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Reprocessing of polymer blends from WEEE: A methodology for predicting embrittlement

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ABSTRACT

For recycling purposes, the thermal degradation of post-consumed (pc) ABS/HIPS and PP/PE blends derived from waste electrical and electronic equipment (WEEE) was obtained by multiple extrusions. The evolution of molar mass (M_w), melt flow index (MFI), and ultimate elongation (ε_r) of reprocessed blends was evaluated as a function of extrusion cycles. The degradation mechanism of ABS/HIPS blends corresponds to a random chain scission as indicated by a diminution of ε_r correlated to an increase in MFI and decrease in M_w after 30 cycles of extrusion. The same type of degradation mechanism occurs on the PP/PE blend as shown by the drop in M_w and thus an increase in MFI by a factor of six but only after 11 cycles, thus suggesting the higher thermomechanical resistance of ABS/HIPS. The beginning of the critical molar mass for embrittlement (M'_c) zone was reached around 130 and 200 kg/mol for ABS/HIPS and PP/PE, respectively, which can be related to the beginning of the critical MFI zone around 12 and 63 g/10 min (230 °C/2.06 kg), respectively. As a result, we propose an innovative embrittlement criterion using MFI measurements that allow a quick and easy analysis of post-consumed polymer blends.

1. Introduction

Polymer materials are mainly found in food packaging, construction materials, textiles, transport, and many other commodities with electrical and electronic equipment (EEE). EEE comprises 11 to 30 %wt of the plastic share [1], which represents an annual production of almost 50 million tons, and 8 %wt of solid plastic waste (SPW) produced worldwide in 2016. In the EEE family, acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS), and polypropylene (PP) are the predominant polymers due to their good processability as well as their mechanical and chemical properties [2,3]. For the past few years, EEE has raised concerns because of the presence of brominated flame retardant (around 5–25 %wt) [4,5] and heavy metals (around 0.5–3 % wt) [6,7], which are highly toxic for the environment and human health. For this reason, it is necessary to manage waste EEE (WEEE) in a suitable way other than landfilling.

Several alternatives including recycling have been developed over the past few decades [8,9]. Primary recycling consists of the direct reprocessing of uncontaminated SPW, which is quite similar to virgin material, while secondary recycling requires sorting, shredding, and then reprocessing steps to obtain a material as pure as possible in order to manufacture new products. Tertiary (or chemical) recycling aims to recover raw material (oil, wax, or even initial monomer in the case of polyesters or nylons) using different chemical processes (depolymerisation [10], pyrolysis [11], gasification [12], etc.). Finally, quaternary recycling involves SPW incineration for energy recovery. Considering the different types of materials used for only one application, sorting is an essential step to avoid impurities [13–15]. Further, chemical recycling generates very high expectations, although today it remains far too expensive to implement on an industrial scale. Consequently, mechanical recycling is the most rewarding method. Nevertheless, reprocessing is known to induce the thermomechanical degradation of polymers because of temperature and shearing, thus implying a loss of chemical, physical, and mechanical properties [16–18].

Regarding the literature on ABS degradation occurring by mechanical recycling, impact properties seem to be the most affected parameter [19–21]. Indeed, the successive extrusions using a twin screw extruder of ABS demonstrate the loss of impact resistance of 35% [22] and 40% [23] after six and ten cycles, respectively. ABS with a higher polybutadiene (PB) content seems to be more sensitive to thermomechanical degradation. However, no variation in the melt flow index (MFI) or mass average molar mass (M_w) is visible, suggesting that the chemical

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structure of styrene-acrylonitrile (SAN) is less affected than the PB phase [23,24]. Furthermore, some authors have observed an effect on strain at break (ε_r) with a threefold reduction and a slight increase in MFI after five steps extrusion for ABS [25], while others have not remarked any changes [26]. Regarding HIPS, ε_r seems to be the most sensitive parameter to processing. As a matter of fact, five steps of injection moulding applied to HIPS lead to a higher MFI and a lower viscosity of 20%, which are correlated to a decline in tensile properties, thus suggesting a diminution of M_w (i.e., chain scission) [27]. Moreover, HIPS shows a reduction of ε_r of around 40% and an augmentation of MFI of around 45% after nine cycles of extrusion, which tends to be in agreement with previous observations [28].

The thermal degradation of polyolefins has been widely studied [29–31]. In the case of PP, it is largely admitted that the thermomechanical process causes a diminution of viscosity (i.e., diminution of M_w) due to chain scission, which notably affects strain at break [16,32]. Polyethylene (PE) shows different behaviours assimilated to a coupling of chain scission and branching depending on the processing conditions and polymer architecture [31,33]. For example, high density polyethylene (HDPE) and low density polyethylene (LDPE) will highlight a more predominant MFI decrease during reprocessing by injection moulding, thus altering ε_r (around 50–70%) after 10 cycles [34]. It is important to observe that the use of additives before reprocessing such as stabilisers can increase the resistance of the material against thermal oxidation [35].

Polymer blends could be an interesting compromise between virgin and recycled polymers of a similar nature [21,36,37] to recover their initial properties at best, or in the case of SPW, different polymer types such as ABS and HIPS or PP and PE, which are difficult to separate during the sorting step. Indeed, a polymer blend can be complex to achieve considering the chemical interaction between the components. For example, ABS is partially miscible with HIPS, and thus the control of the morphology is quite complex and dependent on the composition, substantially affecting the mechanical properties such as strain at break and impact resistance [19]. Similarly, PP and PE are also not miscible [38], and their blend can lead to a dramatic reduction in ε_r depending on the nature of PE [39,40]. For this reason, in the case of both olefins and styrenes, the use of compatibilisers may be needed to reduce the interfacial tension and favour interactions between the components [41,42]. Depending on the material structure and processing conditions, the thermomechanical degradation of polymer blends can lead to the migration of low molecular species as radicals over phase boundaries and create cross reactions with macromolecular entities. In many ways, this formation of grafted copolymers could affect the thermal stability of the blend [43,44].

The literature review points to the lack of information regarding the degradation of polymer blends and the existence of a criterion governing the ultimate mechanical properties. As a result, specific tests must be performed to verify whether the blend retains its properties, especially in terms of mechanical behaviour after multiple extrusions or injection moulding. Since mechanical tests are not possible on post-consumed polymers in granular form (i.e., before reprocessing), we propose characterising MFI, which can be a good indicator of thermal degradation [45], in the materials to be recycled by reprocessing. Another advantage when using MFI as the characterisation method is its low cost and simplicity of use. The ultimate mechanical properties such as strain at break are governed by M_w in the case of linear polymers, i.e., thermoplastics [46]. The use of MFI as a criterion for possible recycling is because a critical MFI value can be associated with a ductile-brittle transition. In other words, given that MFI can be correlated to M_w [47,48], for a given polymer and blend of polymers, we can expect the existence of a critical MFI value for plastic deformation during a tensile test.

The aim of this study is to investigate the degradation of post-consumed (pc) ABS/HIPS and PP/PE blends from WEEE by reprocessing and to determine a criterion governing strain at break in terms of the critical MFI value. For this purpose, successive extrusions of the blends were made with a twin screw extruder in order to ensure the most severe conditions with a combination of oxygen, temperature, and shearing. The evolution of the polymer structure was evaluated by Fourier transform infrared (FTIR) spectrometry, MFI, and gel permeation chromatography (GPC), and its mechanical properties were characterised by uniaxial tensile testing.

2. Material and methods

2.1. Samples

Four model materials mainly found in WEEE were used: commercial LG Chem acrylonitrile-butadiene-styrene (ABS) HI121H, ($T_g = 105$ °C, $\rho = 1.04$; MFI = 1.2 g/10 min (230°C-2.06 kg)); high impact polystyrene (HIPS) Edistir R850E from Eni Versalis ($T_g = 97$ °C, $\rho = 1.04$ g/cm^3, MFI = 4.2 g/10 min (230°C-2.06 kg)); polypropylene (PP) PPH 7060 ($T_f = 168$ °C, $\rho = 0{,}905$ g/cm^3, MFI = 15 g/10 min (230°C-2.06 kg)) supplied by Total; and high density polyethylene (HDPE) 6070 UA ($T_f = 134$ °C, $\rho = 0.96$ g/cm^3 MFI = 12.6 g/10 min (230°C-2.06 kg)) provided by Sidpec.

Small solid plastic waste (SPW) without brominated flame retardant (BFR) came from a French sorting centre after being preliminarily shredded and sorted. Only samples without brominated flame retardant has been sorted by using X-ray fluorescence (XRF) for this study. EDS (X ray spectroscopy) measurements have been performed to verify this point. Overall, 30 pieces (≈55 g) consisted of PP and PE (named samples A) and 20 pieces (≈38 g) of ABS and HIPS (named samples B) were selected for identification according to their size (minimum ≈ 3 cm × 3 cm), shape (flat, curved, tubes, etc.), and colour (white, black, grey, and other). All samples were washed with water and detergent (Paic from Colgate).

2.2. Sample processing

Pc ABS/HIPS blend was first dried for 16 h at 70 °C. Strips of PP/PE then pc ABS/HIPS blend were manufactured with a twin-screw extruder from Thermohaake equipped with a volumetric flow controller, twin screws with a 16 mm diameter and length-to-diameter ratio of 40, and a 30 × 2 mm slit flat die. The temperature profile of the barrel was set to 200 225 225 225 225 225 225 225 °C, and the die was heated to 230 °C. Chill rolls were heated to 70 °C for ABS-HIPS and 40 °C for PP-PE blends with a variable speed of 40–60 cm/min depending on the irregular flow. They were put into contact with each other to obtain a smooth surface. Final thickness of PP/PE and ABS/HIPS was measured at around 1 mm and 2 mm, respectively. The samples were subsequently shredded at 930 tr/min with a Lancelin device fitted with a grid composed of 7 mm diameter holes to extract flakes.

2.3. Infrared spectrometry

Infrared spectrometry experiment was Bruker IFS 28 at 4 cm^{-1} resolution. Attenuated total reflectance (ATR) mode was used for the WEEE identification, with an average of four scans being made. Some samples were sanded and polished with a Leitz Metallovert device, first using 300 and then 800 sandpaper to probe the sample core. The sample thickness was measured before and after polishing, and about 1 mm layer thickness was removed from the samples.

2.4. Oxidation induction time

Samples were analysed with a Q10 apparatus provided by TA Instruments according to the following protocol:

Heating scan of 10 °C/min to 170 °C for ABS/HIPS and 180 °C for PP/PE under nitrogen.

Isothermal step for 5 min before switching gas from nitrogen to

oxygen.

The oxidation induction time is assimilated to a slope variation corresponding to the exothermal signal appearance when the stabilisers are consumed and the oxidation of polymers begins.

2.5. Gel permeation chromatography

GPC measurements were performed using a Waters 717 plus chromatograph for styrene samples equipped with two columns from Waters (stationary phase) and then a refractive index and ultraviolet (UV) detectors in tetrahydrofuran (mobile phase). The elution method consisted of an isocratic step at 1 ml/min for 30 min at 35 °C. Calibration was performed using SM-105 PS standards from Shodex from which values were implemented in Breeze software to calculate the M_w.

Agilent HT 220 apparatus was employed with olefin samples equipped with a refractive index detector in 1,2,4-trichlorobenzene stabilised with 0.0125% BHT at 135 °C (mobile phase) and two PLgel Olexis columns from Agilent Technology (stationary phase). The elution method consisted of an isocratic step at 1 ml/min for 30 min at 135 °C. Calibration was performed using SM-105 PS standards from Shodex. M_w was determined using universal constant $K = 12.1 \times 10^5$ dg/L and $\alpha = 0.707$ for PS, $K = 16.6 \times 10^5$ dg/L and $\alpha = 0.733$ for PP, and $K = 40.6 \times 10^5$ dg/L and $\alpha = 0.725$ for PE [49].

2.6. Tensile test

Tensile tests were performed with an Instron 5966 device equipped with 10 kN force cell on 5A specimens that respect the dimensions given by ISO 527–2 at 5 mm/min for ABS/HIPS and 1 mm/min for PP/PE. Tests were carried out at room temperature and 50% relative humidity on series of 7–10 samples. Using the tensile test, changes in ε_r were followed after each extrusion cycles.

2.7. Rheology

Frequency sweep tests from 100 to 0.01 Hz at 230 °C and 0.5% deformation were conducted with an Anton Paar MCR 502 rheometer equipped with parallel plates and 1 mm gap. The Cox-Merz rule is considered applicable to this case, and thus angular frequency ω and shear rate $\dot{\gamma}$ are assumed to be equivalent as complex η* and dynamic η viscosity.

2.8. Melt flow index

MFI measurements were made according to international ISO 1133 standard using a Kayeness instrument with a cylindrical barrel diameter of 0.475 cm and a cylindrical die diameter of 0.2095 cm. A 2.016 kg load is applied at 230 °C through a piston, and material is collected per 30 s for ABS/HIPS and 10 s for PP/PE to determine MFI calculated as the mass of the material in grams flowing per 10 min.

3. Results

3.1. Characterisation of shredded material

3.1.1. Identification of matrix before reprocessing

The ATR FTIR spectroscopy allows an identification of the selected shredded WEEE (spectra can be viewed in Fig. 1 and Fig. 2). Regarding the FTIR spectra comparison between all 20 styrenes and 30 olefins selected as SPW and virgin polymers, it appears that PP and ABS are the primary materials in the sample series as previously observed [2,3] with 76 %wt for PP versus 13 %wt for PE and 65 %wt for ABS versus 35 %wt for HIPS. These values correspond to the proportion in terms of weight percentage for each polymers by sorting 50 samples by using FTIR method. ABS is mostly remarkable by the nitrile C≡N signal at 2233 cm^{-1} and the two peaks of aromatic C–H bending observed at 700 and 760 cm^{-1}. Stretched aromatics are visible above 3000 cm^{-1} and

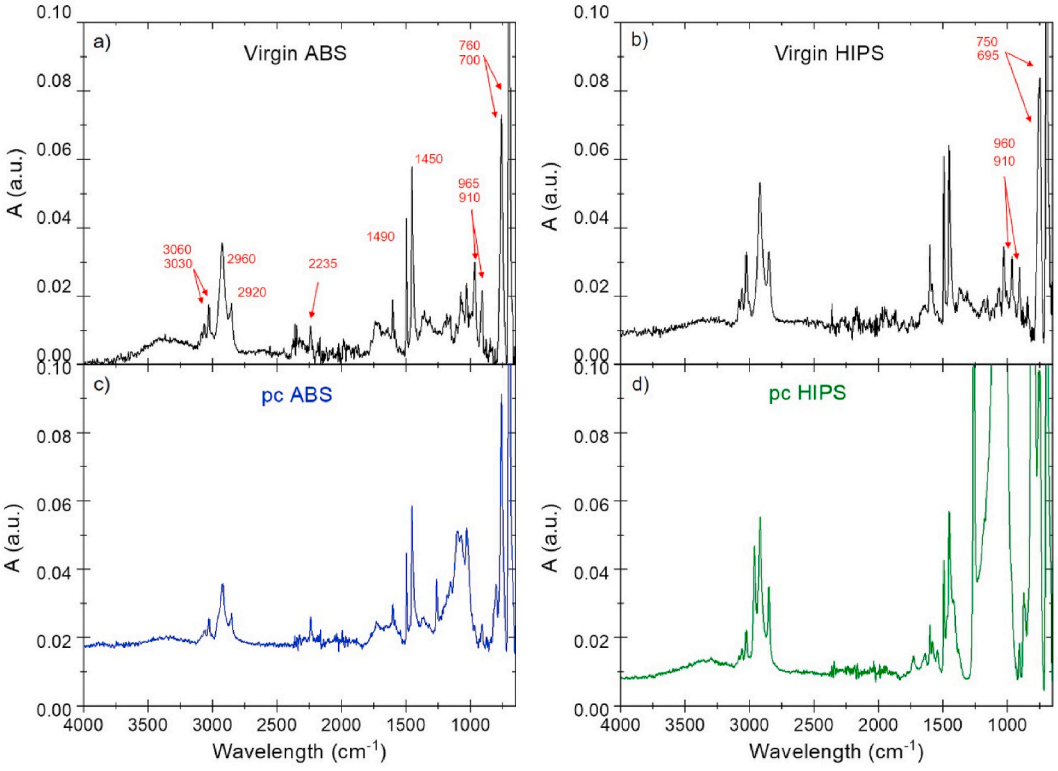


Fig. 1. Fourier transform infrared (FTIR) spectra in attenuated total reflectance (ATR) mode corresponding to virgin ABS a) and HIPS b) and then pc ABS c) and HIPS d).

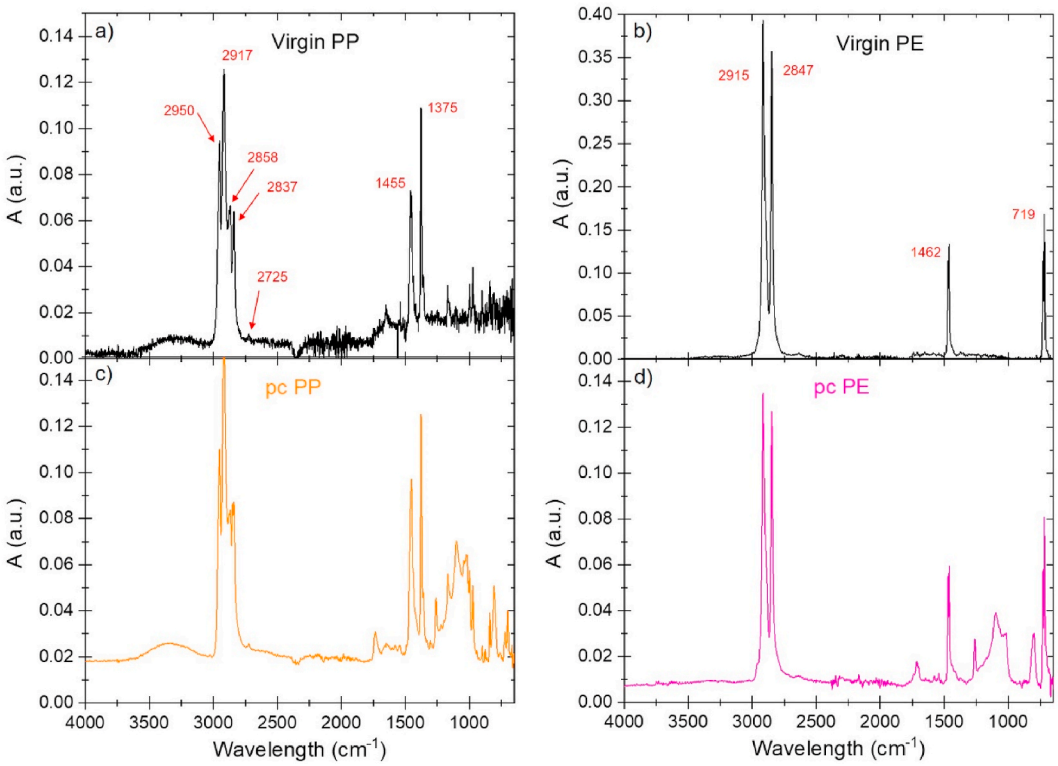


Fig. 2. Fourier transform infrared (FTIR) spectra in attenuated total reflectance (ATR) mode corresponding to virgin PP a) and PE b) and then pc PP c) and PE d).

aliphatics just below this value [50,51]. Finally, the two peaks visible for ABS and HIPS samples at 910 and 965 cm^{-1} are related to vinyl-1,2 and *trans*-1,4 C═C of the butadiene phase, respectively. PP is identifiable by the presence of peaks at 2950 and 2917 cm^{-1} and then 1375-1360 cm^{-1} in relation to C–H stretching and bending of the CH_3 group, respectively. PE is recognisable with signal positions at 2195 and 2847 cm^{-1} corresponding to aliphatic C–H followed by 1462 and 719 cm^{-1} for C–H bending of the CH_2 group [52].

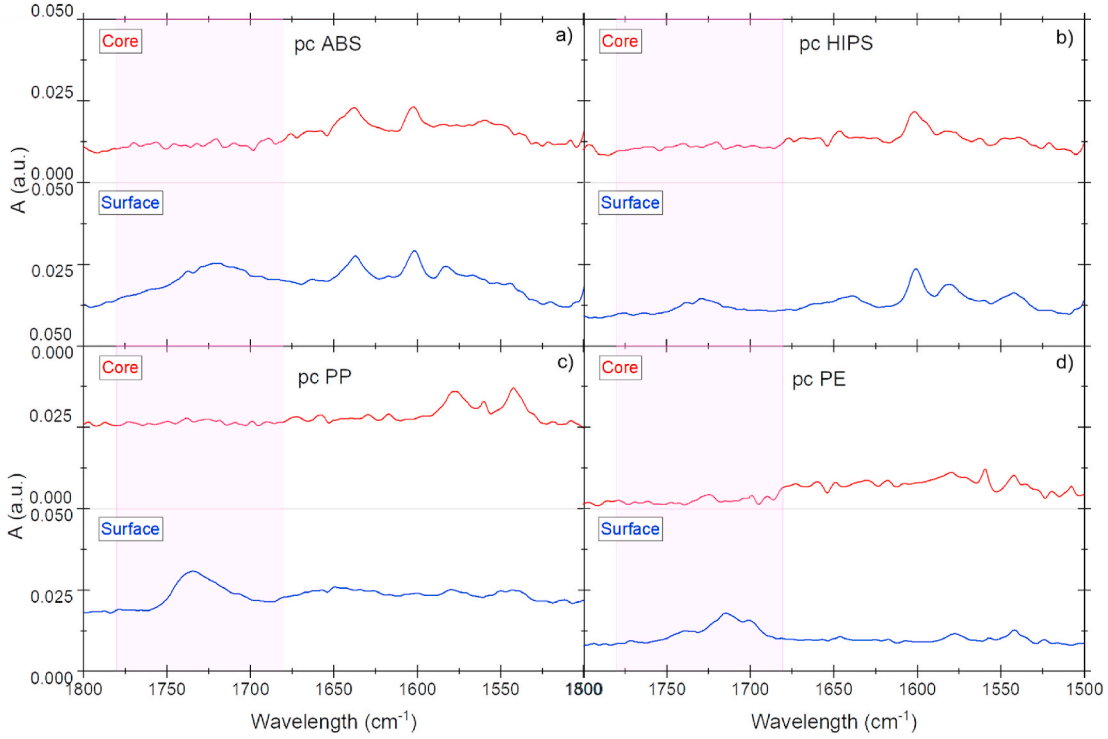


Fig. 3. Fourier transform infrared (FTIR) spectra in attenuated total reflectance (ATR) mode of the surface and core of a pc ABS a), pc HIPS b), pc PP c) and pc PE d) shred. The pink area designates the carbonyl region. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.1.2. Characterisation of degradation level before reprocessing

Oxidation products were probed on pc shreds using infrared ATR (Fig. 3), more specifically in the 1600-1800 cm^{-1} wavelength region where carbonyl peaks are known to grow during ageing [53]. In our case, there is no evidence of oxidation in most of the tested samples, while for those with slight oxidation at the surface, no oxidation is visible in the core. The FTIR characterization of the core sample has been performed after remove 1 mm from the surface, knowing 1 mm is far above the oxidation layer thickness expected A previous study highlighted an oxidation layer of ≈200 μm for LDPE [54]. Consequently, WEEE samples, which are considered to have a previous "lifetime" of 5–10 years, are first very slightly oxidised, but this oxidation only corresponds to a layer that is assumed not to be representative of the whole sample. Therefore, the thin oxidation layer will be diluted during the reprocessing step. For this reason, mean infrared, which is widely used in laboratories, is not a suitable technique for determining material oxidation, as it cannot be employed to separate materials as a function of their oxidation level. Near infrared is mostly used in sorting centres thanks to the high speed of automatic execution [55], although the wavelength range does not span the oxidation marker signals.

Table 1 shows clearly that the M_w of pc materials is quite scattered, mostly for HIPS with an average value of 194 kg/mol, while the M_w of ABS is around 130 kg/mol. The M_w of the pc PP and pc PE spreads is approximately 278 and 171 kg/mol, respectively. This observation is hardly comparable to virgin materials, because the initial M_w depends on the diversity of grades used for different applications. Moreover, the window of Đ values seems to be rather constant at around 2.5 and 5 for ABS and PP shreds, respectively, regardless of M_w. It is important to notice that M_w values are mainly above M'_C values of PS, PP, and PE [46], which separate the ductile/brittle transition, thus suggesting a limited of chemical degradation in pc plastics so far. Let us recall here that M'_C is the critical molar mass below which the polymer becomes mechanically brittle during a chain scission process and chain scission process is associated to oxidation products formation.

3.2. Investigation of blend reprocessing

3.2.1. Impact on mechanical properties

Table 2 represents the overall tensile properties of pc ABS/HIPS and PP/PE blends as a function of the reprocessing cycles. Regarding the ABS/HIPS blend, the tensile strength and elongation at break diminish after 30 cycles of extrusion as seen in Table 2. Nevertheless, a 12% increase in Young modulus (E) is observed, especially between the first and third cycles, probably due to a thinner dispersion and a better distribution of the butadiene nodule within the morphology, because ABS and HIPS do not show any substantial variation of E with reprocessing [20,28]. It is worth recalling that the morphology will be highly sensitive to the blend proportion considering that ABS and HIPS are partially miscible [19,56,57], which explains why compatibilisers can be used up to 30 %wt to recover or even improve their mechanical properties [58], although this is not conceivable for recycling. The ultimate properties have a greater interest for us in this study, and Table 2 indicates that yield strength and elongation disappear after the 30th cycle, suggesting that the ductile/brittle transition has been reached.

The mechanical behaviour of the pc PP/PE blend is close to the brittle domain as evidenced by the weak ε_r (Table 3) compared to virgin homopolymers PP and PE. However, blending PP with PE can produce a composite material with a very low elongation at break, especially with HDPE [40]. The diminution of ε_r is a more common observation with the reprocessing of PP, generally assimilated to a chain scission phenomenon [16], whereas the drop of ε_r observed for LDPE and HDPE is more due to chain branching or crosslinking effect [34]. Table 3 highlights a diminution of modulus E and ε_r by more than 30% between the first and eleventh step of reprocessing, without greatly altering the yield stress and yield elongation. Considering the majority of PP in the blend, this is not in concordance with the observations made regarding the reprocessing of PP, where E undergoes a 15% increase after five steps of reprocessing [16] or changes slightly with the addition of pc PP or pc resin [41,45]. There is a slight variation in the melting enthalpy from 57 to 54 J/g for PP and a shift toward lower melting temperatures after three cycles of reprocessing (not reported), indicating a decrease in crystallinity and the size of crystals, which can possibly reduce the tensile modulus. Nevertheless, this observation is not in agreement with the phenomenon of chemicrystallisation observed during the thermal oxidation of semicrystalline polymers such as olefin [46], where the chain scission mechanism allows a chain formerly involved in entanglement to form crystalline lamella.

Table 1
Evaluation of average values of tiO, molar mass (M_w), and dispersity (Đ) determined for different ABS, HIPS, PP, and PE shredded materials.

	ABS	HIPS	PP	PE
tiO (min)	52 ± 39	21 ± 10	64 ± 74	42 ± 82
M_w (kg/mol)	130 ± 18	194 ± 59	278 ± 52	171 ± 142
Đ	2.5 ± 0.2	2.6 ± 0.3	5 ± 2	9.2 ± 6.6

Table 2
Overall tensile properties of pc (ABS/HIPS) including Young modulus (E), yield strength (σ_y), yield elongation (ε_y), ultimate strength (σ_r), and elongation at break (ε_r) as a function of reprocessing.

Cycles	E (MPa)	σ_y (MPa)	ε_y (%)	σ_r (MPa)	ε_r (%)
1	1704 ± 83	20 ± 1	5 ± 1	20 ± 1	8 ± 2
3	2094 ± 201	17 ± 3	6 ± 1	16 ± 5	9 ± 2
4	2379 ± 260	22 ± 2	6 ± 2	22 ± 2	7 ± 3
7	2475 ± 213	16 ± 7	4 ± 2	16 ± 7	8 ± 5
11	2370 ± 318	21 ± 7	7 ± 3	21 ± 7	8 ± 4
20	2271 ± 395	16 ± 6	7 ± 2	16 ± 6	8 ± 2
30	1870 ± 45	X	X	8.2 ± 5	2.2 ± 1.5

Table 3
Overall tensile properties of pc PP/PE blend including Young modulus (E), yield strength (σ_y), yield elongation (ε_y), ultimate strength (σ_r), and elongation at break (ε_r) as a function of reprocessing.

Cycles	E (MPa)	σ_y (MPa)	ε_y (%)	σ_r (MPa)	ε_r (%)
1	1942 ± 463	18 ± 1	6.5 ± 1	16 ± 1	11 ± 2
3	1113 ± 138	16 ± 2	8 ± 1	13 ± 1	20 ± 11
4	1258 ± 124	16 ± 1	8 ± 2	13 ± 2	16 ± 7
7	1190 ± 132	18 ± 1	7 ± 1	18 ± 2	7 ± 1
11	1304 ± 156	15 ± 1	5 ± 1	14 ± 1	6 ± 1

3.2.2. Oxidation product analysis

To explain the mechanical properties, the infrared spectrogram of the two pc blends reprocessed several times was carried out (Fig. 4). Firstly, the presence of the nitrile group signal at 2232 cm^{-1} and the aromatics C–H at 697 and 760 cm^{-1} seems to confirm that the pc ABS/HIPS blend is mainly composed of ABS (Fig. 4a). Further, a weak oxidation is highlighted after 30 cycles, as indicated by the presence of a very small peak located at 1730 cm^{-1} and a broader one at 3310 cm^{-1}, corresponding to the formation of carbonyl oxidation and hydroperoxide products, respectively. Moreover, the signals visible at 965 and 910 cm^{-1}, respectively related to "*trans*-1,4" and "vinyl-1,2" unsaturated bonds of the PB phase, seem to remain rather constant, meaning that the oxidation of PB did not occur as frequently as expected. Similar observations can be made with PP/PE blends, which show no valuable change in carbonyl signals between 1800 and 1600 cm^{-1} (Fig. 4b). The presence of PP signals as opposed to PE signals confirms its predominance in the blend.

Comparable remarks on oxidation products have been made with virgin ABS [24], HIPS [28], and PP [16] after reprocessing, although other studies have highlighted the diminution of the diene rubber band

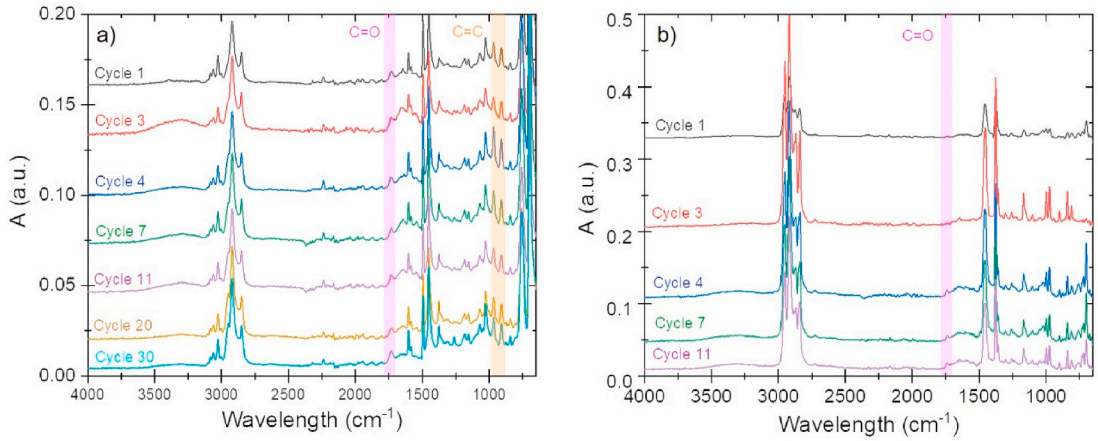


Fig. 4. Fourier transform infrared (FTIR) spectra in attenuated total reflectance (ATR) mode during the different reprocessing steps of the pc ABS/HIPS a) and pc PP/PE blends b). The pink and orange zones indicate carbonyls and double bond regions, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and the increase in oxidation products for ABS resins [25,26] after five steps of twin extrusion. LDPE and PP indicate an slight formation of carbonyl groups after reprocessing using a twin extruder coupled with a torque rheometer [59]. It is known that ABS oxidation is discernible in the more unstable PB phase, but the oxidation process will depend on many parameters such as chemical structure, oxygen concentration, temperature, or stabiliser content within the polymer. In our case, we assume that stabilisers were consumed during the initial use of the polymers and the subsequent reprocessing. Nevertheless, the low oxygen concentration (around 20% from air) incorporated into the barrel of the twin extruder is less aggressive than the thermal ageing process in an oven and thus does not enable a proper oxidation of the pc ABS/HIPS blend.

3.2.3. *Impact on molar mass and dispersity*

The GPC measurements represented in Fig. 5a show a diminution of M_w from 176 to 114 kg/mol after 30 cycles for the ABS/HIPS blend, while dispersity (Đ) remains constant. Concerning the PP/PE blend, a reduction from 260 to 190 kg/mol after 11 steps of processing is observed, while Đ decreases slightly (Fig. 5b). It may be that the thermomechanical degradation of blends composed of macromolecules, which have no interactions, can lead to an additivity effect with the cross recombination and formation of the grafted copolymer [44] of the component depending on the proportions [60]. This would explain the initial increase in M_w after three steps of extrusion. These results suggest a random chain scission mechanism for both blends mostly induced by the thermomechanical effect generated by the successive extrusions. In the case of ABS/HIPS, it is assumed that either the SAN phase contained in ABS and/or the PS phase undergoes the chain scission process or that the PB fraction is separated from SAN or PS. The PP/PE blend seems to follow similar behaviour to that of pure PP [16], while HDPE or LDPE indicates a preferential branching mechanism [34].

3.2.4. *Impact on the melt flow index*

The impact of reprocessing on MFI of the ABS/HIPS and PP/PE blends was investigated (Table 4). MFI of the ABS/HIPS blend gradually increased and doubled after 30 cycles of extrusion. Regarding the PP/PE

Table 4
Evolution of the melt flow index (MFI) (230 °C/2.06 kg) with the reprocessing cycles for ABS/HIPS and PP/PE blends.

MFI (g/10 min)		
Cycles	ABS-HIPS	PP-PE
0	4.7 ± 1.7	13 ± 1.5
1	6.8 ± 0.1	14 ± 1
3	7.8 ± 0.1	15 ± 0.6
4	8.2 ± 0.003	15 ± 0.6
7	8.6 ± 0.5	25 ± 0.6
11	9.5 ± 0.1	63 ± 5
20	11 ± 0.3	X
30	12.1 ± 0.03	X

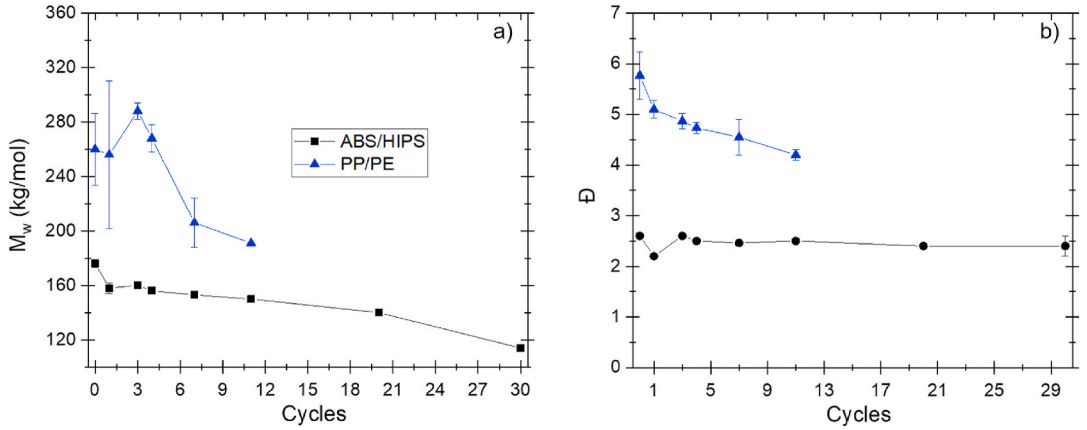


Fig. 5. Variation of molar mass (M_w) a) and dispersity (Đ) b) of pc ABS/HIPS and pc PP/PE blends with their degradation induced by the thermomechanical degradation process.

blend, MFI substantially increased by almost four times the initial value after 11 cycles of reprocessing. These results are in good agreement with previous findings for M_w, which assumed a predominant chain scission phenomenon. Previous studies on the reprocessing of ABS and HIPS homopolymers reveal a more gradual increase in MFI, even after 10 cycles [23–25,28] similar to PP [61], but different to HDPE and LDPE, which tend to present a lower MFI [33]. Moreover, the PP blend with 0–10 %wt of PE shows a fourfold increase in MFI after five extrusions, thus following the same pattern as pure PP because of chain scission [62].

4. Discussion

4.1. Ultimate deformation related to molar mass

To predict the ability to recycle polymer blends from WEEE, the evolution of ε_r as a function of M_w is illustrated in Fig. 6 for ABS/HIPS and PP/PE blends.

On the one hand, it appears that ε_r does not vary with the 21% reduction of M_w after 20 steps of ABS/HIPS reprocessing, although after 30 cycles of extrusion a drop of ε_r occurs by a factor of two and M_w is reduced to 114 kg/mol. Considering that Đ is constant for the successive extrusions, this correlation between ε_r and M_w makes it possible to determine a window M'_c between 100 and 140 kg/mol. Below 100 kg/mol, the degradation induced by the successive extrusions leads to an unacceptable embrittlement for a given application. As a result, provided that ABS is in the majority and the degradation mode leads to chain scission, embrittlement occurs when M_w is below 100 kg/mol. The origin of this value is associated with the molar mass between entanglements (M_e) [63,64] whose destruction provokes embrittlement in the case of amorphous polymers [46].

On the other hand, the evolution of PP/PE ε_r is less drastic compared to ABS/HIPS, but it is spread across a larger window of M_w. Indeed, a loss of nearly half of ε_r, which corresponds to a 27% drop of M_w is visible after 11 cycles of reprocessing. Regarding the value of 200 kg/mol proposed in the literature for PP [65], we can assume that the M'_c area of our PP/PE blend was reached. Furthermore, it is important to stress that the processing became very difficult because of the very low viscosity (i.e., high MFI) of the PP/PE blend. Previous studies have highlighted the identical behaviour of the PP/LDPE 90/10 %wt blend after five steps of extrusion with an alteration of ε_r by a factor of three correlated to a six-fold increase in MFI (i.e., diminution of M_w) [66]. Some authors claim that the blend overcomes the predominant chain scission induced by thermomechanical effect similar to pure PP compared to pure LDPE, which shows a crosslinking reaction during degradation. As mentioned above, the type of PE (i.e., LDPE, LLDPE, or HPDE) can distinctly affect the mechanical behaviour of PP/PE blends [40]. Nevertheless, blending PP with a limited amount of LDPE does not greatly affect the elongation of PP, which would be interesting to investigate in our case given that PP is much more common in WEEE compared to PE [2].

From these observations, it appears that the beginning of the M'_c zone was reached for both ABS/HIPS and PP/PE blends, even if it is less visible in the latter case. Considering the non-negligible variation in M_w and MFI for both blends, the variation of elongation at break values allows us to assume that the ductile/brittle transition is reached after 11 and 30 steps of reprocessing, thus revealing the high thermal resistance of the ABS/HIPS blend compared to the PP/PE blend. We are now interested in correlating this M'_c with the critical value of MFI.

4.2. Relationship between molar mass and melt flow index

The correlation between M_w and MFI can facilitate the characterisation at the industrial scale using, for example, MFI measurements, which is a simple and rapid technique compare to gel permeation chromatography (GPC). Previous studies have established the empirical relation involving a power law equation, where the zero-shear viscosity at the Newtonian plateau is proportional to the average M_w to the power of 3.4 [67]. Considering the simple relationship between viscosity and MFI [48], this equation is remodelled as follows:

$$1/MFI = GM_w^{\alpha} \quad (1)$$

Where G and α are constants depending on the nature of the polymer. The hypothesis of this equation implies a system with Newtonian behaviour. The variation of 1/MFI with M_w is represented in Fig. 7 for ABS/HIPS and PP/PE blends. This figure shows that the previous determined critical molar mass zone around 130 kg/mol and 200 kg/mol can be related to a critical MFI zone around 12 and 63 g/10 min (230 °C/2.06 kg) for ABS/HIPS and PP/PE blends respectively. Therefore, the embrittlement process can be correlated to MFI measurements and this latter parameter can be a useful and simple method to characterise post consumed materials properties for recycling industry. Furthermore, it appears that the linear fit applied to the ABS/HIPS blend has a slope value (i.e., α coefficient) of 3.9, which corresponds to the same order of magnitude of 3.4. Nevertheless, the linear fit does not include the final dot, which corresponds to the 30th cycle of extrusion

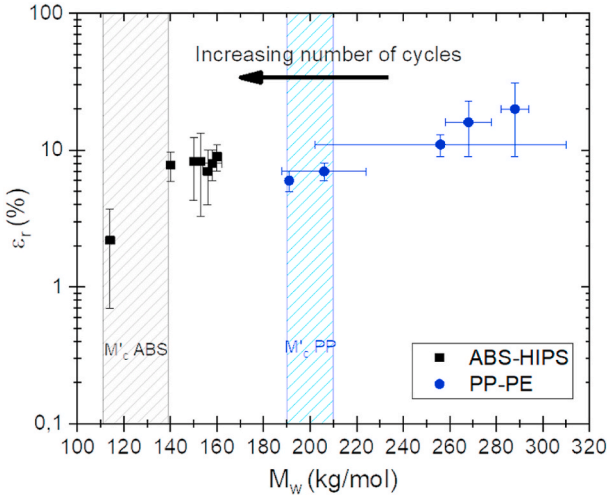


Fig. 6. Variation of the molar mass (M_w) as a function of the ultimate elongation (ε_r) of ABS/HIPS and PP/PE blends.

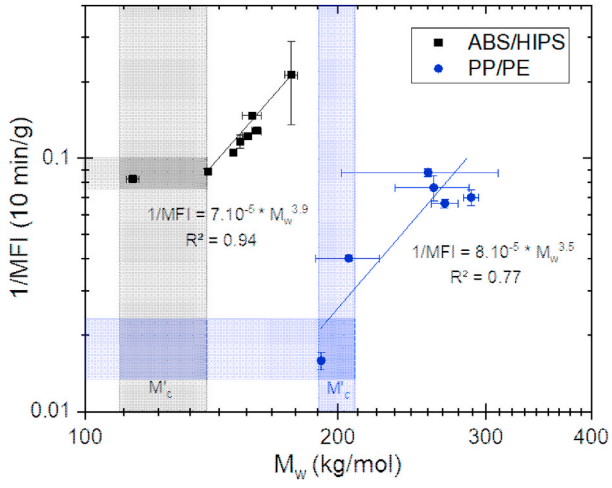


Fig. 7. Variation of molar mass (M_w) with the melt flow index (MFI) (230 °C/2.06 kg) after multiple reprocessing of ABS/HIPS and PP/PE blends. The grey and blue rectangles delimit the M'_C and MFI'_C zones for each blends. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

where the ductile/brittle region is assumed to be reached. As a result, even if the ABS/HIPS blend does not highlight Newtonian behaviour (not reported), the power law seems to be adequate for a range of values that are above the M'_c (i.e., critical MFI), although a deviation is clearly visible in Fig. 4 when embrittlement is reached (i.e., under M'_c). Regarding PP/PE, the use of the power law works well for whole range of data, as demonstrated by the value of the α coefficient equal to 3.5. This can be explained by the fact that the ductile/brittle transition is reached after only 11 cycles of extrusion without greatly affecting ε_r compared to the ABS/HIPS blend. The application of equation (1) seems to work for several grades of virgin PP but less for recycled PP obtained from the recycling of SLI Pb-acid batteries because of the presence of impurities or fillers [68]. Indeed, some authors have demonstrated that the melt flow was not only dependent on M_w but also on the molecular architecture, including the branching for different PE, with M_w increasing from 65 to 638 kg/mol and Đ from 3 to 20 [69]. In our case, it is clear that the blend effect complicates the predictability of the relationship between MFI and M_w, as shown by the R^2 value of both linear fits, which was quite low especially for the PP/PE blend. This can be used to explain the deviation of α from 3.4.

5. Conclusion

This paper investigated the thermal degradation of pc ABS/HIPS blends derived from WEEE performed by multiple extrusions. The post consumed shred samples of ABS, HIPS, PP, and PE, which were selected and characterised, indicate no degradation or oxidation compared to virgin materials. Regarding the reprocessed ABS/HIPS blends, the evolution of the molar mass, melt flow index, and ultimate elongation was evaluated as a function of extrusion cycles. Although the modulus slightly varies for the ABS/HIPS blend, ultimate stress and elongation were reduced after 30 cycles of reprocessing, while the pc PP/PE blend shows a diminution of the ultimate mechanical properties after the 7th cycle, suggesting behaviour close to the ductile/brittle transition for both blends. It appears that degradation mechanism corresponds to random chain scission induced by the thermomechanical effect in both cases. The ductile/brittle transition is governed by the chain scission when molar mass becomes below a critical value M'_C which corresponds also to a critical value MFI'_C. Therefore, embrittlement can be studied using MFI measurements that allow a quick and easy analysis of post-consumer material properties from an industry perspective. Furthermore, a preliminary simple predictive model using a power law was used to connect the molar mass to the melt flow index and determine a critical value of the melt flow index for embrittlement. This preliminary work could be useful in the future when investigating the degradation of WEEE and thus provide good guidance to optimise sorting.

Author statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We understand that the Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

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.

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Appendix A. Supplementary data

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