Full length article

Simulating the recycling of milk bottles in the UK: Influence of blending virgin and repeatedly melt-extruded high-density polyethylene

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ABSTRACT

The UK Dairy Roadmap has set a target of achieving 50 wt.-% high density polyethylene (HDPE) recyclate in their HDPE milk bottles. Such high recyclate content will lead to the accumulation of HDPE recyclates that have been subjected to different number of melt extrusion cycles in the supply chain. This work investigates the structure-property relationship of blending virgin HDPE (vHDPE) with these different grades of repeatedly melt-extruded HDPE (rHDPE). HDPE was subjected to 10, 20 and 50 melt-extrusion cycles and blended with vHDPE. No significant difference in terms of melt rheology, tensile properties and overall migration in acidic and aqueous environments of the blends of the different rHDPEs with vHDPE was observed when compared to vHDPE. This study demonstrates the feasibility of blending up to 50 wt.-% rHDPE of different grades with vHDPE as set out in the UK Dairy Roadmap.

1. Introduction

In the 2018 United Kingdom Budget, a new tax on plastic packaging manufactured in or imported into the United Kingdom with less than 30 wt.-% recycled content was announced. The rate of tax is £200 per tonne and has taken effect from the 1st April 2022 (H.M. Government, 2022). The UK government estimates that this initiative could lead to *ca.* 200, 000 tonnes of carbon savings. As consumers are price sensitive, it is highly unlikely that this tax cost will be transferred down the supply chain as the retailers would keep their product prices down to increase product sales. Therefore, product manufacturers will be forced to absorb this tax cost. Based on the estimate that *ca.* 2.3 million tonnes of plastic packaging are placed on the UK market every year (WRAP, 2021), the plastic packaging tax will cost product manufacturers an additional £480 million annually. This provides a clear economic incentive for businesses to increase the recycled content of their plastic packaging. In addition to this, a recent survey among a wide UK demographic indicated that 93% of the UK population expect their plastic packaging to contain recycled materials (RECOUP, 2018). The combination of public's growing demand for plastic packaging with lower carbon footprint

and environmental legislative pressure on businesses has stimulated research into the reuse and recycling of post-consumer plastics, diverting them away from landfill and incineration (Schyns and Shaver, 2021; Singh et al., 2017).

The incorporation of post-consumer recyclates (PCRs) into plastic packaging still represents a significant technical challenge particularly for food contact applications (Cecon et al., 2021; Vogt et al., 2021). Contaminants from PCRs may appear in the final food-contact plastic packaging product. Due to inefficient sorting, PCR materials that are not regulated for food-contact use may be accidentally incorporated into food-contact packaging containing PCRs. Nonetheless, the UK dairy industry has made a real progress towards the use of PCRs in high density polyethylene (HDPE) milk bottles. Since 2008, efficient closed loop HDPE recycling infrastructure is in place in the UK, which covers the collection and sorting of post-consumer HDPE bottles, as well as grinding, washing and melt-extrusion of the sorted HDPE to produce clean HDPE recyclates (Biffa, 2019). These recyclates are then sent back to milk bottle manufacturers to be melt-compounded with virgin HDPE to produce new milk bottles (Smith et al., 1999; Welle, 2005).

Numerous studies have investigated the effect of recycling on the

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properties of HDPE. A study by Loultcheva et al. (1997) has shown that the repeated melt extrusion of HDPE up to 5 cycles in a twin-screw extruder did not reduce the melt viscosity and the tensile strength of the HDPE significantly. Similar observation was also reported by other studies that have subjected HDPE to up to 10 melt-extrusion cycles (Apone et al., 2003; Boldizar et al., 2000; Strömberg and Karlsson, 2009). When HDPE is repeatedly melt-extruded by more than 20 cycles, structural changes to HDPE occur. Oblak et al. (2015) reported that chain scission becomes dominant after the 30th extrusion cycle. As a result, a ~17% reduction in tensile modulus was observed. Similarly, Benoit et al. (2017) found that when HDPE was subjected to 50 melt-extrusion cycles, the tensile strength decreased by 29%, from 24 MPa to 17 MPa. The reduction in the tensile strength is associated with the chain scission of HDPE.

The UK dairy sector is set to improve the design of dairy packaging by increasing the recycled HDPE content in milk bottles to 50 wt.-% in the near future (Dairy UK, 2018). This will lead to a scenario in the future whereby the closed loop supply of HDPE recyclates will consist of HDPE molecules that have been subjected to different number of melt-extrusion cycles. Whilst the influence of recycling on the physical properties of HDPE is well characterised, there is however, very little published information on melt blending different grades of HDPE recyclates, *i.e.*, HDPE that had been subjected to different number of melt-extrusion cycles, with virgin HDPE and its effect on the physical properties of the resulting HDPE blend for food contact packaging applications. Therefore in this work, we report the structure-property relationship of HDPE blends containing virgin HDPE with various grade of HDPE recyclates. The influence of different grades of HDPE recyclates on the molecular weight distribution, rheological properties, colour change, migration of HDPE molecules in acidic and aqueous environments, as well as the mechanical properties of the various HDPE blends are reported and discussed.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) granules (BorPureTM MB7541) were purchased from Borealis AG (Vienna, Austria). 1,2,4-Trichlorobenzene (Honeywell Research Chemicals, purity ≥ 99%), stabilised with 250 ppm of butylated hydroxytoluene (Thermo Scientific Acros, purity ≥ 99%), was purchased from Fisher Scientific (Loughborough, UK). Acetic acid (TECHNICAL, purity ≥ 98%) and ethanol (GPR REC-TAPUR®, purity ≥ 99.8%) were purchased from VWR International Ltd. (Lutterworth, UK). All chemicals were used as received without further purification.

2.2. Preparation of virgin and repeatedly melt-extruded HDPE samples

The various types of HDPE samples prepared in this work were processed using a co-rotating twin-screw extruder (Eurolab XL, ThermoFischer Scientific, Karlsruhe, Germany) equipped with two 16 mm diameter screws. The screw length-to-diameter ratio of the extruder was 25. Virgin HDPE (vHDPE) granules were first fed into the extruder at a rate of 0.5 kg h^{-1} and melt extruded at 170 °C. A screw speed of 30 rpm was used (residence time = 3 min). The extrudate was then pelletised into *ca.* 3 mm long pellets using Haake VariCut (ThermoFischer Scientific, Karlsruhe, Germany). The vHDPE pellets were then subjected to 10, 20 and 50 of the aforementioned melt extrusion-pelletisation cycles and the resulting repeatedly melt-extruded HDPE (rHDPE) are herein termed rHDPE-**10**, rHDPE-**20** and rHDPE-**50**, respectively. To produce binary HDPE blends consisting of vHDPE and rHDPE-**10** (Blend-**1**), vHDPE and rHDPE-**20** (Blend-**2**) as well as vHDPE and rHDPE-**50** (Blend-**3**), the vHDPE and rHDPE pellets were dry mixed in batches of 50 g at a mass ratio of 1:1 prior to subsequent melt compounding. Ternary and quaternary HDPE blends consisting of vHDPE, rHDPE-**10** and rHDPE-**20**

(Blend-**4**) at a mass ratio of 1:1/2:1/2, as well as vHDPE, rHDPE-**10**, rHDPE-**20** and rHDPE-**50** (Blend-**5**) at a mass ratio of 1:1/3:1/3:1/3 were also produced following the previously described dry mixing and melt compounding steps. Fig. 1 presents a schematic diagram showing the screw configuration of the extruder, as well as the various HDPE samples prepared in this work.

2.3. Materials characterisation

2.3.1. Molecular mass of vHDPE, rHDPE and vHDPE/rHDPE blends

Molecular mass distribution was determined using a 1260 Infinity High-Temperature Gel Permeation Chromatography (GPC) (Agilent, Santa Clara, United States) calibrated with polystyrene calibrants (based on refractive index). A Mark-Houwink correction was applied to the results in accordance with ASTM D6474-18. HDPE sample was dissolved in 1,2,4-trichlorobenzene at a concentration of 1.44 mg mL^{-1} for 4 h and the measurement was then conducted at a flow rate of 1.0 mL min^{-1} with an injection volume of 200 μL at 160 °C. The GPC results were analysed using the Agilent GPC/SEC software (version 2.1.9).

2.3.2. Attenuated total reflection fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra of the various HDPE samples were obtained using Spectrum One FTIR spectrometer (Perkin Elmer, Massachusetts, USA). The spectra were collected between 600 and 4000 cm^{-1}. The resolution of the spectra was 2 cm^{-1} and a total of 128 scans were performed to obtain each spectrum.

2.3.3. Discolouration of HDPE

The discolouration of HDPE due to repeated melt-extrusion or blending vHDPE with rHDPE was quantified by evaluating their CIELAB colour space. Prior to the measurement, the samples were compression moulded (Model 4122, Carver, Inc., Wabash, USA) at 180 °C under a weight of 1.5 t for 1 min into circular disks with a diameter of 60 mm and a thickness of 1 mm. The circular disk was then scanned using a flatbed scanner (HP LaserJet Managed MFP E57540dn, HP Inc., California, USA) to produce an image with 300 dpi resolution. The perceptual lightness (L^*), redness-greenness (a^*) and yellowness-blueness (b^*) values were determined using Adobe Photoshop CS6 (version 13.1.2) colour sampler tool. The degree of discolouration of the samples was calculated as the total colour difference relative to vHDPE (ΔE) using (Berns, 2019):

$$\Delta E = \sqrt{\left(L^* - L^*_{\text{vHDPE}}\right)^2 + \left(a^* - a^*_{\text{vHDPE}}\right)^2 + \left(b^* - b^*_{\text{vHDPE}}\right)^2} \tag{1}$$

2.3.4. Rheological properties of vHDPE, rHDPE and vHDPE/rHDPE blends

Rheological measurement was conducted using a Haake MARS 40 rheometer (ThermoFischer Scientific, Karlsruhe, Germany). A 60 mm diameter cone-plate geometry (C60 2°/Ti – 02190045) was used. Prior to the measurement, the various types of HDPE samples were compression moulded following the previously described protocol into 60 mm diameter circular disks with a thickness of 1 mm. The circular disk sample was then placed between the cone and the plate. The axial gap between the cone and the plate was set to be 0.1 mm. A frequency sweep at a constant shear stress of 300 Pa was conducted in oscillatory mode at a temperature of 200 °C from 0.1 to 100 Hz.

2.3.5. Migration of HDPE molecules in aqueous and acidic environments

As repeatedly melt extruding HDPE will lead structural changes and hence, the leeching and migration of lower molecular weight HDPE molecules from the bulk, migration studies of the various HDPE samples in aqueous and acidic environments were conducted in accordance with European Union Commission Regulation No. 10/2011 on plastic materials and articles intended to come into contact with food. The simulant for an aqueous environment was 10% (v/v) ethanol and the simulant for
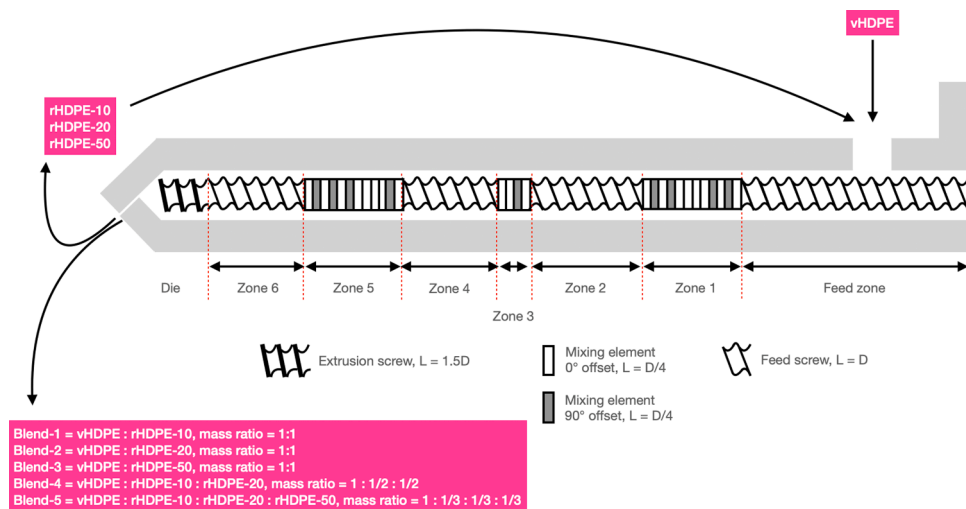
Fig. 1. Schematic diagram showing the screw configuration of the extruder and the various HDPE samples produced.

an acidic environment was 3% (v/v) acetic acid. The various HDPE samples were first compression moulded at 180 °C under a weight of 2 t for 1 min to produce 300 μm thick films. Prior to this characterisation, the films were cut into 15 mm × 15 mm squares using a Zwick/Roell ZCP 020 manual cutting press, rinsed with deionised water and dried in a vacuum oven at 90 °C overnight. The initial weight (w_i) of each film was recorded (Entris124l-1S, Sartorius Lab Instruments GmbH, Göttingen, Germany) prior to immersion in 20 mL of the simulant at 20 °C. The film was taken out of the simulant at different time points (250, 600 and 1200 h) and rinsed with deionised water, followed by oven drying at 90 °C under vacuum overnight to obtain the final weight (w_f) of the film. The overall migration value (*OM*) was then calculated using:

$$OM \; [\text{mg} \, / \, \text{kg}] = \frac{w_i - w_f}{w_{\text{food simulant}}} \qquad (2)$$

where $w_{\text{food simulant}}$ is the weight of the food simulant.

2.3.6. Differential scanning calorimetry (DSC) of HDPE

The crystallisation and melt behaviour of HDPE was characterised using DSC (Discovery DSC, TA Instruments, Elstree, UK). A heat-cool-heat regime was employed. Approximately 10 mg of sample was heated from 20 to 210 °C using a rate of 10 °C min^{-1} before cooling to 20 °C using a rate of 50 °C min^{-1}. The sample was then re-heated to 210 °C using a rate of 10 °C min^{-1}. The crystallinity (χ_c) of the sample was calculated using:

$$\chi_c (\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \qquad (2)$$

where ΔH_m is the melting enthalpy evaluated from the DSC curve and ΔH_m^o is the melting enthalpy of purely crystalline HDPE (301.5 J g^{-1}) (Runt et al., 1980).

2.3.7. Tensile properties of vHDPE, rHDPE and vHDPE/rHDPE blends

Tensile test was conducted in accordance with ASTM D638-14 using a universal testing machine (Model 4502, Instron, High Wycombe, UK) equipped with a 10 kN load cell. Prior to the test, the various HDPE samples were injection moulded using Haake Minijet Pro (Thermo-Fischer Scientific, Karlsruhe, Germany) into dog bone shaped test specimens that possessed an overall length of 65 mm, a gauge length of 10 mm, a thickness of 3 mm and the narrowest width of the specimen was also 3 mm. The barrel and mould temperatures of the injection moulder were set to be 160 °C and 40 °C, respectively. The injection moulding process was carried out at an injection pressure of 650 bar for 30 s, followed by a post-pressure of 650 bar for a further 90 s. Before

mounting the dog bone test specimen on the testing machine, dots were marked on its surface of in the direction of the applied load using a stamp (IMT-ACC001, iMetrum Ltd., Bristol UK). Tensile test was conducted at a crosshead displacement speed of 10 mm min^{-1} (corresponded to a strain rate of 0.1% min^{-1}). The strain of the test specimen was evaluated by monitoring the movement of the previously applied dots in the gauge section using a non-contact optical extensometer (iMetrum Ltd., Bristol, UK). Five specimens were tested for each HDPE sample and the average is reported.

3. Results and discussion

3.1. Molecular mass of vHDPE, rHDPEs and vHDPE/rHDPE blends

The molecular mass distribution of the various HDPE samples prepared in this work is presented in Fig. 2. Table 1 summarises the number-average molecular mass (M_n), weight-average molecular mass (M_w) and polydispersity index (Đ) of the various HDPE samples. Our vHDPE has a M_w of ~106,000 g mol^{-1} and a broad dispersity distribution (Đ = 13.4). When HDPE was subjected to 10 and 20 melt extrusion cycles (corresponding to samples rHDPE-**10** and rHDPE-**20**, respectively), M_w did not change significantly. However, a narrowing of the dispersity distribution was observed. Subjecting HDPE to 50 melt extrusion cycles (corresponding to sample rHDPE-**50**) led to a significant decrease in M_w to only ~69,000 g mol^{-1} and the narrowing of dispersity distribution (Đ = 11.3).

During polymer melt extrusion, shear-induced and oxidative-induced chain degradations are known to affect molecular mass (Gol'dberg and Zaikov, 1987). Shear-induced carbon-carbon scission of the polymer generates alkyl radicals (R·), which can cause the propagation of kinetic chains and the growth of the polymer chains through chain branching (El'darov et al., 1996). Thermal oxidation of the polymer chains during melt extrusion could also occur in the presence of oxygen, generating peroxyl radicals (ROO·) that cause a reduction in molecular mass. It should be noted that oxygen molecules could also react with R· to produce ROO· and the reaction of ROO· with R-H will produce R· and ROOH (Gol'dberg et al., 1988). The latter molecule can decompose into alkoxy radicals (RO·). As the number of melt-extrusion cycles increases, oxidative products accumulate in HDPE, leading to the observed reduction in M_w of rHDPE-**50** (see Section 3.2 for further confirmation). Apart from the aforementioned shear-induced and oxidative-induced degradations, repeated pelletisation may also play a role in the reduction of M_w in rHDPEs. This process could reduce the length of the polymer chains mechanically each time the extrudate was being pelletised into 3 mm length. It can also be seen from Table 1 that
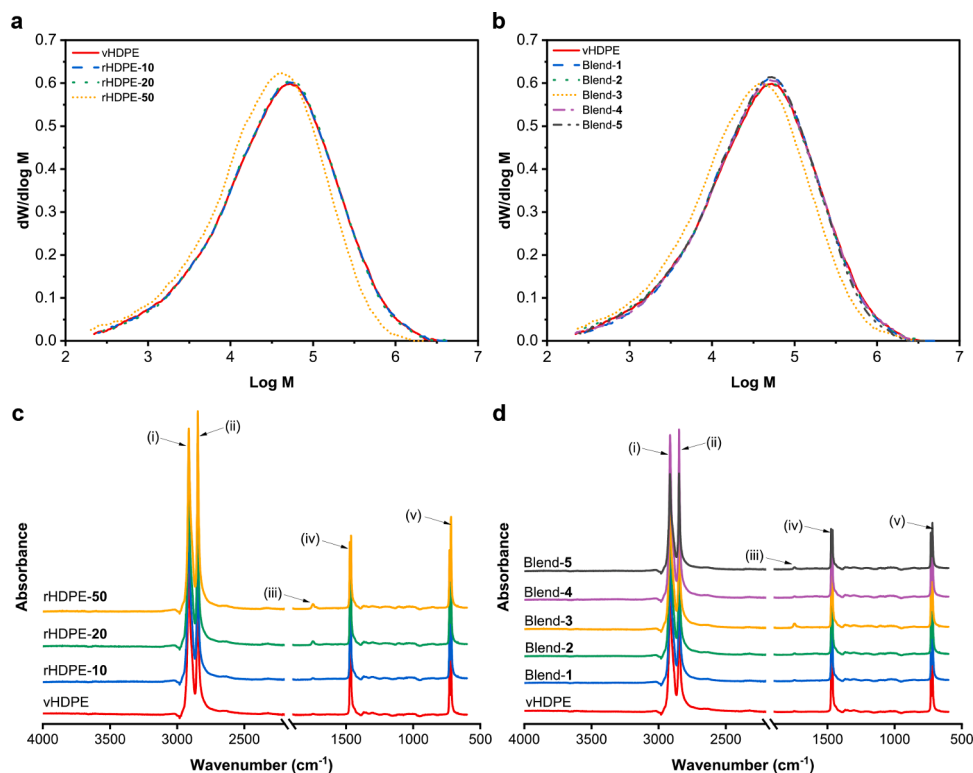
Fig. 2. The molecular mass distribution of the various (a) rHDPEs and (b) vHDPE/rHDPE blends, compared against vHDPE, as well as the ATR-FTIR spectra of the various (c) rHDPEs and (b) vHDPE/rHDPE blends.

Table 1

Number-average molecular weight (M_n), weight-average molecular weight (M_w), polydispersity index (Đ), ratio between absorbance peak at 1743 cm^{-1} and 730 cm^{-1} (R), L^*, a^*, b^* and ΔE of vHDPE, rHDPEs and vHDPE/rHDPE blends.

Sample	M_n (g/mol)	M_w (g/mol)	Đ	R	L^*	a^*	b^*	ΔE
vHDPE	7945	106,240	13.4	0.01	99	0	2	0.0
rHDPE-10	8211	106,352	13.0	0.04	99	0	7	5.0
rHDPE-20	8363	103,573	12.4	0.06	96	0	7	5.8
rHDPE-50	6088	68,606	11.3	0.08	89	1	10	12.8
Blend-1	8688	102,474	11.8	0.03	98	0	5	3.2
Blend-2	7502	103,833	13.8	0.06	98	−2	4	3.0
Blend-3	6247	78,984	12.6	0.08	97	−2	9	7.5
Blend-4	8203	105,412	12.9	0.03	99	−2	6	4.5
Blend-5	7953	95,893	12.1	0.06	99	−2	8	6.3

the M_w of the various blends of virgin and repeatedly melt extruded HDPE is the weighted average between the M_w of vHDPE and rHDPE subjected to different number of melt-extrusion cycles.

### 3.2. ATR-FTIR spectra of vHDPE, rHDPEs and vHDPE/rHDPE blends

Fig. 2c,d show the ATR-FTIR spectra of the various HDPE samples. The peaks at positions (i), (ii), (iv), and (v) correspond to CH$_2$ asymmetric stretching, CH$_2$ symmetric stretching, bending deformation and rocking deformation, respectively (Gulmine et al., 2002). In the rHDPE and vHDPE/rHDPE blend samples, the appearance of an absorption band at ~1750 cm^{-1} (labelled as peak (iii) in Fig. 2) that corresponds to carbonyl band (C=O), can be observed (Almond et al., 2020). This is associated with the oxidative degradation of HDPE that gives rise to products containing the carbonyl functional group, such as ketones and esters (Gardette et al., 2013; Yang et al., 2006). We further calculate the

ratio (R) between the absorbance peak at ~1750 cm^{-1} and 730 cm^{-1} (see Table 1). It can be observed that R increases with increasing melt-extrusion cycles. This confirms the accumulation of carbonyl containing oxidative degradation products in HDPE after repeated melt-extrusion.

3.3. Colour of rHDPEs and vHDPE/rHDPE blends compared to vHDPE

Discolouration of HDPE due to repeated melt-processing has been commented on (Mendes et al., 2011; Pock et al., 2004) but received little attention. In 2011, the UK Waste and Resource Action Programme (WRAP) commissioned a study to improve the recyclability of HDPE milk bottles (WRAP, 2011). The study reported a change in the colour of HDPE milk bottles from white to a greener hue when the content of HDPE recyclates was increased. The discolouration was attributed to the contamination of coloured HDPE milk bottle caps (in the UK, the colour of the milk bottle caps is used to differentiate the type of milk) in the HDPE recyclates stream. The same study also concluded that the repeated melt-extrusion process itself had minimal impact on discolouration of HDPE. However, our study shows otherwise. Fig. 3 presents the variation of the colour of HDPE (additives free) subjected to different number of repeated melt-extrusion cycles. A gradual change in colour from white for vHDPE, towards a slightly darker hue for rHDPE-10 and rHDPE-20 was observed. HDPE that has been subjected to 50 repeated melt-extrusion cycles (rHDPE-50) showed the darkest hue. It is worth mentioning that previous works on the discolouration of repeatedly melt-processed HDPE focused on the effect of antioxidant (del Teso Sánchez et al., 2016, 2012). In our work, the HDPE used was pure without any antioxidant.

The changes in the colour of the various HDPE samples were further quantified in terms of their L^*, a^*, b^* colour parameters and ΔE (see Table 1). It can be seen from the table that subjecting HDPE to higher number of repeated melt-extrusion cycles increases the ΔE value. The ΔE value is 5.0 for rHDPE-10 and 5.8 for rHDPE-20. rHDPE-50 shows the
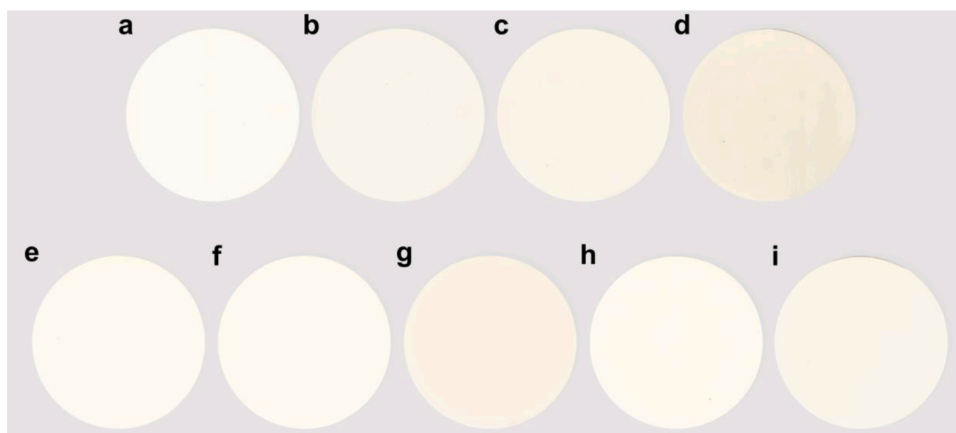
Fig. 3. Scanned image of various HDPE samples. (a) vHDPE, (b) rHDPE-**10**, (c) rHDPE-**20**, (d) rHDPE-**50**, (e) blend-**1**, (f) blend-**2**, (g) blend-**3**, (h) blend-**4** and (i) blend-**5**.

highest ΔE value of 12.8. This is not surprising as rHDPE-**50** has the highest level of degradation when compared to other samples. The change in ΔE of the various HDPE grades is largely influenced by a decrease in the perpetual lightness (L^*) and an increase in the yellowness-blueness (b^*). This implies that, apart from the gradual change into darker hue, HDPE also becomes more yellow with increasing melt-extrusion cycle. This corroborates with the ATR-FTIR spectra presented in Fig. 2. Carbonyl is a known chromophore that could affect light absorbability, subsequently leading to a change in the colour of a material (Lizundia et al., 2017; Allen et al., 2000). The increase in carbonyl content has previously been associated with the darker hue and yellowing of HDPE (Baum, 1959). Subjecting HDPE to a higher number of melt-extrusion cycles increases the concentration of carbonyl in the sample, leading to a higher ΔE.

As shown in Fig. 3, blend-**1**, blend-**2** and blend-**4** (blends containing vHDPE, rHDPE-**10** and rHDPE-**20**) exhibit colour close to that of vHDPE. In comparison, blends containing rHDPE-**50** (i.e., blend-**3** and blend-**5**) have a slightly darker hue but are still noticeably lighter than that of rHDPE-**50**. Table 1 shows that the blending of the various grades of rHDPE with vHDPE leads to a lower ΔE. Blend-**1**, blend-**2** and blend-**4** (blends containing only vHDPE, rHDPE-**10** and rHDPE-**20**) have ΔE of 3.2, 3.0 and 4.5, respectively. These values are smaller compared to the ΔE of rHDPE-**10** and rDHPE-**20**. Blend-**3** and blend-**5**, which contain rHDPE-**50**, have ΔE of 7.5 and 6.3; values higher than that of blend-**1**, blend-**2** and blend-**4**. These values however, are still significantly lower than that of rHDPE-**50** (ΔE=12.8). Dark-yellow appearance, as observed in the repeatedly melt extruded HDPE (i.e., rHDPE-**10**, rHDPE-**20** and rHDPE-**50**) may not be appealing to consumer and therefore will not be accepted by retailers. These results show that blending vHDPE with different grades of repeatedly melt extruded HDPE, including rHDPE-**50** could reduce the dark hue and yellowing of the sample, subsequently improving its overall appearance.

3.4. Dynamic viscosity of vHDPE, rHDPEs and vHDPE/rHDPE blends

Fig. 4a displays the complex viscosity ($|\eta^*|$) of the various HDPE melt as a function of frequency at 200 °C. It can be observed that the melt rheology of HDPE exhibits a Newtonian-plateau at low frequency. This is due to the entanglement of the polymer chains, which maintains a constant resistance to flow. Shear thinning behaviour, characterised by a decrease in $|\eta^*|$ with increasing frequency, was observed when the frequency was greater than 0.5 Hz. At high shear, the HDPE molecules start to align in the direction of shear and thus can slip over each other easily as they are no longer entangled, leading to the observed shear thinning behaviour. Due to the similarity in M_w (see Table 1), the melt rheology of vHDPE, rHDPE-**10** and rHDPE-**20** are similar. The noticeable decrease in
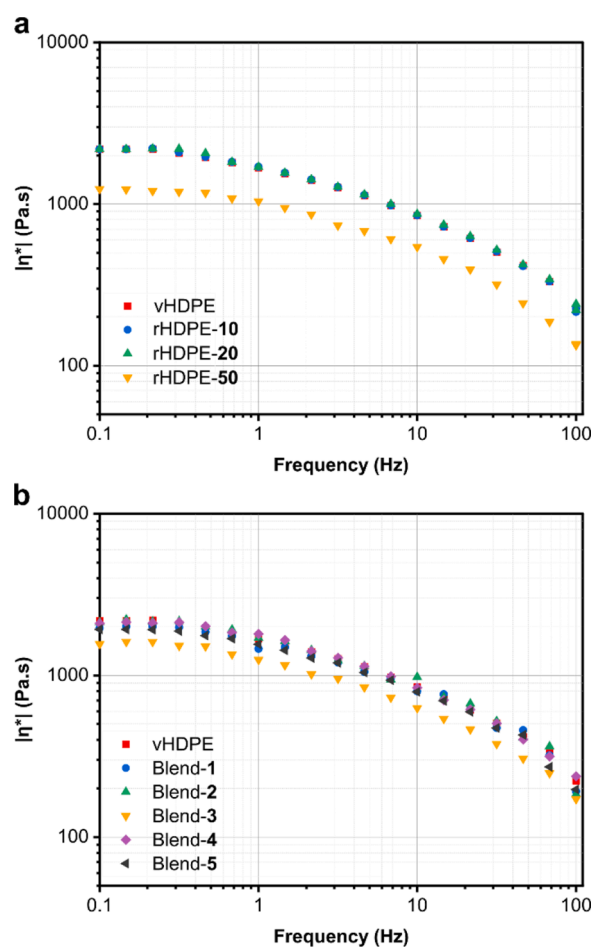
Fig. 4. Evolution of complex viscosity with frequency of (a) rHDPEs and (b) vHDPE/rHDPE blends, compared against the complex viscosity evolution of vHDPE.

$|\eta^*|$ of rHDPE-**50** compared to vHDPE, rHDPE-**10** and rHDPE-**20** can be attributed to its lower M_w. Nevertheless, all vHDPE/rHDPE blends possess similar melt rheological properties to that of vHDPE (Fig. 4b). This also implies that blending vHDPE with different grades of repeatedly melt extruded HDPE, including rHDPE-**50**, would be able to offset the lower melt viscosity due to chain degradation.

3.5. Overall migration of vHDPE, rHDPEs and vHDPE/rHDPE blends in acidic and aqueous environment

An important parameter when a polymer is used for food contact packaging applications is the diffusion of low molecular weight molecules, such as plasticisers, antioxidants, light stabilisers, lubricants, antistatic agents, slip compounds and thermal stabilisers into the food in contact (Bhunia et al., 2013). This may affect the safety of the final product. As the repeated melt-extrusion of HDPE causes chain scission and generates thermal oxidative products that accumulates in the polymer (see Table 1), overall migration studies were further conducted in this work. Fig. 5 presents the overall migration of substances from vHDPE, rHDPE and the various vHDPE/rHDPE blends when in contact with aqueous (ethanol 10% v/v) (Fig. 5a,b) and acidic (acetic acid 3% v/v) (Fig. 5c,d) environments for up to 1200 h. It can be seen that in both environments, migration of substances from the HDPE samples occurred and increasing the number of melt-extrusion cycles increased the amount of substance migrating into the food simulating liquids. The overall migration values of vHDPE in aqueous and acidic environments at 1200 h immersion time were found to be 4.5 mg kg^{-1} and 4.0 mg kg^{-1}, respectively. After 10 repeated melt-extrusion cycles (rHDPE-**10**), the overall migration values in aqueous and acidic environments increased to 5.5 mg kg^{-1} and 4.8 mg kg^{-1}, respectively. A further increase in the number of repeated melt-extrusion cycles to 20 (rHDPE-**20**) increased the overall migration values to 6.8 mg kg^{-1} and 6.0 mg kg^{-1} in aqueous and acidic environments, respectively. Sample rHDPE-**50** possesses the highest overall migration value of 9.0 mg kg^{-1} and 8.0 mg kg^{-1} in aqueous and acidic environments, respectively. As the HDPE samples used in this study do not contain any additives, the increase in overall migration value is thought to be a direct result of the increase in the concentration of low molecular weight thermal oxidative products due to repeated melt-extrusion.

It can also be seen in Fig. 5b,d that blending rHDPE with vHDPE suppresses the migration of substances into the food simulating liquids. Blend-**3** (vHDPE with rHDPE-**50**) has an overall migration value of only

5.8 mg kg^{-1} and 5.3 mg kg^{-1} in aqueous and acidic environments, respectively. This is a 35% decrease from the overall migration value of neat rHDPE-**50**. The migration process can be divided into (i) the diffusion of the migrating substance through the polymer, (ii) the accumulation of the migrating substance at the polymer–simulant interface and (iii) the desorption of the migrating substance into the simulant in which it is in contact with. Blending vHDPE with the various rHDPE samples reduces the concentration of low molecular weight thermal oxidative products, as well as reducing their diffusion coefficient. It is worth mentioning that the overall migration values of the various HDPE samples are well below the 60 mg kg^{-1} limit set in the Commission Regulation (European Union) No. 10/2011 on plastic materials and articles intended to come into contact with food.

3.6. Crystallisation and melt behaviour of vHDPE, rHDPEs and vHDPE/rHDPE blends

Chain branching and chain scission due to repeated melt-extrusion are known to influence the degree of crystallinity of HDPE (Oblak et al., 2015). This would consequently complicate the delineation of the effects of HDPE crystallinity and the blending of different grades of rHDPE when analysing the mechanical properties of the various HDPE samples reported in Section 3.7. Therefore, DSC was first conducted. A single melting peak in both the first and second heating curves can be observed at ~130 °C for all the HDPE samples (see Fig. S1 in the supplementary information). Subjecting HDPE to 10, 20 and 50 repeated melt-extrusion cycles does not affect the melting temperature of the samples. Similarly, blends consisting of vHDPE and the various rHDPE showed similar melting behaviour to that of virgin counterpart. The degree of crystallinity (based on first heating) of the repeatedly melt extruded HDPE samples (rHDPE-**10**, rHDPE-**20** and rHDPE-**50**) were found to be similar at ~65% (see Table S1 in the supplementary information), implying that the mild oxidative degradation that led to chain branching and scission in rHDPE did not affect their crystallisation behaviour. Blending vHDPE with various grades of HDPE has also
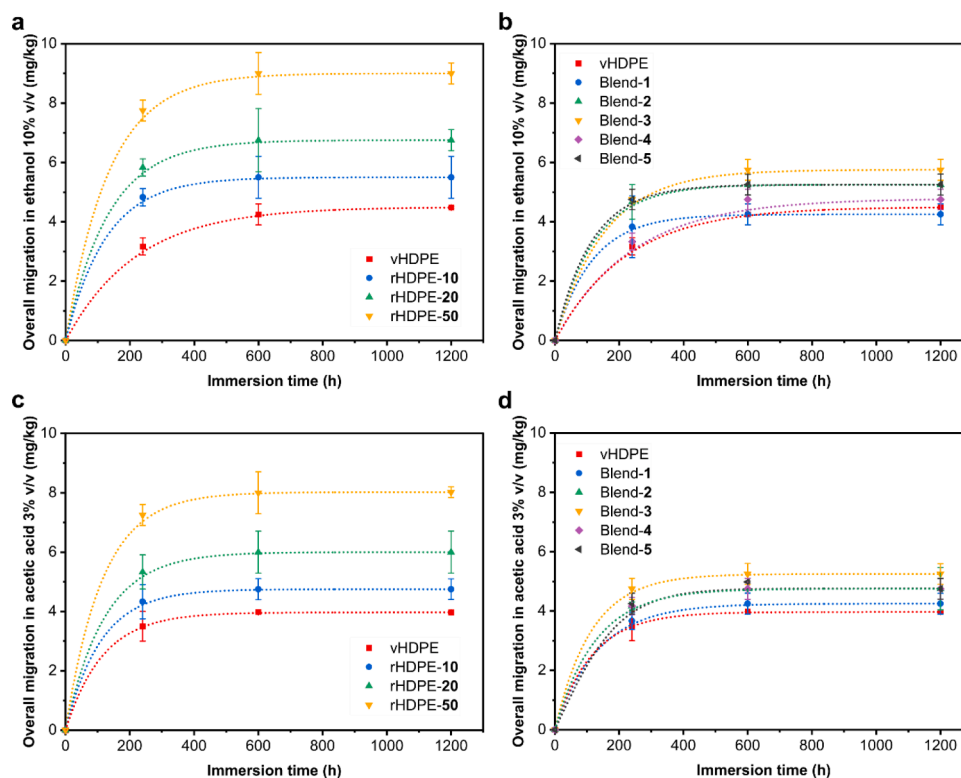

Fig. 5. Overall migration of vHDPE, rHDPEs and vHDPE/rHDPE blends immersed in (a,b) ethanol 10% (v/v) and (c,d) acetic acid 3% (v/v) for up to 1200 h.

resulted in χ_c of ~64%. The similarity in the χ_c of vHDPE, various rHDPE and vHDPE/rHDPE blends based on first heating suggests that a direct comparison in the tensile properties of the samples can be made.

3.7. Tensile properties of vHDPE, rHDPE and vHDPE/rHDPE blends

Fig. 6 presents the tensile properties of vHDPE, rHDPE and vHDPE/rHDPE blends. As shown in the figure, the tensile modulus (E) and strength (σ) of HDPE subjected to 10 cycles (rHDPE-**10**) and 20 cycles (rHDPE-**20**) of repeated melt extrusion are similar to that of vHDPE. The E and σ of vHDPE, rHDPE-**10** and rHDPE-**20** are ~1.8 GPa and ~31 MPa, respectively. However, a slight decrease in ε_b from 65% (vHDPE) to 54% for rHDPE-**10** and 52% for rHDPE-**20** can be observed. This could be attributed to chain branching (as reflected in the increase of M_w) that increases the rigidity of rHDPE-**10** and rHDPE-**20**. Consequently, this resulted in the earlier onset failure of the samples. A decrease in E and σ of rHDPE-**50** was observed and this reveals the negative impact of repeatedly melt extruding HDPE. It can also be seen that the E and σ of rHDPE-**50** is 13% lower than those of vHDPE. This is due the mild degradation as observed in the decrease of M_w in rHDPE-**50** (see Table 1 and Fig. 2).

The ε_b of rHDPE-**50** was found to be 92%; a value that is significantly higher than that of vHDPE. This may be attributed to the cross-linking of HDPE molecules that could also occur due to the repeated melt extrusion and pelletisation of rHDPE-**50**. vHDPE/rHDPE blends containing rHDPE-**10** and rHDPE-**20** have tensile properties similar to that of vHDPE. Blend-**1**, blend-**2** and blend-**4** show E and σ of 1.88 GPa and ~31 MPa, respectively. Different from rHDPE-**10** and rHDPE-**20** that exhibited a decrease in ε_b, blend-**1**, blend-**2** and blend-**4** have ε_b of 63%; comparable to the ε_b of vHDPE. Blends containing rHDPE-**50** (i.e., blend-**3** and blend-**5**) have similar σ (~30 MPa) but slightly lower E (1.69 GPa) compared to those of vHDPE. Nevertheless, the E of blend-**3** and blend-**5** are higher than the E of rHDPE-**50**. The ε_b of blend-**3** and blend-**5** are also comparable to that of vHDPE. The tensile properties of vHDPE/rHDPE blends demonstrate that blending recycled plastics (of various grades) with virgin HDPE would be a straightforward method to recover the mechanical properties of repeatedly melt extruded HDPE.

4. Conclusion

In this work, we found that oxidative chain scission and branching occurred when HDPE was subjected to repeated melt-extrusion. The M_w of HDPE decreased from ~106 kg mol^{-1} for vHDPE, to only ~69 kg mol^{-1} for rHDPE-**50**. ATR-FTIR confirmed the accumulation of carbonyl-containing oxidative products within HDPE after repeated melt-extrusion. This also resulted in samples with darker hue, as reflected in the higher ΔE of rHDPE-**50**. The oxidative degradation resulted in lower melt rheological properties and higher overall migration in both aqueous and acidic environments. rHDPE-**50** possessed the lowest $|\eta^*|$ (e.g., $|\eta^*|$ = 573 Pa s at 10 Hz) and highest overall migration (9.0 mg kg^{-1} in ethanol 10% v/v and 8.0 mg kg^{-1} in acetic acid 3% v/v). By comparison, vHDPE have $|\eta^*|$ = 867 Pa s at 10 Hz and overall migration of 4.5 mg kg^{-1} and 4.0 mg kg^{-1} in aqueous and acidic environments, respectively. The HDPE samples that have been repeatedly melt-extruded for 50 cycles also possessed lower E and σ of 1.5 GPa and 28 MPa, respectively; 13% lower than that of vHDPE. Blending vHDPE with different grades of repeatedly melt extruded HDPE, including rHDPE-**50** resulted in $|\eta^*|$ and overall migration comparable to that of vHDPE. Blend-**3** and blend-**5** which contain rHDPE-**50** possessed σ of ~30 MPa and E of 1.69 GPa, respectively. These values are also comparable to those of vHDPE and higher than those of rHDPE-**50**. In addition, the ΔE of the vHDPE/rHDPE blends are lower than their respective rHDPE counterparts.
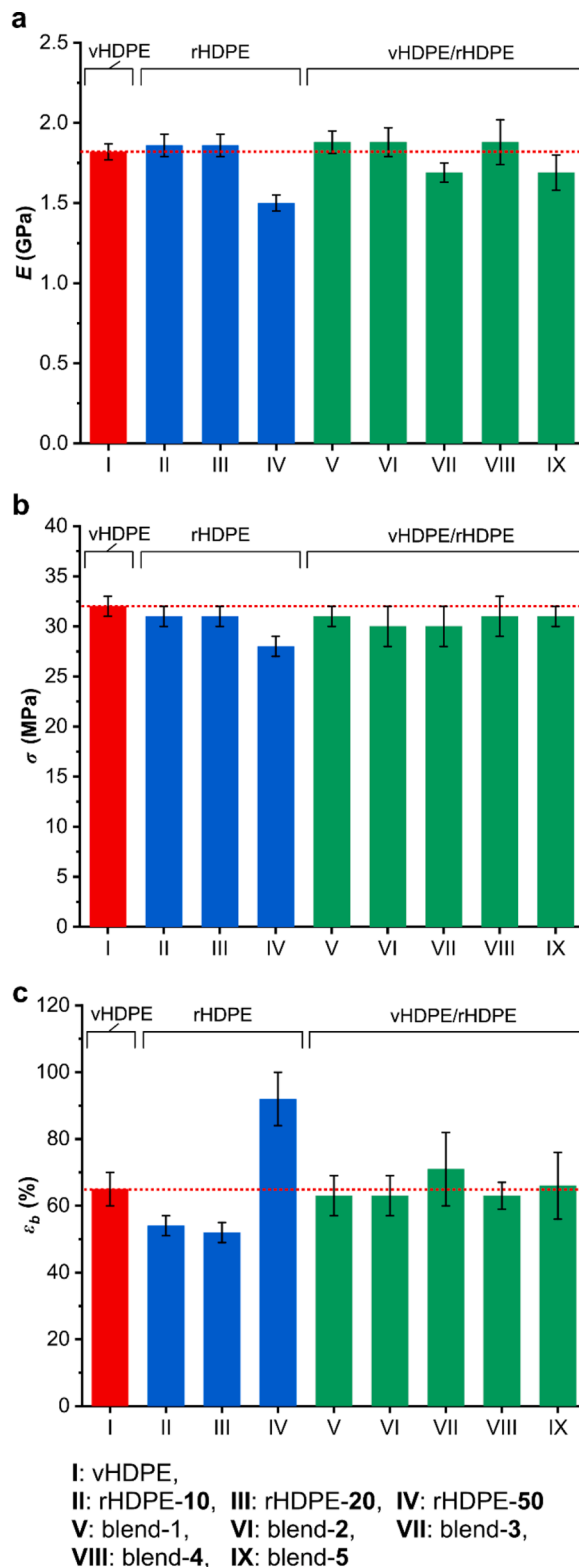

Fig. 6. Tensile properties of vHDPE (red), rHDPEs (blue) and vHDPE/rHDPE blends (green). (a) Tensile modulus, (b) tensile strength and (c) strain at break of the various HDPE samples. The red dotted lines represent the tensile properties of vHDPE.

CRediT authorship contribution statement

Andre N. Gaduan: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization.

Joanne Li: Investigation, Formal analysis, Writing – review & editing.
Gavin Hill: Investigation, Formal analysis, Writing – review & editing.
Christopher Wallis: Resources, Writing – review & editing. **Christoph Burgstaller:** Resources, Writing – review & editing. **Koon-Yang Lee:** Conceptualization, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2022.106734.

References

Almond, J., Sugumaar, P., Wenzel, M.N., Hill, G., Wallis, C., 2020. Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. e-Polymers 20 (1), 369–381.

Apone, S., Bongiovanni, R., Braglia, M., Scalia, D., Priola, A., 2003. Effects of thermomechanical treatments on HDPE used for TLC ducts. Polym. Test. 22 (3), 275–280.

Baum, B., 1959. The mechanism of polyethylene oxidation. J. Appl. Polym. Sci. 2 (6), 281–288.

Benoit, N., González-Núñez, R., Rodrigue, D., 2017. High density polyethylene degradation followed by closed-loop recycling. Prog. Rubber Plast. Recycl. Technol. 33 (1), 17–38.

Berns, R.S., 2019. Billmeyer and Saltzman's Principles of Color Technology, 4th ed. Wiley.

Bhunia, K., Sablani, S.S., Tang, J., Rasco, B., 2013. Migration of chemical compounds from packaging polymers during microwave, conventional heat treatment, and storage. Compr. Rev. Food Sci. Food Saf. 12 (5), 523–545.

Biffa, 2019. Plastic surgery: Managing waste plastics. https://www.biffa.co.uk/-/media/files/sustainability/biffa-plastic-surgery-managing-waste-plastic_reality-check-series_issue-4.pdf. (Accessed 25th October 2022).

Boldizar, A., Jansson, A., Gevert, T., Möller, K., 2000. Simulated recycling of post-consumer high density polyethylene material. Polym. Degrad. Stab. 68 (3), 317–319.

Cecon, V.S., Da Silva, P.F., Curtzwiler, G.W., Vorst, K.L., 2021. The challenges in recycling post-consumer polyolefins for food contact applications: a review. Resour. Conserv. Recycl. 167, 105422.

Dairy UK, 2018. The UK Dairy roadmap: Showcasing 10 years of environmental commitment. https://www.dairyuk.org/publications/the-dairy-roadmap/. (Accessed 25th October 2022).

del Teso Sánchez, K., Allen, N.S., Liauw, C.M., Edge, M., 2016. Effect of polymerization catalyst technology on the melt processing stability of polyethylenes, Part 3: additives blends performance. J. Vinyl Addit. Technol. 22 (2), 117–127.

del Teso Sánchez, K., Allen, N.S., Liauw, C.M., Edge, M., Johnson, B., Catalina, F., Corrales, T., 2012. Effects of polymerization catalyst technology on the melt processing stability of polyethylenes. part 2. single stabilizer performance. J. Vinyl Addit. Technol. 18 (1), 26–39.

El'darov, E.G., Mamedov, F.V., Gol'dberg, V.M., Zaikov, G.E., 1996. A kinetic model of polymer degradation during extrusion. Polym. Degrad. Stab. 51 (3), 271–279.

Gardette, M., Perthue, A., Gardette, J.-.L., Janecska, T., Földes, E., Pukánszky, B., Therias, S., 2013. Photo- and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. Polym. Degrad. Stab. 98 (11), 2383–2390.

Gol'dberg, V.M., Vidovskaya, L.A., Zaikov, G.E., 1988. Kinetic model of the mechanism of high-temperature inhibited oxidation of polymers. Polym. Degrad. Stab. 20 (2), 93–121.

Gol'dberg, V.M., Zaikov, G.E., 1987. Kinetics of mechanical degradation in melts under model conditions and during processing of polymers—a review. Polym. Degrad. Stab. 19 (3), 221–250.

Gulmine, J.V., Janissek, P.R., Heise, H.M., Akcelrud, L., 2002. Polyethylene characterization by FTIR. Polym. Test. 21 (5), 557–563.

H.M. Government. 2022 Plastic packaging tax, https://www.gov.uk/government/collections/plastic-packaging-tax (Accessed 25th October 2022).

Lizundia, E., Nguyen, T.-.D., Vilas, Jose L., Hamad, W.Y., MacLachlan, M.J., 2017. Chiroptical, morphological and conducting properties of chiral nematic mesoporous cellulose/polypyrrole composite films. J. Mater. Chem. A 5 (36), 19184–19194.

Loultcheva, M.K., Proietto, M., Jilov, N., La Mantia, F.P., 1997. Recycling of high density polyethylene containers. Polym. Degrad. Stab. 57 (1), 77–81.

Mendes, A.A., Cunha, A.M., Bernardo, C.A., 2011. Study of the degradation mechanisms of polyethylene during reprocessing. Polym. Degrad. Stab. 96 (6), 1125–1133.

Oblak, P., Gonzalez-Gutierrez, J., Zupančič, B., Aulova, A., Emri, I., 2015. Processability and mechanical properties of extensively recycled high density polyethylene. Polym. Degrad. Stab. 114, 133–145.

Pock, E., Kiss, C., Janecska, Á., Epacher, E., Pukánszky, B., 2004. Effect of chain structure on the processing stability of high-density polyethylene. Polym. Degrad. Stab. 85 (3), 1015–1021.

Runt, J., Harrison, I.R., Dobson, S., 1980. Heat of fusion of polyethylene crystal suspensions: variation with crystallization temperature. J. Macromol. Sci. Part B 17 (1), 99–115.

Allen, N.S., Edge, M., Rodriguez, M., Liauw, C.M., Fontan, E., 2000. Aspects of the thermal oxidation, yellowing and stabilisation of ethylene vinyl acetate copolymer. Polym. Degrad. Stab. 71 (1), 1–14.

RECOUP, 2018. Plan for plastics. https://www.veolia.co.uk/sites/g/files/dvc1681/files/document/2018/09/Veolia%20UK%20_%20Plan%20for%20plastics%20report.pdf. (Accessed 25th October 2022).

Schyns, Z.O.G., Shaver, M.P., 2021. Mechanical recycling of packaging plastics: a review. Macromol. Rapid Commun. 42 (3), 2000415.

Singh, N., Hui, D., Singh, R., Ahuja, I.P.S., Feo, L., Fraternali, F., 2017. Recycling of plastic solid waste: a state of art review and future applications. Compos. Part B Eng. 115, 409–422.

Smith, D.N., Harrison, L.M., Simmons, A.J., 1999. A survey of schemes in the United Kingdom collecting plastic bottles for recycling. Resour. Conserv. Recycl. 25 (1), 17–34.

Strömberg, E., Karlsson, S., 2009. The design of a test protocol to model the degradation of polyolefins during recycling and service life. J. Appl. Polym. Sci. 112 (3), 1835–1844.

Vogt, B.D., Stokes, K.K., Kumar, S.K., 2021. Why is recycling of postconsumer plastics so challenging? ACS Appl. Polym. Mater. 3 (9), 4325–4346.

Welle, F., 2005. Post-consumer contamination in high-density polyethylene (HDPE) milk bottles and the design of a bottle-to-bottle recycling process. Food Addit. Contam. 22 (10), 999–1011.

WRAP, 2011. HDPE milk bottle research and development. https://wrap.org.uk/resources/report/hdpe-milk-bottle-research-and-development#download-file. (Accessed 25th October 2022).

WRAP, 2021. Plastics market situation report. https://wrap.org.uk/resources/report/plastics-market-situation-report-2021. (Accessed 25th October 2022).

Yang, R., Liu, Y., Yu, J., Wang, K., 2006. Thermal oxidation products and kinetics of polyethylene composites. Polym. Degrad. Stab. 91 (8), 1651–1657.