and the lamp was set for normal operation maintaining 5000 h of continuous operation for the lamps. The irradiance sensor was calibrated every 400 h of lamp operation during the UV cycle under normal test temperature. The equipment used was cleaned every 800 h to remove scale deposits resulting from water evaporation during the condensation cycles. The film samples in this work were exposed to the midpoint of degradation and maximum threshold limit (e.g. time before total sample deterioration). These are equivalent to 7.5 days and 15 days for the case of the 100/0 and 75/25 samples; and 5.5 days and 11 days for the 50/50 and 25/75 samples as determined previously [29]. This will allow the determination of the degradation profile across as much as possible of the time period the polymers might be exposed to outdoor applications as a plastic product.

Differential scanning calorimetry (DSC)

A Perkin Elmer (Model Jade, US) equipped with a PYRIS analysis software was used to test control and exposed samples using a 5 ± 0.1 mg sample weight taken from the middle section of the specimens. Al_2O_3 crucibles were used for both samples and reference materials. Crystallinity measurements were determined using scans of the second heating cycle between 50 and 230 °C based on the peak area of the heat flow curve between 60 °C and 130 °C, with a nitrogen (N_2) gas flowrate of 20 ml min^{-1} and a heating rate of 10 °C min^{-1} . The degree of crystallinity (%) was calculated from the software by dividing the melting enthalpy over the melting enthalpy of a 100% crystalline PE (293.6 g J^{-1}). PP was excluded in the calculations as it is of minimal presence in the blends making up only 2 wt% of PSW used. Cooling rate was set at 15 °C min^{-1} in similar conditions [36, 37]. The second heating cycle was used in the crystallinity analysis following the initial heating run, as it will eliminate inherited effects of thermal histories and weathering on the specimens [37]. Oxidation induction temperature (OIT) in dynamic scan mode was conducted using similar weight for the studied samples. Samples were heated using a rate of 10 °C min^{-1} with a N_2 flowrate of 20 ml min^{-1} . Samples were then held for 5 min at 70 °C to settle followed by the introduction of oxygen (O_2) gas flowrate of 20 ml min^{-1} . Samples were then heated from 70 to 230 °C at a rate of 2 °C min^{-1} [38].

Thermogravimetric analysis (TGA)

Thermal degradation of virgin/waste blend samples was investigated using a Shimadzu TGA-50 thermobalance equipped with a data acquisition/analysis software (TA Instrument) set to record the data every second under five heating rates (β) (i.e. 5, 10, 15, 20 and 25 °C min^{-1}). A constant flow of pure (99.99%) dry nitrogen with a flow rate of 50 ml min^{-1} was maintained throughout the experiments. The measurements were conducted using 5 ± 0.1 mg samples from room temperature to 550 °C made with triplicates showing high repeatability with standard deviation not exceeding 1% in accordance with the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendations previously published in Vyazovkin et al. [39, 40] for non-isothermal (dynamic) thermogravimetry; to diminish sample size influences on the kinetics [41, 42].

FTIR-spectroscopy

The equipment used was a Perkin Elmer UK (Spectrum Two Model) FTIR-spectrometer. Spectra were recorded with a resolution of 4 cm^{-1} using a Diamond Universal Attenuated Total Reflection (ATR) attachment (Perkin Elmer UK) with four interferogram scans averaged to give the spectra from 500 to 5000 cm^{-1} using the ATR technique. At least two replicas of samples were used to record each spectra.

Scanning electron microscopy (SEM)

The sample surfaces were placed on a double-sided carbon tape positioned on a metal holder then coated with a layer of platinum with a thickness of 8–10 nm by sputtering using a JEOL-JFC-1600 sputter coater for 30 s. Samples were then analysed by placing them under JEOL-JSM-6010 LA SEM using a voltage of 5 kV, to prevent damage of the polymeric film [19, 43, 44]. All samples were stored in the dark before analysis at laboratory temperature with controlled relative humidity (RH) of 50%.

Results and discussion

Effect of weathering and thermal analysis

Weathering of the film samples showed apparent and visible changes on the surface of the materials. This was noted with a perceptible discolouration and fading of colour as the waste content increased, especially with the materials containing 50 wt% and 75 wt% of PSW. The total change in colour parameters (ΔE) was measured as a function of weathering time and reported previously in Al-Salem et al. [29]. ΔE showed values between 2.2 ± 0.1 and 5.7 ± 0.2 for the various materials tested between 48 and 360 h of accelerated weathering exposure [31]. Colour parameters were generally less stable and changed more rapidly with the increase in waste content and exposure duration. This can be attributed to the change in surface chemistry due to UV exposure which leads to the photo-degradation of the polymers, which in the case of PSW the materials are exposed to additional heating cycles due to reclamation, preparation and processing. Heating and cooling of PO polymers at compounding stages will produce larger crystalline zones that can lead to an apparent alteration in the colour parameters [45]. The longer materials were exposed to UV inside the weathering chamber, the more they were susceptible to change in colour. This is due to longer exposure time spans to spray/condensation cycles in the testing procedure simulating outdoor weather [29, 46]. A correlation was established between natural (outdoor) weathering and accelerated weathering tests for the studied materials in this work [46]. It was revealed that 1 h of accelerated weathering is equivalent to 1 day of natural exposure based on statistical ranking and properties loss reported with exposure time.

The degree of crystallinity determined from the DSC analysis is presented in Table 1. The virgin LLDPE (100/0 samples) unexposed to accelerated weathering, exhibited a similar degree of crystallinity to the other sample blends tested in this work (34%). PO polymers are known to be semi-crystalline materials by their nature. The structure of the materials allows rapid photo-degradation to the polymeric matrix with weathering due to the high degree of permeability accessible to oxygen molecules because of their structure and crystallinity degree [47]. The average glass transition temperature (T_g) reported for PE is -70 °C, which is well below the UV exposure and condensation temperatures used in this work. This facilitates the following phenomena to occur: (1) rearrangement of the crystalline phase due to the mobility of the amorphous region; (2) surface contraction leading to cracks on the materials surface (as it will be revealed at later stages of this communication with SEM results); and (3) loss of chain ends due to oxygen permeability [19, 24, 44]. This can explain the reason behind the increase in crystallinity after weathering the virgin LLDPE to the midpoint of total degradation time (7.5 days) reaching a 40% crystallinity degree.

Table 1

Degree of crystallinity (%) measurements established from DSC thermograms of the second heating cycle in inert atmosphere

Material (v/w wt%)	Exposure duration (days)	Degree of crystallinity (%)
100/0	0	34
	7.5	40
	15	35
75/25	0	35
	7.5	35
	15	41

Material (v/w wt%)	Exposure duration (days)	Degree of crystallinity (%)
50/50	0	34
	5.5	32
	11	34
25/75	0	34
	5.5	34
	11	35
0/100	0	34
	5.5	33
	11	35

Mechanical profiling using tensile pull tests was conducted on the studied specimens in past efforts [29, 31, 35]. The pre-weathered blends formulated in this work were acceptable in terms of international market standards [31, 35]. This confirms the blends applicability for upgrading into marketable products resulting from mechanical recycling [35]. The degradation with respect to accelerated weathering exposure was previously discussed in Al-Salem et al. [29, 31]. The results are depicted in the Supplementary Materials File for the reader's consideration. The properties estimated include Young's modulus (MPa), stress at break (MPa), strain at break (%) and force at break (N). The alteration in the mechanical integrity of the LLDPE samples studied in this work, namely in Young's modulus, strain and stress at rupture, indicate the loss of amorphous region at 7.5 days of exposure [29]. This points towards the excessive cross-linking and branching reactions that the polymer undergoes due to photo-degradation which are evident with the increase in crystallinity. On the other hand, the decrease in crystallinity at 15 days of exposure was expected due to the increase in the evolution of chemicals (and eventually making the polymer's matrix saturated) from the termination reaction in the photo-degradation mechanism of PE [43]. These products include oxygenated groups, chain ends, double bonds and branch sites [19, 23]. This is also supported by previous authors' findings depicting an increase of crystal size with the rapid degradation of LLDPE [28, 48, 49]. It was observed that the properties of the 75/25 and 100/0 materials were more stable than other formulations. This will complement the analysis conducted in this research work and shown in later section of this communication.

The incorporation of 25 wt% of waste has led to a stable degree of crystallinity estimated at 35% by the time the UV exposure duration was 7.5 days. The bulk polymer (i.e. LLDPE) served as a suitable matrix material for the blend, considering that 98 wt% of the PSW used consisted of PE. This can also explain the reason behind the constant crystallinity estimated for the other materials with respect to weathering duration (Table 1). However, towards the end of the weathering test, the degree of crystallinity was denoted as 41%. This can be attributed to the dispersion of the waste polymers fraction in the blend considering their thermal history and photo-degradation. It also indicates the change in crystal size due to incorporation of waste polymers and impurities with it.

The virgin LLDPE material showed a melting endothermic peak at 122 °C (Fig. 1a). The melting peak which indicates the melting point (T_m) of the polymer was noted to be constant and did not exhibit detected changes with exposure to weathering. The melting peaks also did not change with waste content and can be related to the LLDPE fraction of the blend (Fig. 1b–d). Thermal energy absorption curves in the shape of shoulders, started to develop prior to the melting peaks for the 75/25, 50/50 and 25/75 blends (Fig. 1b–d). These shoulders became more prominent with respect to waste content, which indicate a change in both crystal size and molecular weight of the polymeric blend [19]. These shoulders also point towards the physical immiscibility of the blends

[22] as they can describe and characterise the bulk of the waste material in the blend. Linear and branched PO polymers will typically show two distinct peaks in DSC melting curves [50]. This is noted in this work where the waste (recycled) plastics will have a higher polydispersity index due to chain scission and oxidation after thermal treatment, indicated by the shoulders evolved. This also indicates that the waste material is well mixed and the LLDPE from waste is blended with the virgin LLDPE resulting in two distinct phases depicted by the two curves in the blends calorimetric endotherms. The changes that occur within PO polymer due to the recrystallization post-cooling in the second heating cycle of the DSC test increases the broadness of these shoulder peaks. All the energy absorption shoulder peak points which indicate the T_m of the waste were noted to increase with the weathering duration. The unexposed samples of the blends has a peak point of 108 °C while the samples exposed to accelerated weathering ranged between 111 and 115 °C. The increase in the peak values can also be attributed to the chain breaking brought by the photo-degradation as noted previously with PO polymers constituting the blends in this work [51].

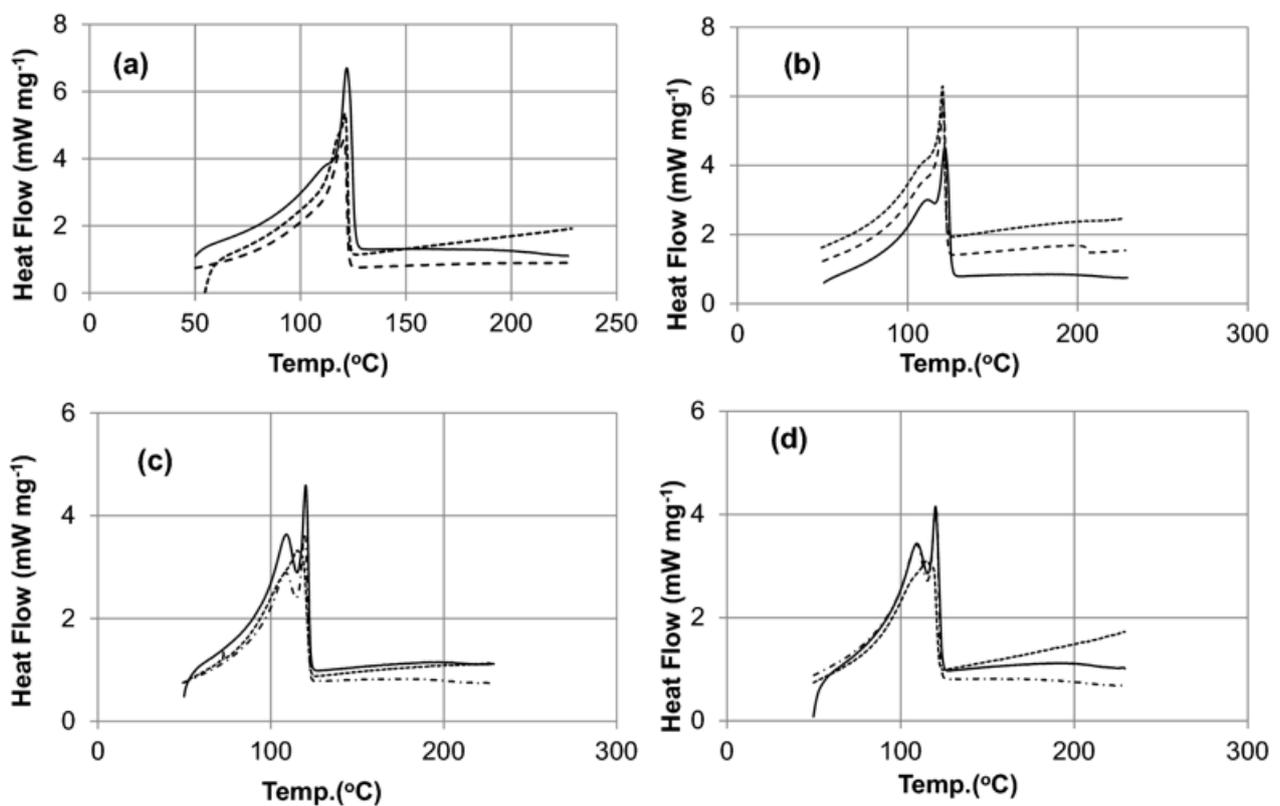


Fig. 1

DSC calorimetric thermogram for **a** 100/0, **b** 75/25, **c** 50/50 and **d** 25/75. Materials showing results obtained for: line: unexposed; dotted line: midpoint and threshold limit; (-.-.): duration of Exposure

OIT analysis was conducted in this work to provide a comparative assessment of the samples degradation and thermal stability in oxygen atmospheres. The dynamic (non-isothermal) scans revealed that the materials are susceptible to weathering. The OIT results are depicted in Fig. 2. The changes in OIT are taken as an indicator to the materials performance in real-life (natural) exposure scenarios. A notable reduction can be seen in the virgin LLDPE (100/0) samples where the OIT has decreased from 200 to 181 °C with respect to the 15 days weathering duration (Fig. 2). LLDPE possess a linear structure that is susceptible to chain breakage with weathering [18, 21, 29]. This leads to the reduction in thermal stability in oxygen atmospheres which also

facilitates oxygen permeability as it diffuses with photo-oxidation. The incorporation of the PSW material used in this work leads to the addition of thermally stable reclaimed PO polymers in the form of LLDPE and HDPE to the virgin LLDPE, making up an accumulative amount of 47 wt% of the waste. This is of course in comparison to LDPE and PP, which are noted to be less thermally stable in oxygen environments [28].

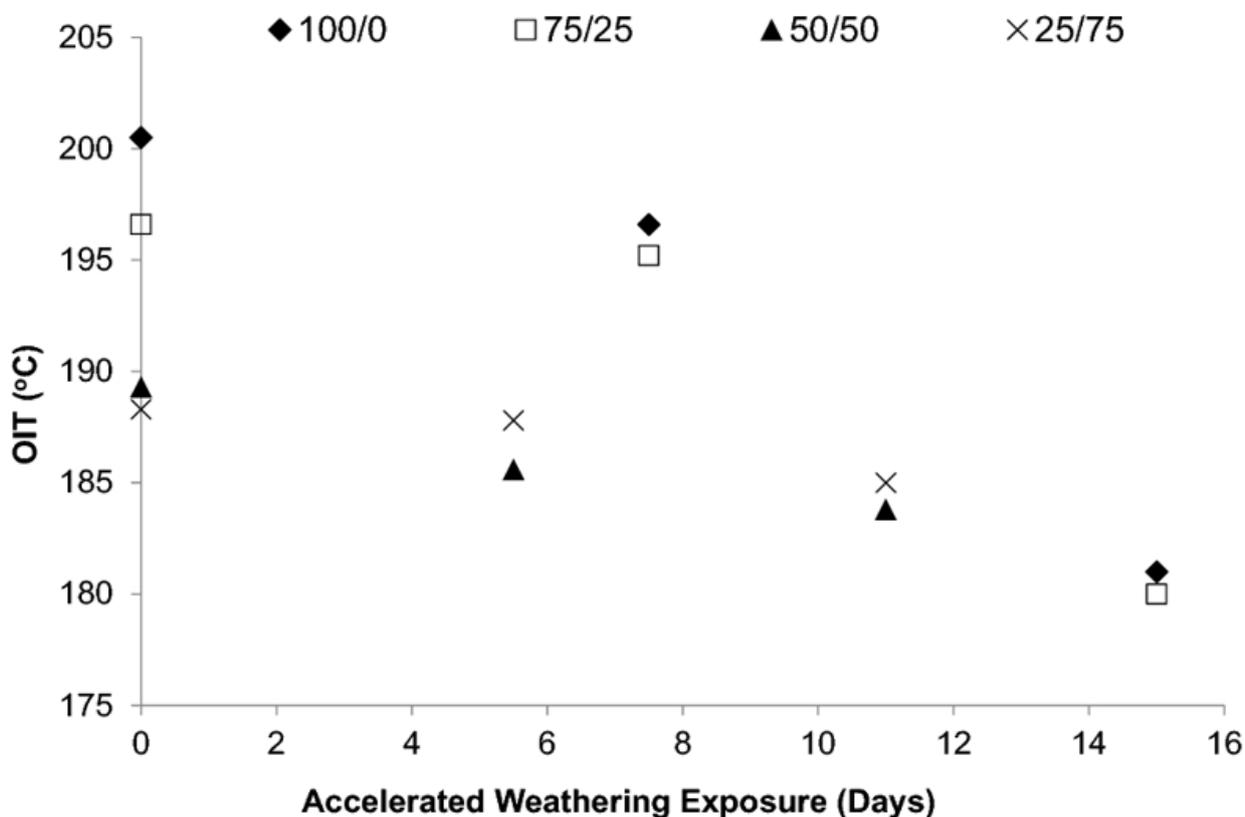


Fig. 2

Variation in oxidation induction temperature (°C) estimated from DSC scans in reactive atmosphere as a function of accelerated weathering time (days)

Gulmine et al. [19] noted that tertiary carbon radicals are more thermally stable than primary and secondary ones present in abundance in LDPE. This is due to their stimulation in DSC scans in reactive atmospheres (e.g. oxygen) for the case of LDPE leading to a lower thermal resistance by comparison to other PO polymers. This can be supported by the findings in this work, where a noted reduction for all blends is witnessed for unexposed (control) samples. However, as the bulk of the blends consists of LLDPE, the change in OIT is very subtle. The OIT estimated for the 75/25 blends hardly changes within the first 7.5 days of exposure (≈ 196 °C) and reaches 180 °C by the end of the accelerated weathering test. In the case of the 50/50 and 25/75 blends, the OIT for the unexposed samples was estimated as 188 °C and 189 °C, respectively. The value was estimated as 183 °C and 185 °C for the 50/50 and 25/75 blends by the 15 days mark, respectively (Fig. 2).

Thermogravimetry was also used to study the weight loss of the materials and their thermal stability. To study the behaviour of the samples, degradation behaviour and their thermal response, the TGA thermograms onset temperature (T_{os} , measured at 5 wt% loss), midset temperature (T_{ms} , at 50 wt% degradation), maximum degradation temperature (T_{max}) and inflection point (T_{if}) are reported in Tables 2, 3, and 4 for the various materials. Figure 3 also shows an example of the TGA thermograms for the weight loss and first derivative (DTG) against

temperature reporting the behaviour of the 100/0 (LLDPE) samples before exposure to accelerated weathering. The incremental shift in the weight loss responding to the change in heating rate (β) is attributed to the change in the LLDPE degradation mechanism with faster degressive reaction time [42].

Table 2

TGA thermograms for the unexposed materials

Sample formulation (virgin/waste) (wt%)	Heating rate ($^{\circ}\text{C min}^{-1}$)	Onset temperature ($^{\circ}\text{C}$)	Midset temperature ($^{\circ}\text{C}$)	Maximum temperature ($^{\circ}\text{C}$)	Inflection point ($^{\circ}\text{C}$)
100/0	5	404	448	512	452
	10	415	460	526	464
	15	422	468	536	473
	20	427	473	542	478
	25	430	478	547	483
75/25	5	404	448	511	451
	10	415	460	528	464
	15	422	468	537	473
	20	427	473	544	479
	25	430	478	549	485
50/50	5	404	448	512	453
	10	415	461	527	465
	15	422	468	536	472
	20	427	474	543	479
	25	430	478	546	483
25/75	5	404	448	512	452
	10	415	461	526	465
	15	422	468	535	472
	20	427	474	542	478
	25	430	478	547	484

Table 3

TG thermograms for the materials exposed to midpoint duration

Sample formulation (virgin/waste) (wt%)	Heating rate ($^{\circ}\text{C min}^{-1}$)	Onset temperature ($^{\circ}\text{C}$)	Midset temperature ($^{\circ}\text{C}$)	Maximum temperature ($^{\circ}\text{C}$)	Inflection point ($^{\circ}\text{C}$)
	5	404	448	512	453
	10	415	460	527	466

Sample formulation (virgin/waste) (wt%)	Heating rate (°C min⁻¹)	Onset temperature (°C)	Midset temperature (°C)	Maximum temperature (°C)	Inflection point (°C)
100/0	15	422	468	536	474
	20	426	473	543	480
	25	430	477	548	484
	5	404	447	512	454
	10	415	459	527	466
75/25	15	421	467	536	474
	20	426	473	543	482
	25	430	477	548	484
	5	404	448	512	454
	10	414	460	527	466
50/50	15	421	467	537	474
	20	426	473	544	479
	25	430	477	548	483
	5	404	448	512	453
	10	415	461	526	466
25/75	15	422	468	544	473
	20	426	474	549	479
	25	430	478	547	483

Table 4

TG thermograms for the materials exposed to threshold limit

Sample formulation (virgin/waste) (wt%)	Heating rate (°C min⁻¹)	Onset temperature (°C)	Midset temperature (°C)	Maximum temperature (°C)	Inflection point (°C)
	5	404	448	513	453
	10	414	460	528	456
100/0	15	421	467	537	473
	20	426	473	543	480
	25	430	477	549	485
	5	404	447	512	454

Sample formulation (virgin/waste) (wt%)	Heating rate (°C min ⁻¹)	Onset temperature (°C)	Midset temperature (°C)	Maximum temperature (°C)	Inflection point (°C)
	10	414	460	527	466
75/25	15	421	467	536	475
	20	426	473	543	483
	25	430	477	548	485
	5	404	448	512	453
	10	414	460	526	465
50/50	15	421	468	543	473
	20	426	473	549	479
	25	430	477	547	483
	5	404	448	515	453
	10	414	460	529	465
25/75	15	421	468	543	473
	20	426	473	549	479
	25	430	477	549	483

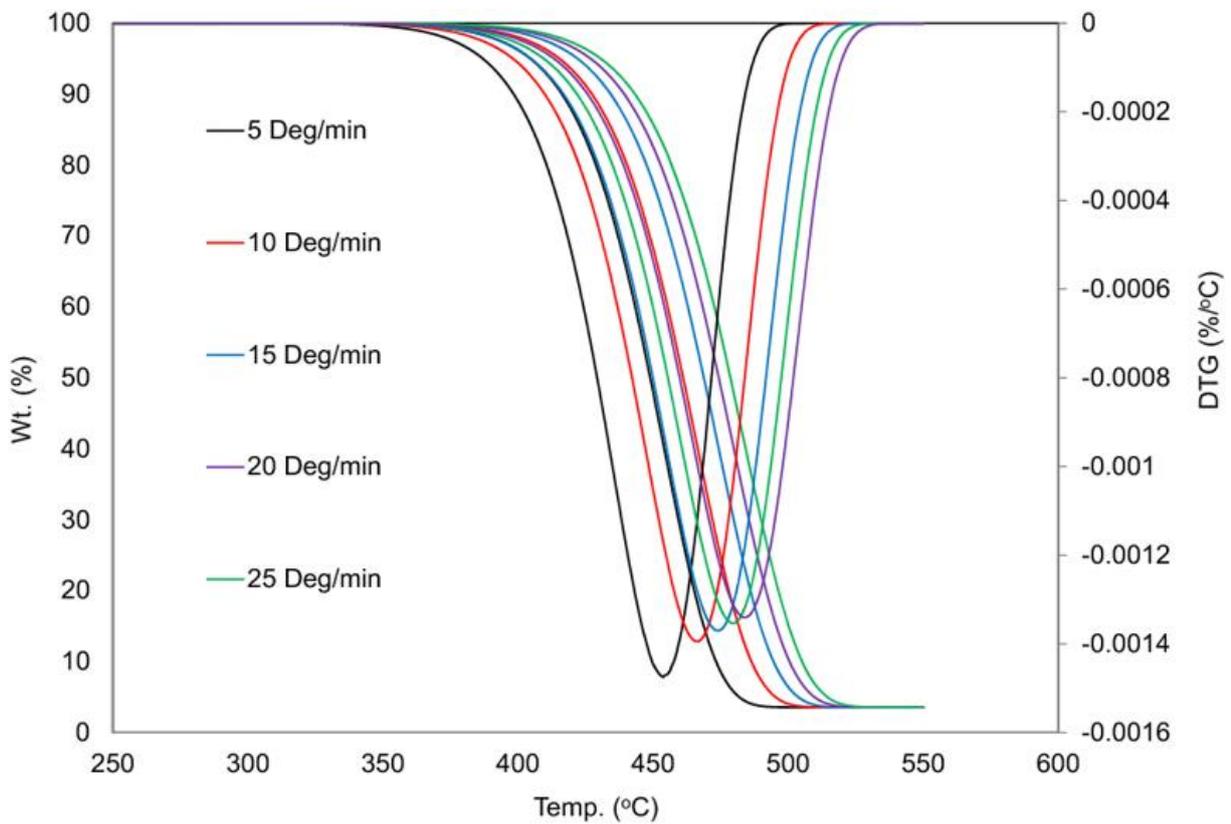


Fig. 3

TGA thermogram of the 100/0 unexposed sample in N₂ atmosphere

T_{os} for the unexposed 100/0 samples (also the peak point of the DTG curve) ranged between 404 and 430 °C. This is in agreement with past reports for LLDPE TG behaviour [52]. There was a notable change in the T_{ms} and T_{if} depending on the change in the heating rate (β) used. This can be attributed to the increase in the rate of chain scission reaction and the evolution of free radicals in PE degradation mechanism [53]. There was no clear distinction in the TGA thermograms for the virgin LLDPE samples after both spans of UV exposure of 7.5 days and 15 days (Tables 3, 4). This is with the exception of the T_{if} which increased proportionally as a exposure to time increased. This behaviour was previously reported by Weon [54] relating it to the acceleration of cross-linking process initiation and the cross-linking density in aged LLDPE. In the case of the blend materials, it was noted that specimens subjected to thermogravimetry did not show more than one stage of decomposition unlike past investigations on polymer blends [41, 42].

The TGA thermograms supported PE degradation behaviour. This can be related to the fact that PP represented only 2% by weight of the PO waste used. The 75/25 samples showed a decrease in the start of degradation point (T_{os}) and the T_{ms} as UV exposure progresses. This can be related to reduction in molecular weight of the material as a consequence of the weathering [44]. Figures 4 and 5 show a representation of the 50/50 TGA thermograms for the unexposed and exposed materials to 7.5 and 15 days of weathering, respectively. The value of the T_{os} did not change with waste content addition. In fact, the constant value of T_{os} reported in this work indicates thermal stability for industrial mass production of the blends studied. The stable T_{os} indicates that processing and manufacturing temperature profile could be similar for the blends studied [22]. At β value equal to 25 °C min⁻¹, it can be noted that T_{max} shifts to higher values (Tables 3, 4). This indicates that the thermal stability for a prolonged service life of the blends can alter in real-life conditions. The same was noted for the 25/75 blends and supported by findings of the DSC studies conducted in this work where the increase of cross-linking is suspected after 7.5 days of accelerated weathering (Table 4). Taking into consideration the natural weathering correlation established previously, the thermal analysis of the samples reveals that the blends with 75% of PO PSW can substitute the virgin LLDPE films for outdoor service with a duration of 1 year. The various TGA thermograms are illustrated for the readers' consideration as Supplementary Material (Figs.S1-S8).

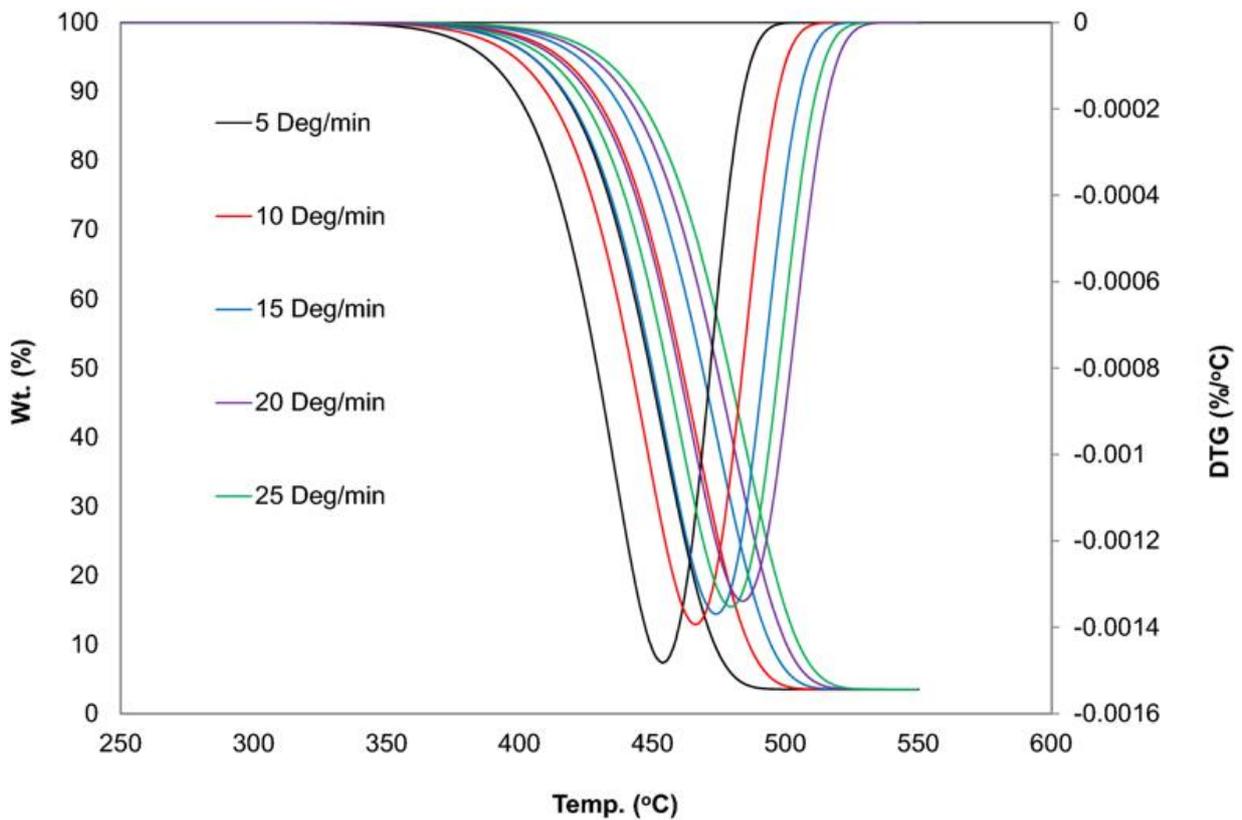


Fig. 4

TGA thermogram of the 50/50 unexposed sample in N₂ atmosphere

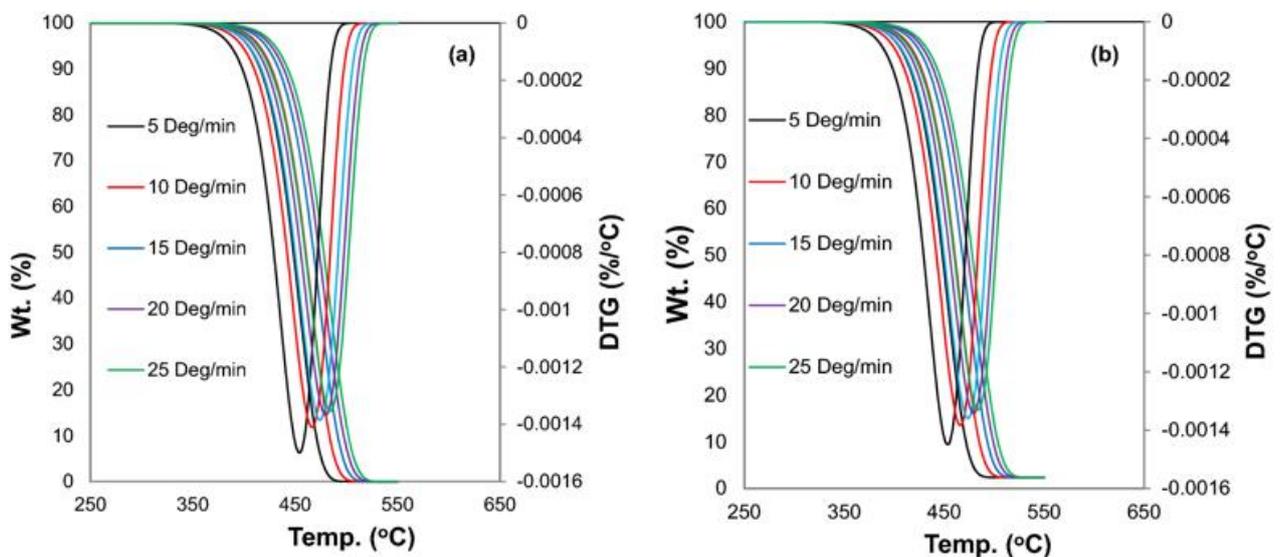


Fig. 5

TGA thermogram of the 50/50 samples exposed to **a** 7.5 days and **b** 15 days in N₂ atmosphere

FTIR-spectroscopy

Spectroscopy using ATR is a useful technique noted for detecting the absorption in the range of mid-infrared region. This is considered ideal for our case mainly to be able to detect the polymers surface degradation. The distinctive absorption peaks are listed in sequential order with their assigned groups (Table 5). The prominent peaks noted for the aged LLDPE and LLDPE/waste bands were observed between 1770 and 1698 cm⁻¹. Figure 6 shows the main differences witnessed for the virgin LLDPE (100/0) material exposed to accelerated weathering. The material

used in this work is of a commercial grade used for film extrusion. There were two notable bands in the regions between 2800 and 3000 cm^{-1} , and 1600–1800 cm^{-1} . Both intervals were noted to become more broader with increase in weathering duration. Both regions are related to light-transforming additives and UV stabilisers embodied in commercial PO resins. The former band region is related to the phenolic OH chemical group present in Irganox additive whilst the latter corresponds to aromatic rings (C=C) in antioxidant and stabilisers [19]. In the case of the blend materials, the same regions mentioned previously were clearly notable and can be seen to be more pronounced with increasing waste content (see Figs.S9–S10). This can be attributed to the fact that PO polymer grades used will typically include stabilisers and antioxidants that are used in more abundance for HDPE and LDPE plastics. This is due to consumers demand on these grades are their application for outdoor service. The 25/75 material exposed to 15 days of weathering has both regions showing prominently even after clear evidence of oxidation due to weathering as discussed below (Fig.S10-S11). The band at 1640 cm^{-1} was showing in the spectra of the materials and can be seen to be more prominent for the recycled polymers. This band can be linked to the double bonds between carbon as a consequence of PE thermal-oxidation (at processing stage) and degradation [54]. The band was more prominent after exposure to UV in the accelerated weathering chamber as a result of the double-bond formation due to PE photo-degradation.

Table 5

Assignment of absorption bands of IR spectrum

Wave number (cm^{-1})	Assigned group/product	References
2915	CH ₂ Stretching of CH ₂ , CH ₃ (asymmetrical)	Matuana et al. [55]
2847	CH ₂ Stretching (symmetrical)	Matuana et al. [55]
1770	C=O Stretching (lactone)	Gulmine et al. [19]
1733	C–O Stretching (ester/aldehyde)	Gulmine et al. [19]
1714	C=O Stretching (ketone)	Gulmine et al. [19]
1470	PE band	D'Amelia et al. [56]
1698	C=O Stretching (carboxylic acid)	Gulmine et al. [19]
730	CH ₂ Rocking vibration, crystalline	Matuana et al. [55]
718	CH ₂ Rocking vibration, amorphous	Matuana et al. [55]

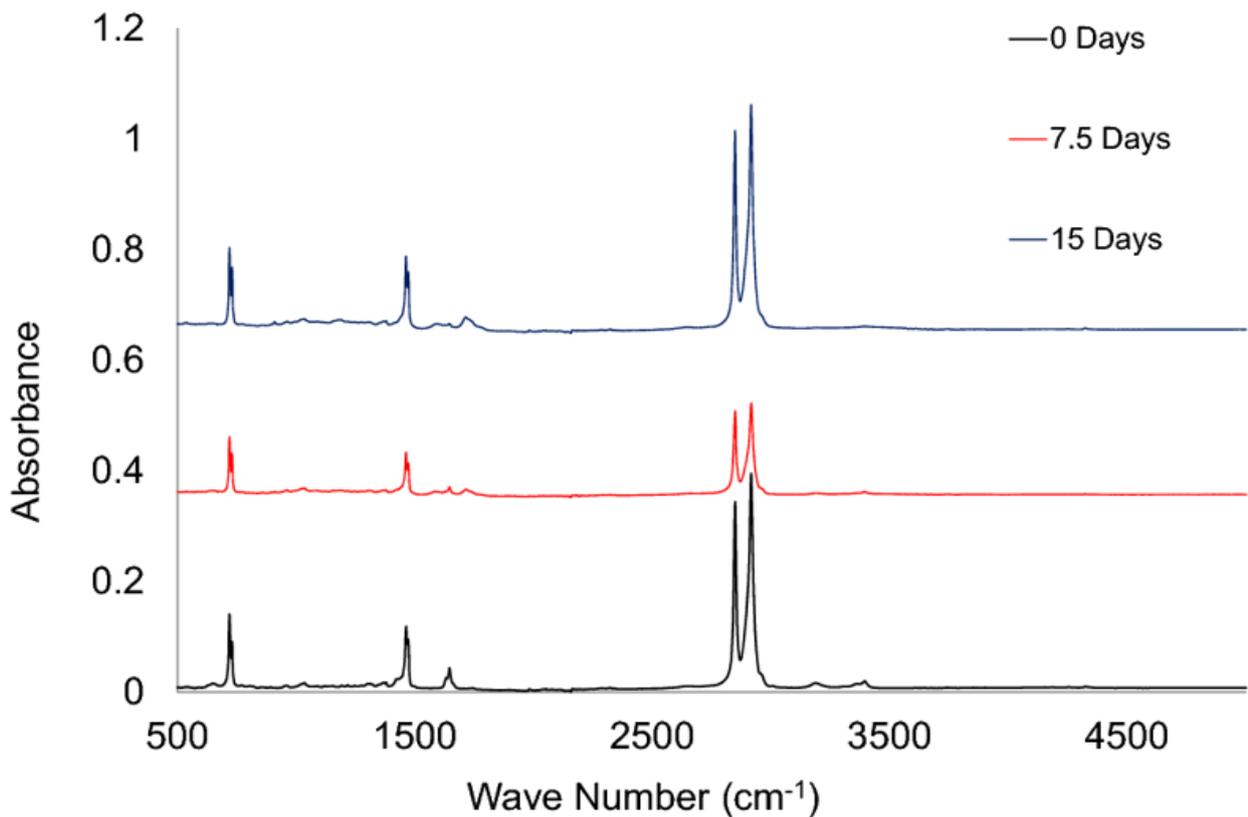


Fig. 6

FTIR-ATR spectra for the 100/0 samples exposed to accelerated weathering
Adapted from Al-Salem [59]

Salt deposition resulting from the water spray inside the QUV chamber was also noted on the FTIR spectra in the region between 960 and 1100 cm^{-1} . The C=O stretching vibration of a ketone absorption band (1714 cm^{-1}) became more pronounced as the weathering exposure started to increase. This band grew in intensity with more exposure to UV. Other bands also started to appear in all the studied samples as illustrated in Fig. 7. This indicates that more than one product as a result of the oxidation process started to evolve as a consequence of the PO polymer degradation. These bands were all assigned to stretching vibration of carbonyl groups.

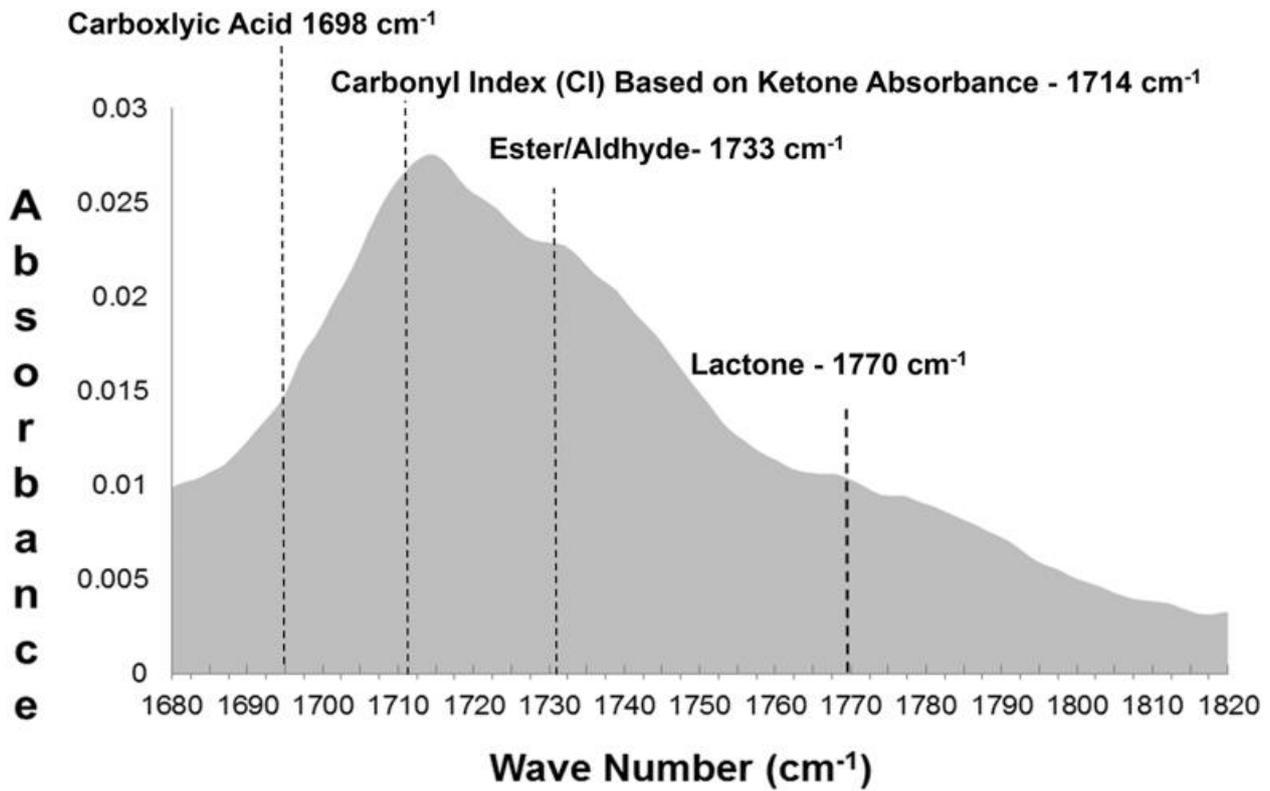


Fig. 7

The spectrum of FTIR for LLDPE and LLDPE/waste blends during the accelerated weathering process showing the formation of bands assigned to carbonyl groups formed by the polymer oxidation processes

To qualitatively assess the changes in the samples studied, the product bands shown in Fig. 7 were used to calculate a number of indices with respect to the PE band absorbance at 1470 cm^{-1} . First, the carbonyl index was estimated as the ratio of the carbonyl group, namely the ketone stretching band, and that of the PE band thus:

$$CI = \frac{\text{Absorbance at } 1714\text{ cm}^{-1}}{\text{Absorbance at } 1470\text{ cm}^{-1}} \quad (1)$$

The band of ketone was the most pronounced out of all carbonyl group products, hence it was considered for the CI calculation. The other product indices were estimated after examining the carbonyl band evolution, and the products targeted were as per the following: lactones, esters/aldehydes and carboxylic acid. Each of these products were assigned an index that was calculated as shown below to monitor the extent of degradation in relation to the reference peak of the PE band:

$$\text{Lactone index} = \frac{\text{Absorbance at } 1770\text{ cm}^{-1}}{\text{Absorbance at } 1470\text{ cm}^{-1}} \quad (2)$$

$$\text{Ester/Aldhyde Index} = \frac{\text{Absorbance at } 1733\text{ cm}^{-1}}{\text{Absorbance at } 1470\text{ cm}^{-1}} \quad (3)$$

$$\text{Carboxylic acid index} = \frac{\text{Absorbance at } 1698\text{ cm}^{-1}}{\text{Absorbance at } 1470\text{ cm}^{-1}} \quad (4)$$

The results of the variation in CI with respect to weathering exposure duration and type of material are shown in Fig. 8. The evolution with exposure time was evident for all the materials

studied. The addition of the waste by 25 wt% stabilised the oxidation and reduced the magnitude of CI. However, an incremental increase was noted by comparison for the 50/50 and 25/75 blends. The addition of waste increases the cross-linked area in the materials. The cross-linking of the materials occurs due to a combination of the reclamation/recycling process and the UV exposure. The reduction of the CI for the 75/25 blend can be related to the increase in content of HDPE and LLDPE which are noted to be more stable PO polymers than LDPE [21]. This behaviour was previously confirmed by the OIT analysis shown in the previous section. On the other hand, the blends have shown an increase in CI magnitude with weathering time and it was noted that the increase in recycled LLDPE and HDPE content will stabilise the trend despite the suspected increased in the cross-linking density. Bernstein et al. [57] showed that ketones will form in the process of PP degradation as a result of the scission of the carbon bonds between the carbon in the methylene and the tertiary carbon. This will ultimately lead to the formation of methylene ketones as a chain end. Their results can explain the increase of the ketone evolved as a consequence of the increase in waste content which has 2% by weight of PP in this study (Fig. 8). The same behaviour of the oxidation products indices was noted for the specific oxidation products that started to evolve as a consequence of the photo-degradation (Fig. 9).

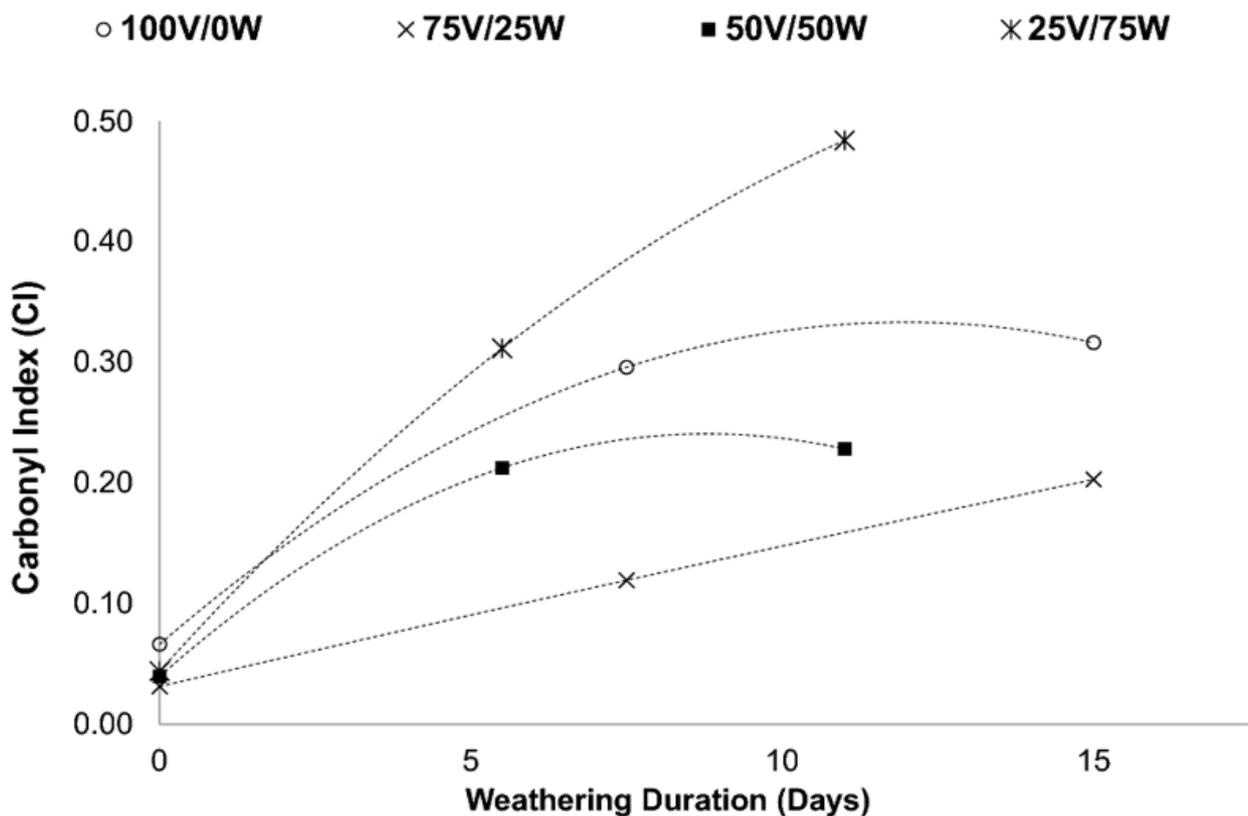


Fig. 8

Variation of carbonyl index (CI) as a function of the accelerated weathering time for the materials considered in this work

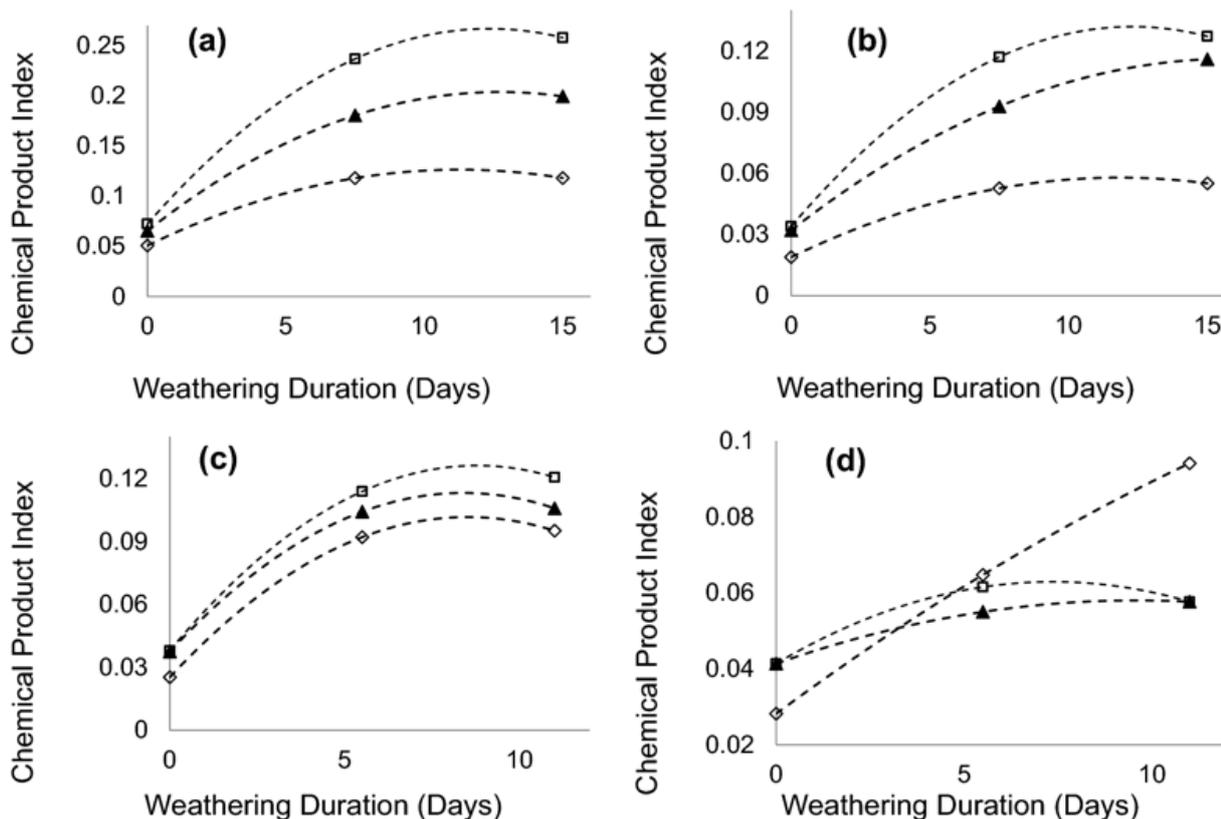


Fig. 9

Variation of diamond: lactone index; square: ester/aldehyde index, filled triangle: carboxylic acid index for samples of **a** 100/0 [59], **b** 75/25, **c** 50/50 and **d** 25/75

Ketones evolve from the PE polymer degradation can lead to the formation of alkyl and acyl radicals by a Norrish type I mechanism [57]. The acyl radicals further react to produce peracids after their reaction with oxygen to form hydroxyl and carboxy radicals. These radicals lead to the increase in the prominence of the bands 1698 cm^{-1} which can be noted to be on the increase with blends containing more PE (Fig. 9a, b). Ester groups are noted to be produced from the carboxylic acid and other hydroxyl groups that result from PE oxidation [58]. Hence, they have been noted to have a compensation effect with respect to exposure duration as quantified by their index (Fig. 9). The increase in PP content will aid in the formation of lactone and vinylene as a result of its degradation as noted previously by Rajkumar et al. [23] as a consequence of hydrogen subtraction (Fig. 9d).

Morphological analysis

Figure 10 shows the photomicrographs of the unexposed samples to accelerated weathering. It can be noted that visible micro-cracks or defects were not detected on the surfaces. Scratches on the surface of the specimens can be attributed to the processing/compounding of the film samples. The scratches on the surfaces can also be related to the cutting of the samples for the SEM analysis. This leads to perpendicular cracks and scratches on the surfaces as noted previously in past works [19, 43]. The virgin LLDPE surface was particularly smooth as compared to the rest of the materials studied (Fig. 10a). As waste content increases, the incompatibility of the polymeric matrix starts to show signs on the morphology of the samples. This could be clearly noticed in the 50/50 and the 75/25 samples (Fig. 10c, d). This could be due to the fact that the plastic waste was reclaimed and processed various times and as a consequence of continues thermal loops it shows immiscibility evidence when blended with the virgin polymer

without any chemical additives or binders [22] The 75/25 samples shows evidence of the lack of matrix bonding and increases in pull-out between the virgin and waste PO polymers (Fig. 10d).

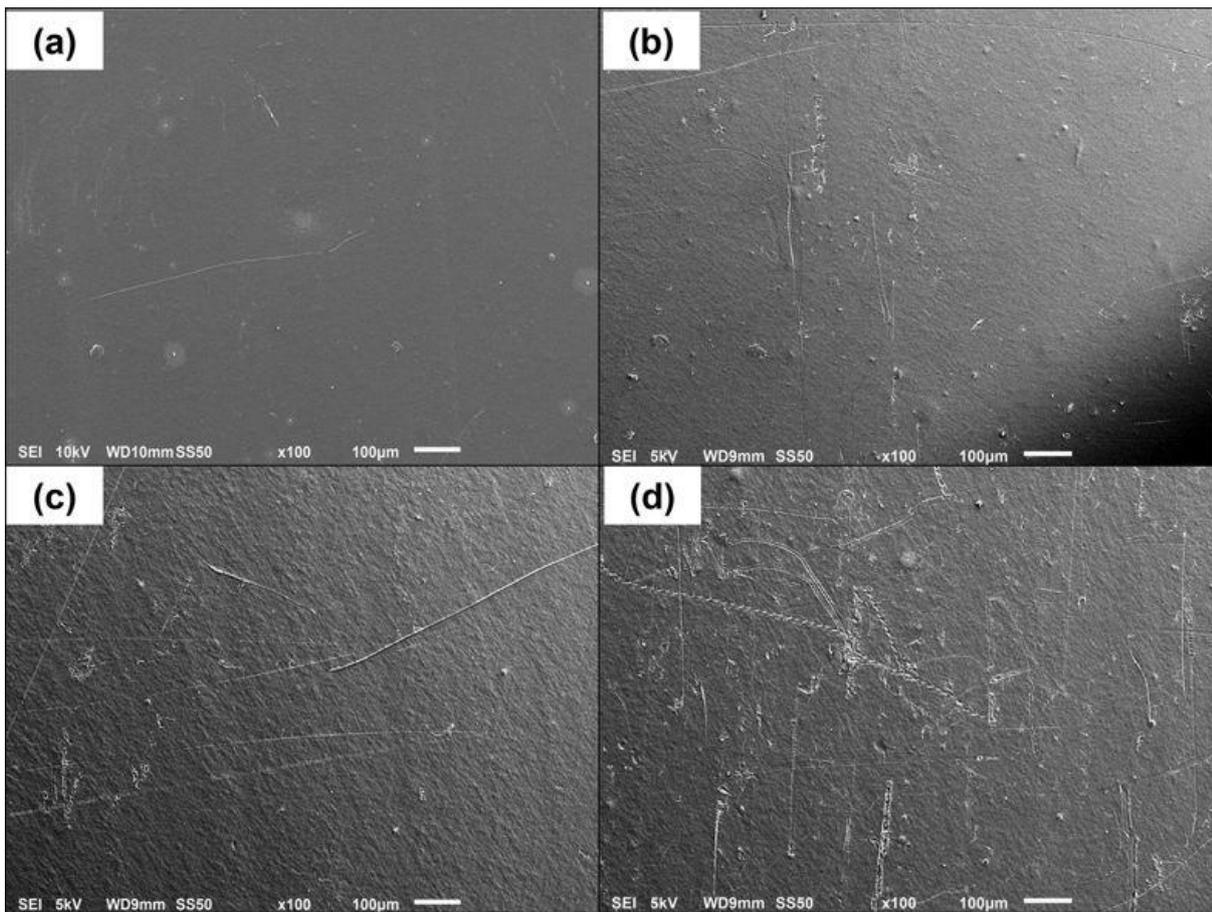


Fig. 10

SEM micrograph of unexposed samples; **a** virgin LLDPE (100/0), **b** 75/25, **c** 50/50 and **d** 25/75 blends

Signs of deterioration started to appear with UV exposure. The 100/0 samples exposed to continuous weathering for the period of 7.5 days started to show surface cracks that accompanied puncture holes on the surfaces (Fig. 11a). The 75/25 blend showed clear and visible cracks as a result of photo-degradation (Fig. 11b–d). Mosaic patterns in the blend samples started to propagate with accompanied surface holes. By comparison to other specimens, it can be noted that the 50/50 and 75/25 samples exposed to 5.5 days of accelerated weathering were clearly more deteriorated on the surfaces as seen in Fig. 12. This leads to the fact that both virgin and waste material will result in an accelerated deteriorating effect due to lack of binder presence as the waste content increases. In combination with the previous analysis conducted, it can be noted that the most appropriate and stable product for market upgrading is the 75/25 blend. This shows the ability of developing mechanically recycled blends for market applications resulting from PSW in Kuwait. Surface cracks and punctures with a diameter exceeding 3 µm were noted on the samples exposed to threshold limit of degradation (Fig. 13). There was no phase segregation notable even after weathering which is due to the fact that all polymers were PO.

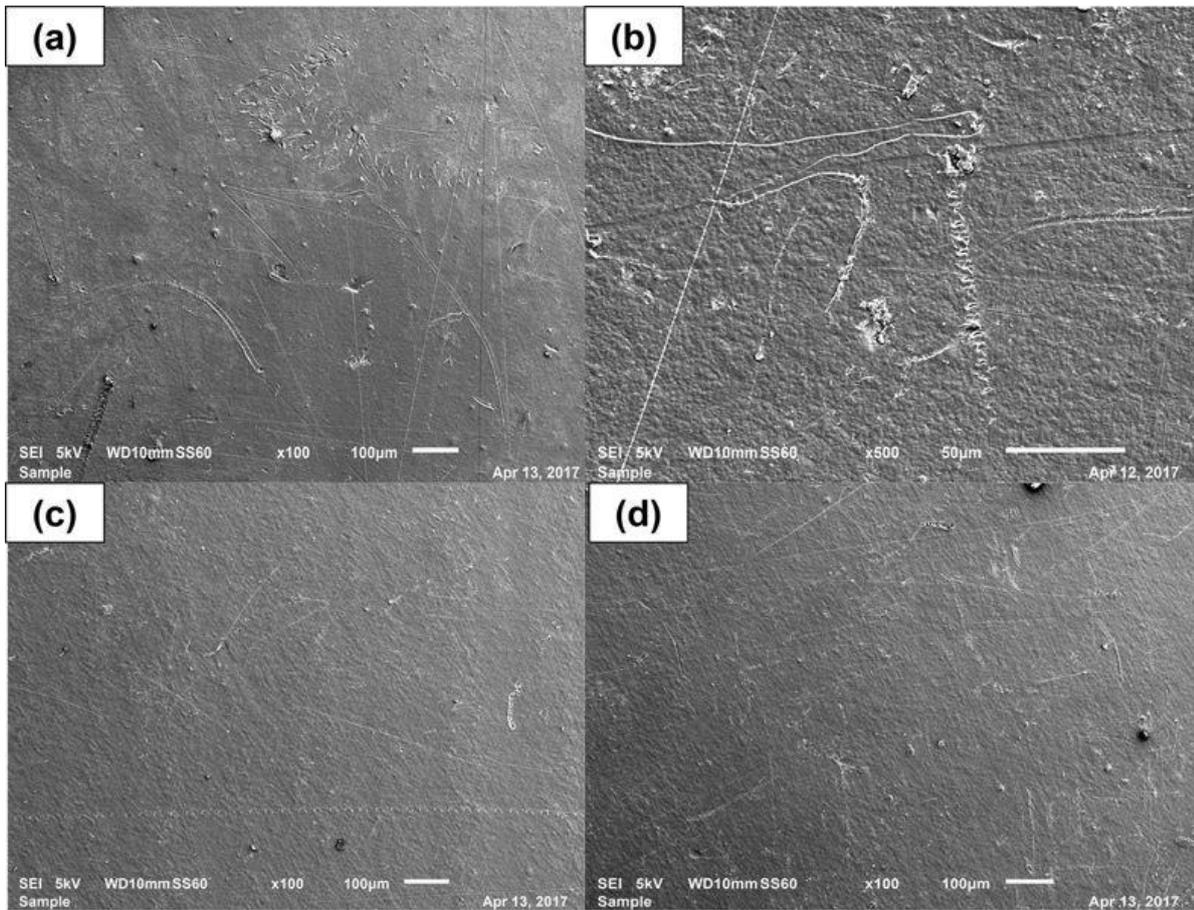


Fig. 11

SEM micrograph of samples exposed to midpoint of degradation; **a** virgin LLDPE (100/0), **b** 75/25, **c** 50/50 and **d** 25/75 blends

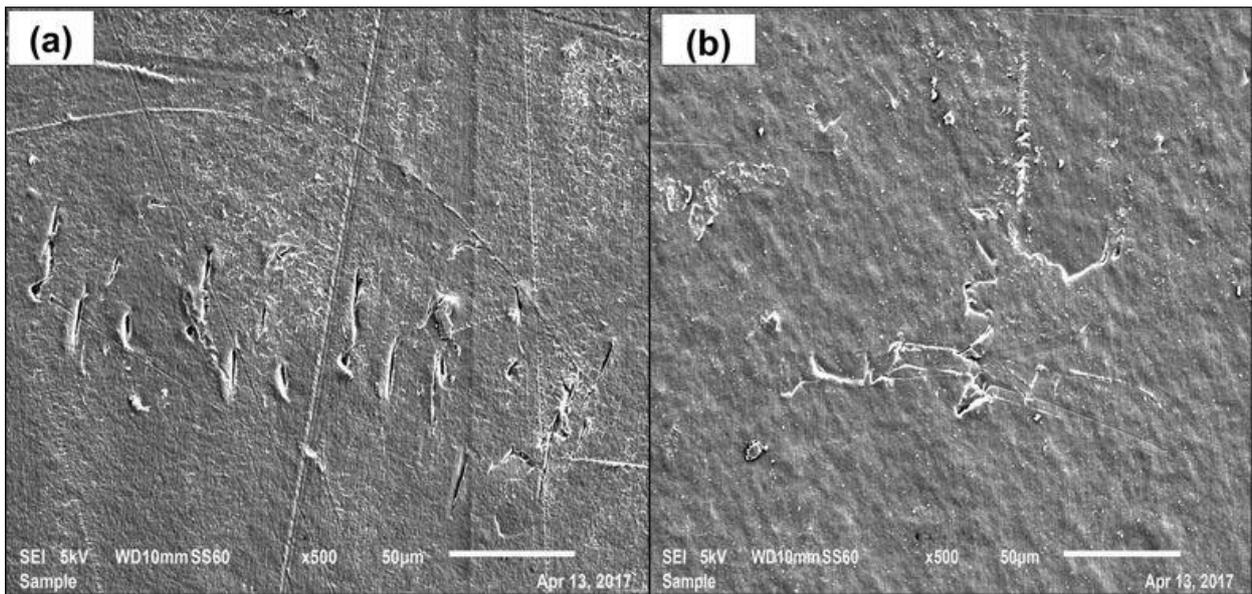


Fig. 12 Propagation of surface micro-cracks on the **a** 75/25 and **b** 50/50 blends samples after 7.5 and 5.5 days of accelerated weathering, respectively

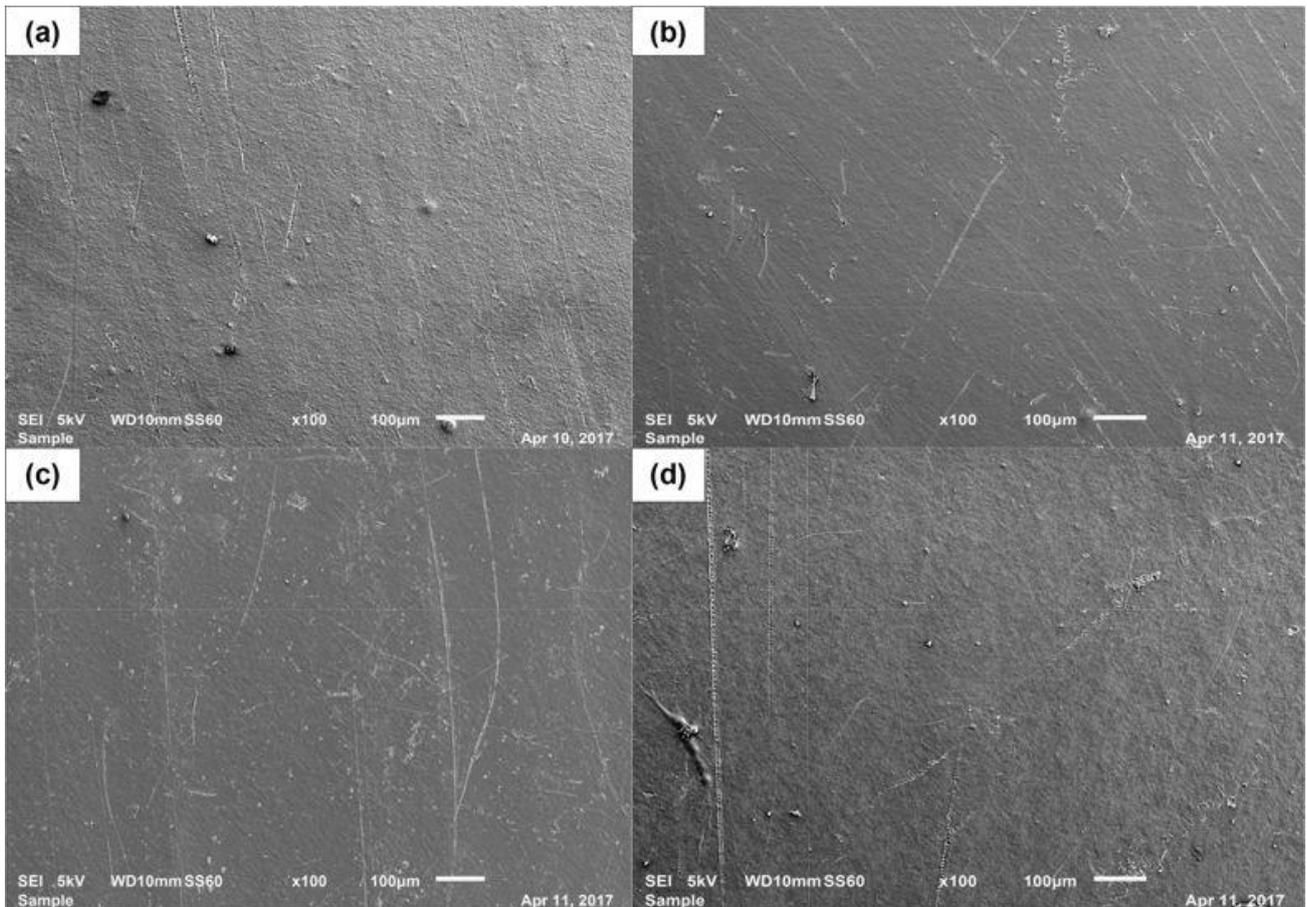


Fig. 13

SEM micrograph of samples exposed to threshold limit; **a** virgin LLDPE (100/0), **b** 75/25, **c** 50/50 and **d** 25/75 blends

Conclusions

Blends of virgin LLDPE and plastic waste were studied under different accelerated weathering durations. The waste material was incorporated by 25–100% (by weight) to showcase the degradation profile of the specimens with respect to different formulations. Thermal characterisation has revealed the behaviour under different conditions, which can be used as a guideline for product development and future modifications. The waste material was previously exposed to various heating cycles and thermo-mechanical degradation conditions. This was a major influencing factor on the degradation profile detected in the waste-rich formulations studied in this work. The degree of crystallinity was noted to be consistent before exposure to weathering tests. Minor changes with respect to the degree of crystallinity were noticed as weathering progresses as a consequence of the change in crystal size. The 75/25 samples showed a change in crystallinity toward midpoint of weathering time resulting in a 41% degree of crystallinity from the 35% originally estimated. This was related to the immiscibility of the polymers and crystal size change due to oxidation. This is supported with the detected energy absorption curves noted in the DSC analysis. The structure of the LLDPE was also noted to be influential in the changes notable in the oxidation induction temperature (OIT) analysis carried out in this study. From the thermogravimetry and DSC studies conducted, the 75/25 was noted to be most stable and can be used as a good material for product development applied for indoor and outdoor purposes. The morphological analysis has led to the detection of mosaic cracks in all directions that progressed as weathering took place. However, the reduction in the carbonyl index determined from the FTIR spectra of the 75/25 supports the claim of the relative stability of the

blend. The work conducted in this study can benefit from density measurements and EDS analysis to support some of the experimental findings. This can lead to the development of a product from waste plastic material that reduced the burden of accumulation in developing and developed societies alike. The thermal degradation kinetics of the blend material should be assessed in the future to determine the materials recycling potential and viability via thermal and chemical means.

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