INCORPORATION OF RECYCLED HIGH-DENSITY POLYETHYLENE TO POLYETHYLENE PIPE GRADE RESINS TO INCREASE CLOSE-LOOP RECYCLING AND UNDERPIN THE CIRCULAR ECONOMY

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Abstract

High-density polyethylene (HDPE) is one of the most used and demanded plastic, not only for packaging, but also for construction and within this application especially for non-pressure and pressure pipes, which makes this material the most abundant in the municipal waste stream. On the basis of the Circular Economy and the sustainable life that promotes, it is important to explore new applications for recycled HDPE (rHDPE) to increase the polymer recycled uptake. However, recycled HDPE is not currently being used in pressure pipes, mainly due to the high structural and loading requirements that must be met. The present study evaluates the potential use of post-consumer rHDPE from different origins in the manufacture of polyethylene pressure pipes. Different rHDPE sources are blended in different ratios with raw HDPE with PE100 grade quality. Blends are fully characterized to determine their feasibility to be used for pipe applications. Properties such as tensile strength at yield, elongation at break and flexural modulus for all blends yield values above the minimum required for PE100 grades. Furthermore, two important mechanical properties of polyethylene pipes, Slow Crack Growth (SCG) and Rapid Crack Propagation (RCP) resistances, are deeply evaluated. Remarkably, a dual correlation of SCG and RCP with the content of recycled PE in blends was established, allowing to develop predictive capabilities that guarantee the requirements and specifications for pressure pipe applications. Finally, through the evaluation of different waste streams, it can be concluded that handling, sorting, separation and selection of polyethylene's waste is critical to achieve the required pipe specifications, and to increase the percentage of post-consumer rHDPE into the final product. This investigation is in line with the sustainability objective and the commitment to boost the circular economy by replacing part of the conventional HDPE raw material with recycled HDPE to increase close-loop recycling on PE for pipe application, and the basis for the recycling of rHDPE from pipe at its end-life, after 50 years in service.

Keywords: Recycled polyethylene; Circular Economy; High-density polyethylene (HDPE); PE100 grade; plastic pipe; Slow Crack Growth (SCG)

1. Introduction

Nowadays, plastics are important materials in our lives and economy due to their excellent properties and low cost, which has led to an increase of twentyfold in the global production of plastics since the 1960s, reaching 360 million tonnes in 2018; and it is expected to double over the next 20 years (Ellen MacArthur Foundation, 2017). Plastics include a large group of different materials, which can be fuel-based or bio-based, both having a wide range of applications.

However, these materials have serious drawbacks often related to their short lifespan. Recent reports show that around 40% of total plastic waste comes from packaging, i.e., single-use applications products that contributes to the generation of tons of plastic waste every year (PlasticsEurope, 2019). Recycling rates have been slowly increasing in the EU in last decade, but it is still unequal across all countries, which cause that landfilling and incinerating are still the main destinies for plastic waste (Figure 1). The low rates in this sector are explained by the difficulties of handling, sorting and recycling plastics, as post-consumer plastic wastes usually consist of mixed plastics of heterogeneous composition. Also, post-consumer plastic waste often contains contaminants, organic and/or inorganic, which requires washing, clean and purifying steps to reduce and prevent contamination in the recycled polymer before being used again (Ragaert et al., 2017). Another limitation of recycled plastic is the deterioration of properties during reprocessing, commonly caused by thermomechanical degradation of the materials. This leads to chain scission, branching and cross linking. The degradation influences crystallinity, which consequently affects material's properties such as stiffness or elongation at break (Mantia, 1999). All these factors, along with the low cost of virgin raw resins brings about restrictions in the use of recycled plastics, even more limited to some specific applications.
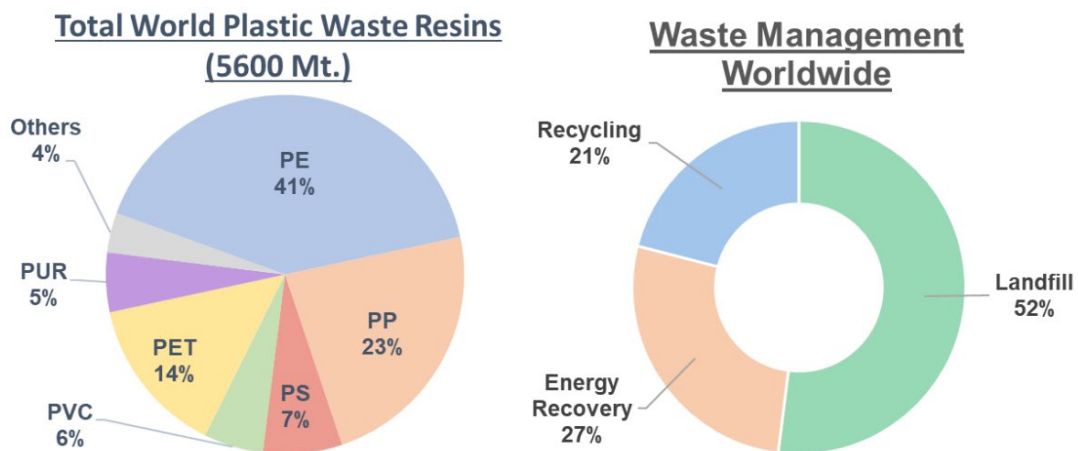
Figure 1. *Total World Plastic Waste Resins generated by the end of 2018 (left) and estimated Waste Management Worlwide rates for these resins (right)* (Geyer, 2020)

This lack of development in the recycling of plastics means that 10 million tons of polymeric materials are discarded every year throughout the world, with the consequent social and environmental impact (Ignatyev et al., 2014). With the aim of combating this issue, in 2018, the first European strategy for plastics was approved in the framework of the Circular Economy, which represents an important change in the way of designing, manufacturing and recycling plastics in the European Union. Landfilling bans, more responsibilities for producers and specific recycling targets will be implemented in the future years to help reducing plastic wastes (European Union, 2018).

Among all plastic waste generated every year, polyolefins constitute the main group in the waste streams. Particularly, polyethylene (PE) is one of the most abundant (Figure 1), as it is widely used in packaging (mostly low-density polyethylene – LDPE), building (Gama et al., 2018) and piping industry (high-density polyethylene) (Geyer, 2020). Post-consumer recycled polyethylene is mainly made of goods such as bottles and packaging, which are sorted, chopped, washed and homogenized to make a reprocessed material that can be used for different applications (Singh et al., 2017). Although recycled polyethylene is already used for the manufacture of low-pressure pipes for gardens and agriculture, in other applications such as high-pressure pipes or packaging, its use is more restricted due to high requirements of these products. In this sense, current EN and ISO standards should be revised in the near future to allow introducing post-consumer recycled PEs.

Industry estimates that the use of recyclates could help to reduce costs and cause a lower environmental impact. However, it is necessary to improve the properties of recycled HDPE to accomplish the goals pursued by the Circular Economy. For example, during the last decade the use of natural fibers, like sisal (Fávaro, 2010) or yute fibers (Satapathy, 2018), to reinforce recycled polyethylene have been deeply explored as it offers good mechanical performance and environmental benefits. Nevertheless, these composites usually require coupling agents to improve the compatibility between fiber and recycled resin (Lei et al., 2007), which could limit its applications. Another contribution to enhance the properties of the recycled material is based on the use of compatibilizers. The presence of small amounts of polypropylene in the PE waste streams is habitual, and compatibilizer agents address the mixture integration, and thus reducing the negative effect of immiscible materials in the polymer matrix, as well as preventing the degradation and possible cross linking during the recycling process (Hope, 1998). Block copolymers have been successfully used for compatibilizing blends containing PE, but other compatibilizers have also been explored such as nanoparticles, ionomers and reactive polymers (Maris et al., 2018). Furthermore, blends of recycled polyethylene with raw resins stands out as one of the best effective alternatives to enhance recyclability, as their performance seems promising for gravity sewer systems (Alzerreca et al., 2015) or for the

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manufacture of corrugated pipes (Board et al., 2018). As a result, new materials with better long-term properties could be fabricated, opening a wide range of industrial applications to post-consumer HDPE, which is of paramount importance to achieve the objectives proposed by the Circular Economy model, without compromising the product's quality.

The aim of this work is to evaluate the incorporation of recycled polyethylene to virgin PE with pipe grade quality to develop new materials that include different percentages of recycling PE to be used in the manufacture of polyethylene pressure pipes, and thus increasing the close-loop recycling on PE for pipe application (Figure 2). The chemical properties and homogeneity of blends prepared are determined by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and temperature rising elution fractionation (TREF) measurements. Physical and mechanical properties are established by using tensile and flexural tests. Resistance to Rapid Crack Propagation (RCP) is ascertained by calculation of the Plane Stress Impact Energy parameter according to the standard ASTM F2231 (ASTM-F2231-02, 2019). Moreover, to effectively predict the long-term performance of these materials to be reused in HDPE pipe applications, the Slow Crack Growth (SCG) resistance is determined. SCG resistance is studied through the Pennsylvania Notch Test (PENT), according to the standard ASTM F1473 (ASTM-F1473-18, 2018). Remarkably, a dual correlation of SCG and RCP with the content of recycled PE in blends was established, allowing to develop predictive capabilities that guarantee the requirements and specifications for pressure pipe applications. Thus, this method of waste management provides new opportunities to introduce rHDPE in the market of PE pressure pipes, where its use has been disclaimed either for industry objections or restrictive laws.
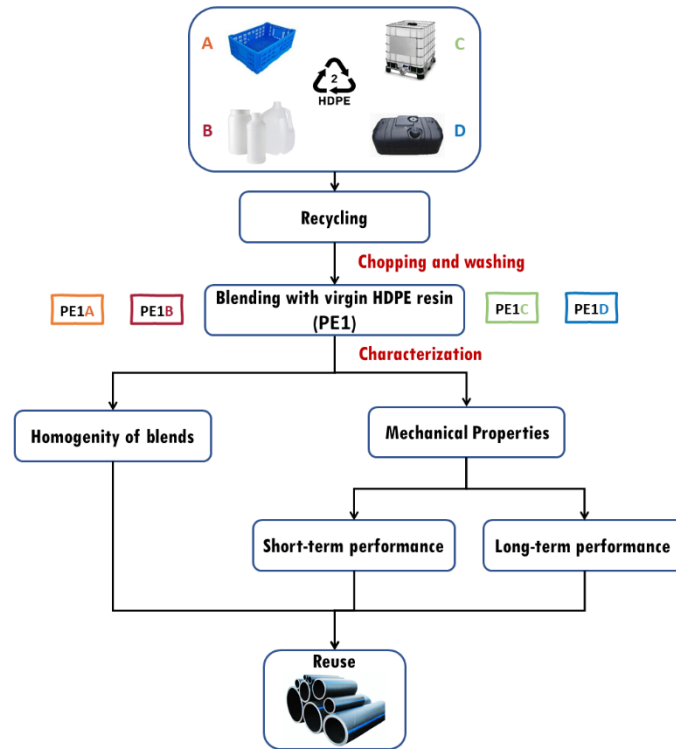
Figure 2. Flowchart of the experimental procedure

2. Experimental

2.1. Materials

Two recycled HDPE materials were provided by two manufacturers from Municipal Solid Waste (MSW). The recycled HDPE *A* were obtained from injection products such as industrial crates and caps, while polyethylene *B* proceed from blow moulding goods, mainly packaging and detergency bottles. Two additional recycled HDPE were obtained from post-consumer industrial containers (*C*) and automobile fuel tanks (*D*) collected from dumps, specifically for scrapyard, by recyclers. As all recycled resins proceed from end-of-life waste, each recyclate has been previously chopped and washed to obtain a homogeneous material, without adding any compatibilizers agents or antioxidants in the process. Blends have been prepared in a Collin ZK 50 twin-screw extruder counter-rotating, containing up to 75 wt% of recycled HDPE, and raw PE100 resin for the remaining portion. The extrusion temperature used goes from 185 to 240 ºC with a screw speed of 60-80 rpm. The raw HDPE is a high quality PE100 pipe grade (according to UNE-EN ISO 12162:2010) that is used for pipe extrusion. This resin has a bimodal molecular mass distribution to fulfil the high requirements of pressure pipes.

2.2. Molecular and physical characterization

To estimate the molecular mass (M_w), the molecular weight distribution (MWD), and the short chain branching distribution (SCBD) measurements were carried out on a Gel Permeation Chromatography (GPC) GPC-IR5 (Polymer Char), a high temperature gel permeation chromatograph. The GPC-IR5 has been equipped with a special set of columns and an infrared detector, which enables the detection of the online concentration and composition to distinguish differences of 1 branch per 1,000 atoms of carbon. Sample solutions at a concentration of 0.75 mg/mL in 1,2,4- trichlorobenzene (TCB), stabilized with BHT (2,6-di-tert-butyl-4-methylphenol) were obtained by gentle stirring at 150 ºC for 2 hours. Analysis were performed at a flow rate of 1 mL/min and a temperature of 160 ºC.

Thermal measurements were performed at a heat rate of 10 ºC/min with a DSC Mettler-Toledo 822e. The degree of crystallinity was calculated from the melting enthalpy values of the samples, using as reference a value of 290 J/g for the enthalpy of fusion for an ideal PE crystal.

TREF experiments to further evaluate the compatibility between virgin and recycled materials were carried out on a commercial CRYSTAF-TREF instrument model 300 (Polymer Char). 80 ± 0.5 mg of sample were dissolved in TCB at 160 ºC. Then the solution was loaded into the column and held at 130 ºC for 45 min. After the stabilization step, the temperature was reduced to 35 ºC under a constant cooling rate of 10 ºC/min where the polymer crystallized into the column. Finally, the sample was eluted with TCB at a constant flow rate of 1 ml/min. The concentration of the polymer eluted was measured by an infrared detector and the first derivative is used to obtain the crystallization curves.

Tensile and flexural tests were developed in a universal testing machine (MTS Alliance RT/5) at 23 ºC and 50 % relative humidity. Tensile tests were carried out on the dumbbell shaped specimens 1BA at a crosshead speed of 50 mm/min, according to UNE-EN ISO 527-2:2012. The yield stress was determined as the first maximum in the stress-strain curves. Flexural tests were accomplished on the rectangular bars samples with a three-point bending geometry according to the ISO 178:2010 standard at a crosshead speed of 2 mm/min.

2.3. Plane Stress Impact Energy

The resistance to RCP is evaluated through the S4 (Small-Scale Steady-State Test) according to ISO 13477-2008. It has been a helpful method to investigate the rapid crack propagation in polyethylene pipes (Yayla and Leevers, 1992). Nevertheless, due to large amount of material needed for this test, alternative methods have been investigated. Brown and Lu developed a method based in the determination of impact resistance at 23 ºC on a specimen previously moulded by compression and notched, showing the existence of a good correlation between

the Plane Stress Impact Energy (PSIE) and the critical temperature determined through the S4 trial (Brown and Lu, 2001). This method was described in the ASTM F2231-02 standard, which is employed in this study to determine the RCP resistance of all blends prepared. RCP focuses on how a fast-moving brittle crack could propagate across the material and is one of the main design criteria for limiting the operational pressures of polyethylene pipes. There are several factors that affect the resin RCP resistance, such as pipe geometry and test conditions (Šindelář et al., 2005). Although there is some controversy with the correlation between the PSIE and the S4 critical temperature (Tc) (Krishnaswamy et al., 2006), this procedure is often used as an indicator of the toughness of the studied materials.

2.4. Pennsylvania edge-notch tensile (PENT) tests

An Instron 3800 Series PENT tester was used to perform tests, according to ASTM F1473, to evaluate the SCG resistance. 10-mm-thick plaques were compression-molded in a hydraulic press at 180 °C and at a nominal pressure of 200 bars. Afterwards, they were cooled slowly for 5 hours at a rate of approximately 0.5 °C/min until reaching room temperature. During the cooling stage, the pressure was decreased naturally. Subsequently, specimens of 50 × 25 × 10 mm were machined from the plaques, followed by notches slowly pressed into the specimen by a razor blade at a speed of about 200 μm/min. Side notches of 1.0 mm and a front notch of 3.5 mm were made according to the ASTM F1473 standard. Under the standard PENT conditions, specimens were exposed to a constant load of 2.4 MPa at a temperature of 80 °C. Afterward PENT test, the fracture surfaces were observed by environmental scanning electron microscopy (SEM) (Philips XL-30) at 0.5 Torr and 15 kV. Slow Crack Growth (SCG) is the main long-term failure in polyethylene pipelines and, hence the most critical parameter to control (Domínguez et al., 2012). Under low stress upon a long period of time, PE fails in a brittle mode (Brown and Bhattacharya, 1985; Lustiger and Corneliussen, 1987). This type of failure is typically considered in the design of pipelines, as these materials must support stresses well below its total yield stress. Eventually, under these conditions, a craze could be formed during transport and installation in the pipe and starts growing slowly until the brittle failure occurs.

3. Results and Discussion

In this work, the potential use of four post-consumer recycled HDPE (namely, Rec-A, -B, -C and –D) in the manufacture of polyethylene pipes blended with raw HDPE (PE1) featuring PE100 grade quality has been evaluated. Table 1 summarizes the main individual properties of PE100 resin and all recycled polyethylene materials used.

1   *Table 1. Physicochemical properties of PE100 resin and recycled polyethylenes.*

| Material	Type	M_w (kg/mol)	M_w/M_n (-)	SCB /1000C[a]	Density (kg/m³)	T_m (ºC)[b]	Crystallinity (%)	MI / HLMI (g/10 min)[c]
PE1	PE100	283	29.4	2.2	962	136.0	64.0	0.06 / 7.01
Rec-A	Recycled HDPE (Injection)	114	16.3	31.6	970	136.4	54.3	3.0 / 160.0
Rec-B	Recycled HDPE (Blow Moulding)	166	18.3	9.6	960	138.6	62.3	0.30 / 34.1
Rec-C	Recycled HDPE (Containers)	277	28.2	1.3	947	133.4	66.1	0.06 / 7.09
Red-D	Recycled HDPE (Fuel Tanks)	296	23.2	0.8	944	130.9	64.4	0.07 / 5.89

2   [a] *SCB /1000C: branch per 1,000 atoms of carbon*

3   [b] *T_m: Melt Temperature*

4   [c] *MI / HLMI: Melt Index / High-Load Melt Index*

5   **3.1.   Blend Compatibility**

6   Plastic blends have been prepared using a twin-screw extruder to mix both virgin and recycled

7   materials (namely, PE1-RecX-Y; where X corresponds to recyclate A, B, C or D; and Y

8   corresponds to wt% of recyclate A, B, C or D). Twin-screw extruders allow a better

9   homogenization of the materials with an intimate blend of the components, as well as a better

10   dispersion of possible contaminants and impurities present in the recycled material that could

11   affect the performance of blends (Mount, 2017). To evaluate whether the intimacy of blending

12   was successful, all the blends were characterized by GPC. Figure 3 shows the MWD curves

13   for raw and recycled HDPE resins. PE1 exhibits the typical bimodal distribution characteristic

14   of the PE resins used for pipe grade, while all rHDPE present unimodal distributions with

15   different M_w. Rec-*A* presents a small peak at low molecular weight, which could be due to

16   impurities or other polymers in small amount present in the sample.
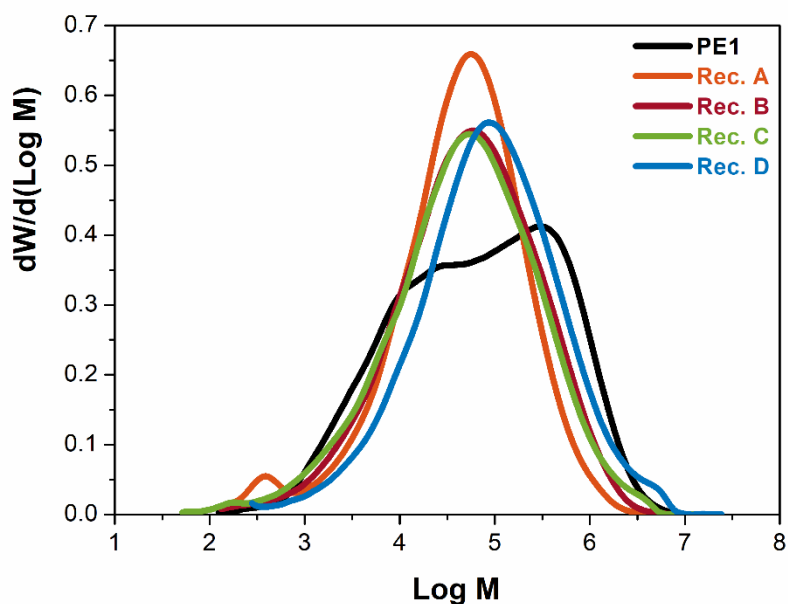
Figure 3. *MWD distribution determined by GPC for virgin HDPE (PE1) and four recycled HDPE (A, B, C, D)*

Furthermore, for comparison, Figure 4 shows the MWD for all the blends, including the MWD of parents PE1 and Rec-*A* through Rec-*D*. The MWD curves of the blends are in intermediate positions between the raw PE1 and recycled HDPEs. Likewise, the MWD's profiles shift from unimodal to bimodal distribution depending on the amount of each component in the blends. This result indicates that the blending process was effective using the twin-screw extruder system.
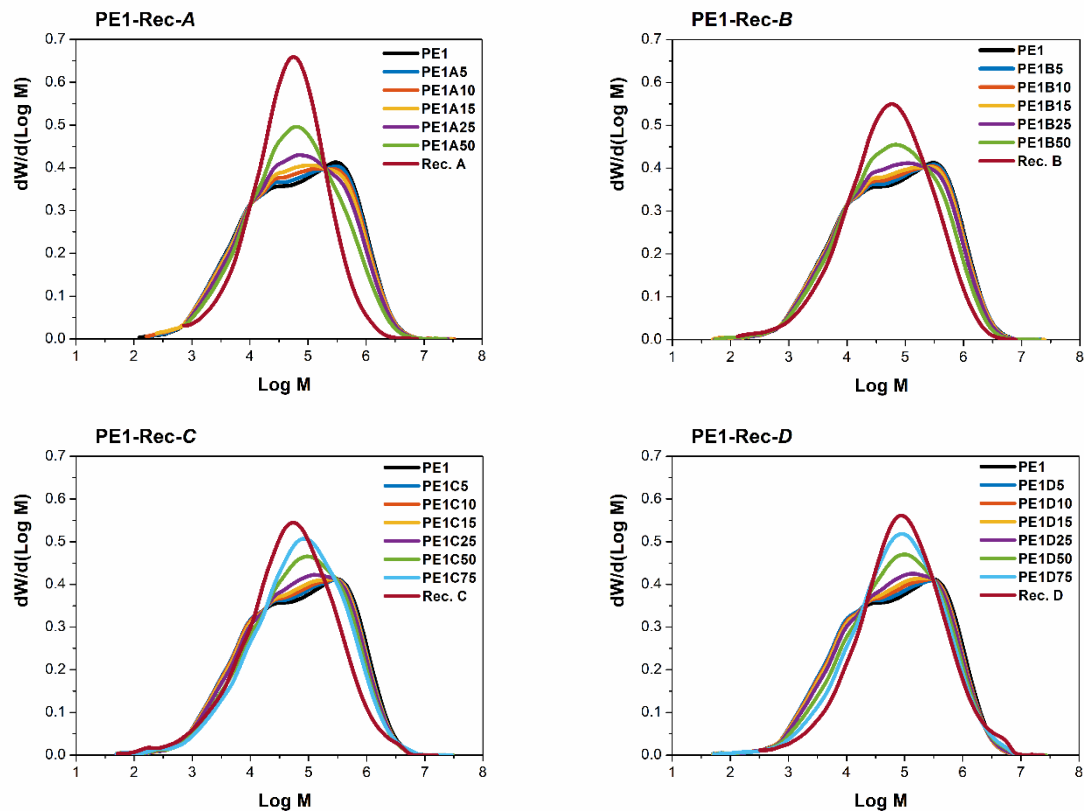
Figure 4. *MWD distribution of blends determined by GPC*

To further confirm the intimacy degree of components on the blend, thermal analyses are determined by DSC. As it is shown in Figure 5, the thermograms of the different blends show one single peak, which indicates good compatibility between the blend components, except for recycled polyethylene *A*. For this material, a small deviation is appreciated around 160 ºC, which could indicate the presence of certain amount of PP. This observation agrees well with the SCBD results (Table 1). Rec-*A* features outstanding high values of short chain branching (31.6 SCB per 1,000 atoms of carbon), which clearly indicates PP contamination and likely lower performance of blends. In addition, thermal analyses of blends corresponding to the system PE1-Rec-*A-25 and-50* (with 25 and 50 % of Rec-*A,* respectively) confirms the presence of PP. For the rest of the explored blend systems, no other additional melting peaks were observed that could reveal other possible impurities that may deteriorate the miscibility.
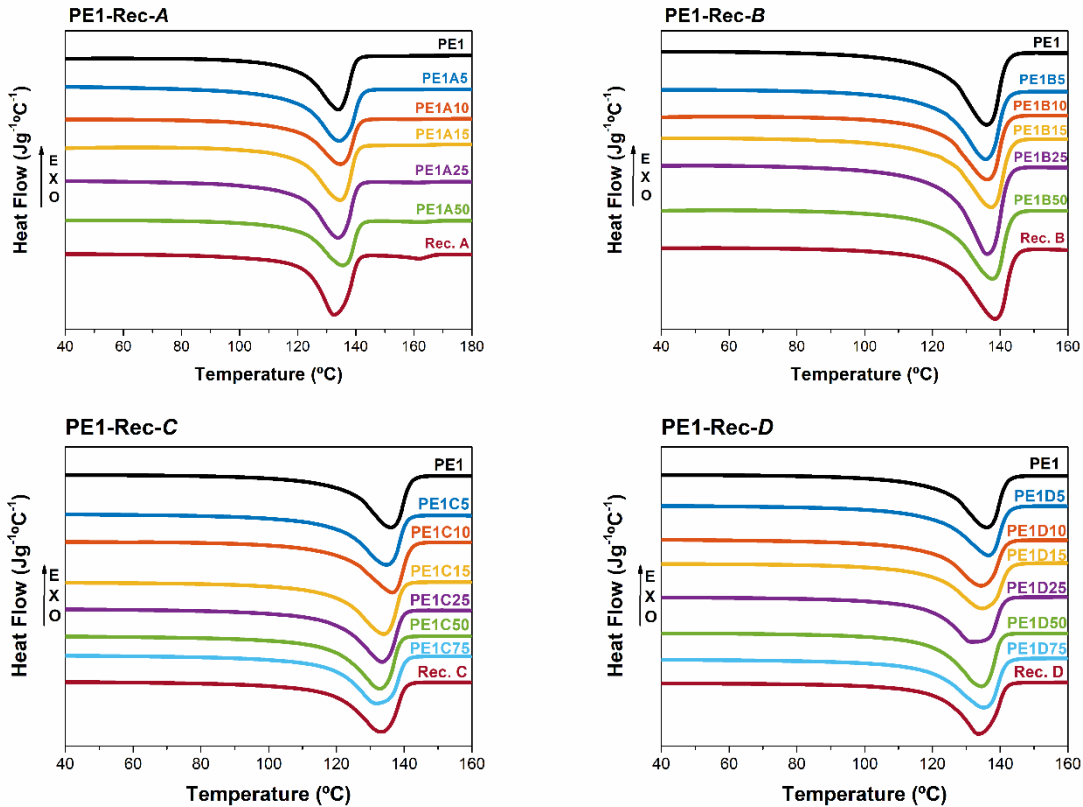
Figure 5. DSC melting thermograms obtained from second heating scanning of blends

Although these results reveal an effective miscibility, analyses of blends by DSC and GPC provide limited information, derived of the possible influence on the blends components by their molecular environment together with the impact of the thermal history that can affect the results obtained (Pasch et al., 2000). TREF analysis may bring more light to the blends compatibility since it studies the crystallization steps of the different components of the blends from very diluted solutions, which avoids the influence of thermal history (Pasch and Malik, 2014). A crystallization cooling rate of 5 ºC/min is chosen to favor the separation between different molecular components of blends (Fonseca and Harrison, 1997). Figure 6.a) shows the TREF analysis for raw and recycled polyethylene samples. The curves' profile is similar for all materials, with the presence of two different peaks, which are related to melting-recrystallization processes that take place during the analysis, favored by high cooling rate. The first sharp peak at around 96 ºC likely corresponds to thinner lamellae populations, composed of chains with a higher degree of branching and content in comonomer. However, slight differences may be observed among all recycled materials. For Rec-*A* and -*B*, this peak eluted at similar temperatures (97 ºC), while for Rec-*C* and-*D* the peak is slightly shifted to lower temperature (96 ºC) and matching well with the first peak of raw PE1. This could be explained by the thermomechanical degradation that suffer rec-*A* and-*B* during the recycling process, which increases the chain scission and branching in these materials, leading to a

significant presence of short (SCB) and long chain branching (LCB), and decreased molecular weight of the polymeric chains. The high SCB values for Rec-*A* and -*B* and low MWs (Table 1) confirm both the degradation and contamination with PP, notably for Rec-*A*, in contrast with Rec-*C* and –*D* resins, which exhibit a lower presence of SCB and higher MWs. The second elution peak is observed at around 102 ºC that may correspond to thicker crystals from linear chains with low content in comonomer. In contrast to recycled PEs, the second peak elution for raw PE1 is appreciated at 99 ºC. A likely explanation lies on both the higher amount of comonomer content and branching included in the high molecular weight chains of standard PE100 pipe grade, sample PE1, in contrast with recycled resins (García et al., 2008). Rec-*A* exhibits an additional elution peak at 118 ºC (around 9 wt%) that corresponds to PP (Fernández et al., 2015; García et al., 2011b), and agrees well with the results obtained by GPC and DSC.
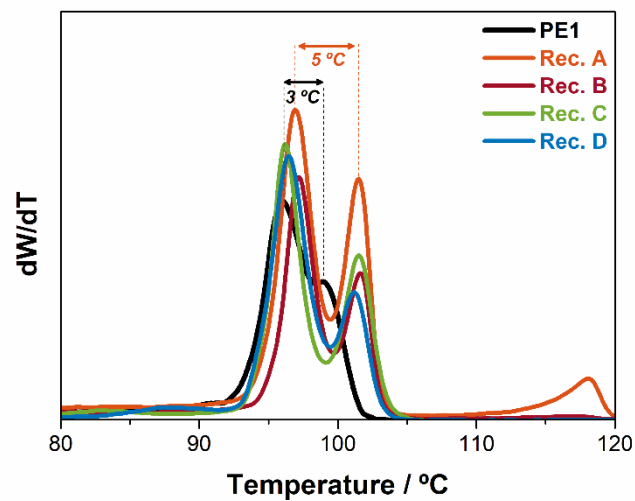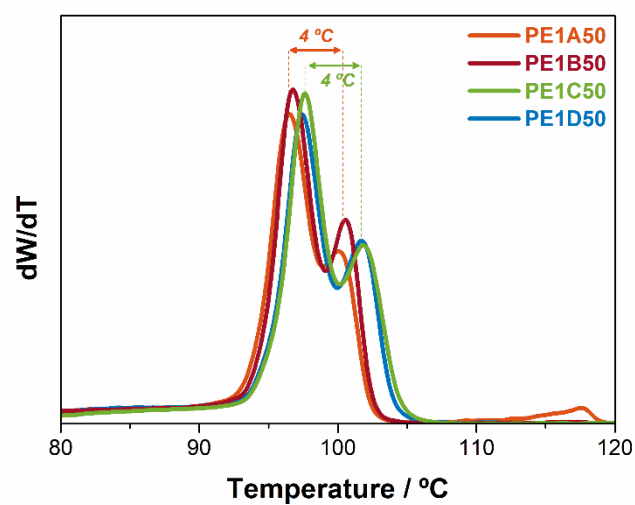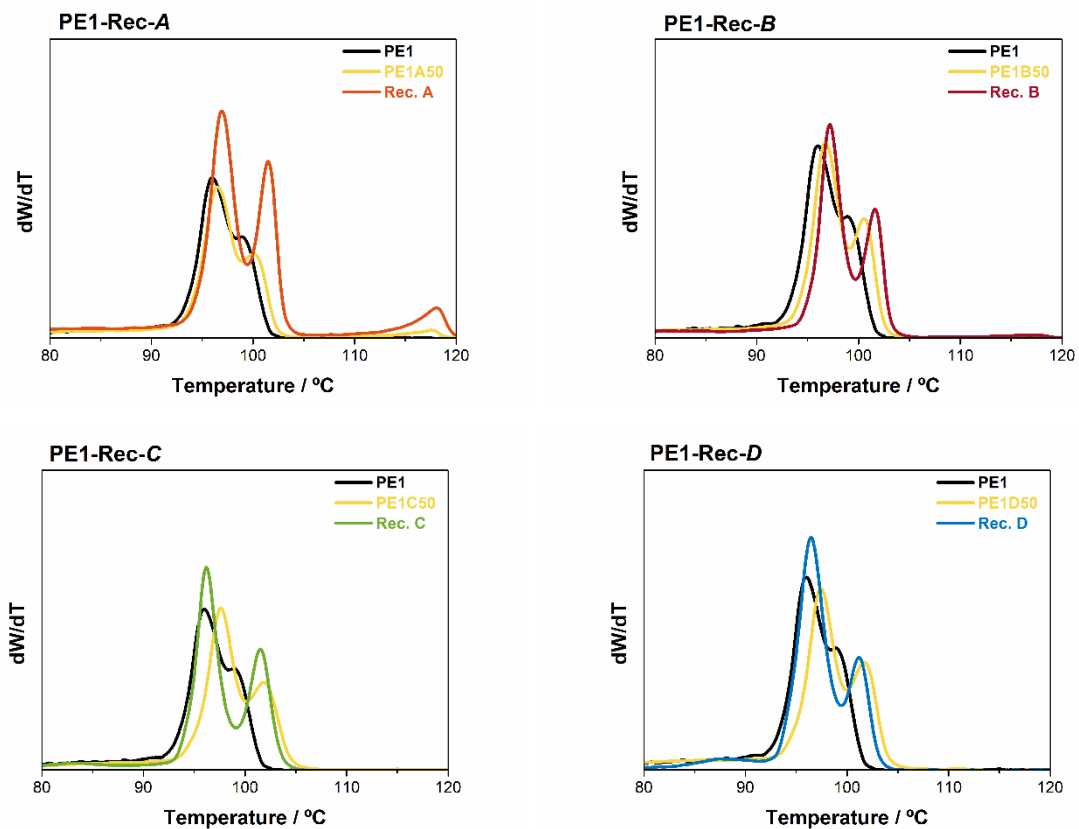

Figure 6. *Analytical TREF curves for raw and recycled resins (a) and blends containing 50 wt% of recycled HDPE (b).*

TREF analysis were also performed for all blends prepared with a recycled HDPE content of 50 wt%. The curves obtained are shown in Figure 6.b). The previous bimodal TREF profile is also observed for all blends with a difference of approximately 4 °C between the first and second eluted peaks, which is another parameter that indicates an effective miscibility among raw and recycled resins. The TREF peaks for PE1-Rec-*C*-50 and PE1-Rec-*D*-50 appears at slightly higher temperatures than blends containing Rec-*A* and -*B*. A likely explanation resides on the increment in molecular weight that experience blends prepared with Rec-*C* and -*D* recycled resins, which may result in improved performance, as discussed later. For PE1-Rec-*A*-50 blend, the peak at 118 °C is also observed, and thus the presence of PP in blends prepared with this recycled resin is confirmed. For comparison, Figure 7 shows the blend system PE1-Rec-*X*-50 plotted with PE1 and each recyclate. As it can be seen, the blends feature intermediate thermograms between those of the raw PE1 and recycled resins, which confirms the good compatibility among the virgin and recycled materials. These results, together with those obtained in GPC and DSC analyses, reveals a good degree of compatibility among all selected polyethylenes for this study. The undesired presence of PP in Rec-*A* resin can entail the modification of some properties during processing that finally might result in deterioration of the blends mechanical performance that presumably makes this rHDPE less suitable for pipe application.

Figure 7. Analytical TREF curves for blends containing 50 wt% of rHDPE plotted with raw and recycled resins.

3.2. Short-term mechanical properties

To evaluate the strength of all blends related to the likely application of post-consumer HDPE in the manufacture of polyethylene pressure pipes, the short-term mechanical properties are studied. It is often the case that recycled HDPE shows lower mechanical performance, mainly due to degradation and contamination, as well as the decrease in the molecular weight that takes place during the recycling process, owing to chain scission and cross-linking contribution.

Thus, tensile stress-strain curves and flexural modulus were determined for all blends at room temperature. For PE100 pipe grades, tensile strength at yield and elongation at break should be above 23 MPa and 500 % respectively, while the flexural modulus must be above 900 MPa (ASTM-D2513-19, 2019; ASTM-D3350-14, 2014; PE100+ Association, 2020; The Plastics Pipe Institute, 2008). Table 2 shows mechanical properties for all blends systems studied. All of them show a similar trend as a function of the recycled content, with values between the raw and the corresponding HDPE recycled material, which agrees well with the additive principle that the measured property depends on the composition of the blend (Gooch, 2011).

Yield strength value for all blends is above 23 MPa, which fulfills with the requirements for PE100 grades. Elongation at break is more sensitive to the recycled material present in the blend that slightly decreases with the presence of Rec-*A* and *-B*. In the case of Rec-*A*, this can be explained by the presence of PP in the polymer matrix. Additionally, these results may be related to the decrease in the molecular weight of the blends as the content of recycled resin increases. This behavior was not observed for Rec-*C* and *-D*, as both have higher M_w because proceed mostly from controlled and closed plastic waste flows and, therefore, are less exposed during their lifetime to external contaminants, which results in recycled PE materials keeping their original physico-chemical properties. Flexural modulus values follow a similar tendency for all blends with values above the minimum required for PE100 grades. Hence, these properties do not represent any limitation related to the potential application of using recycled PE materials for pressure pipe manufacture, with the probable exception of Rec-*A*, which would require either a better separation in origin or using compatibilization strategies (Graziano et al., 2018) to prevent the lower performance of these blends for pipe applications.
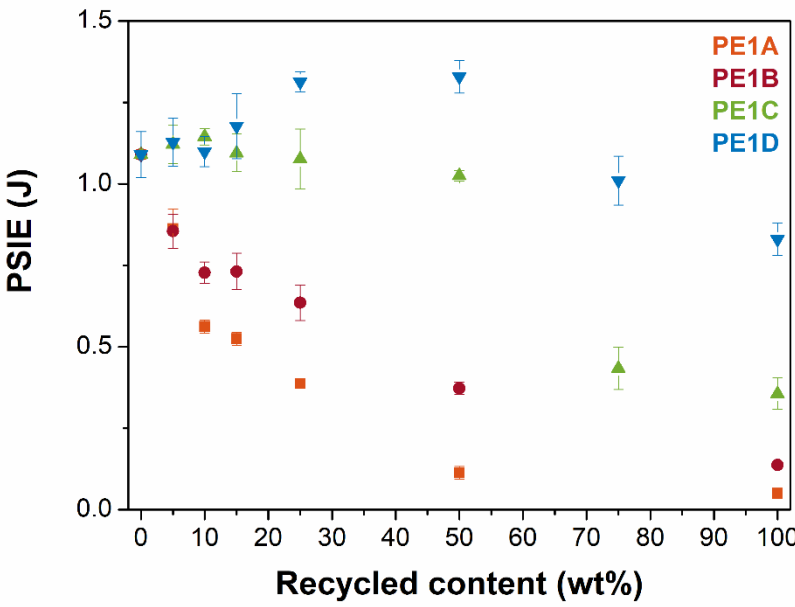
Table 2. *Mechanical properties for all blends systems.*

Blend System	% Recycled HDPE	Yield Strength / MPa	Flexural Modulus / MPa	Density / (kg/m^3)	HLMI (g/10 min)	Mw (kg/mol)	Mw/Mn (-)
PE1-Rec-A	0	24.8	1186	962	7.01	283	29.4
	5	25.0	1121	960	8.29	278	31.2
	10	24.7	1118	963	9.66	273	36.0
	15	24.8	1057	962	11.9	263	33.8
	25	24.1	989	963	16.5	248	34.5
	50	23.9	978	966	31.5	212	31.3
	100	-	999	970	160.0	114	16.3
PE1-Rec-B	0	24.8	1186	962	7.01	283	29.4
	5	24.9	1115	961	6.62	276	32.3
	10	25.2	1121	961	7.46	270	33.5
	15	25.0	1133	962	7.04	264	32.2
	25	25.9	1102	962	8.58	254	29.5
	50	26.2	1106	964	13.9	219	25.8
	100	26.8	1082	960	34.1	166	18.3
PE1-Rec-C	0	24.8	1186	962	7.01	283	29.4
	5	24.7	1221	959	5.94	265	31.3
	10	24.8	1190	960	5.99	262	31.2
	15	24.9	1131	958	6.01	263	30.5
	25	24.7	1151	958	6.26	257	28.7
	50	24.1	1105	956	6.46	244	29.9
	75	23.9	1045	953	6.74	247	28.9
	100	23.4	951	947	7.09	248	28.0
PE1-Rec-D	0	24.8	1186	962	7.01	283	29.4
	5	24.8	1204	960	7.34	269	33.2
	10	24.6	1169	959	7.13	268	31.5
	15	24.5	1099	958	6.00	267	33.1
	25	24.7	1086	958	6.34	269	30.6
	50	24.3	1067	954	6.16	273	28.6
	75	23.9	1037	951	6.02	272	26.3
	100	23.8	1014	944	5.89	256	24.6

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3   Additionally, a key parameter with outstanding impact in the short-term mechanical properties

4   that is needed to be considered to select an adequate polyethylene for pipe application is the

5   resistance to rapid crack propagation (RCP) determined through the measure of the Plane

6   Stress Impact Energy. Thus, Figure 8 shows the values for the impact resistance obtained by

7   the PSIE test at 23 ºC. According to previous results (Domínguez, 2009), PSIE values must

8   be higher than 0.50 and 0.85 J for PE80 and PE100 pipe grades, respectively. For MSW plastic

(Rec-*A* and -*B*), a dramatic decrease in PSIE is observed as higher is the content of the recycled PE into the blend. However, blends with Rec-*B* resins have slightly greater resistance to RCP than those with Rec-A. Impact resistance measurements are more sensitive to the presence of impurities and contaminants than yield stress or flexural modulus essays, which explain the lower PSIE values obtained for blends with Rec-*A* polyethylene.

Instead, it is noteworthy to highlight that the use of recycled resins Rec-*C* and -*D* provides all blends remarkable PSIE values beyond the limits for common pipe grades mentioned above. These materials show an overall good RCP performance mainly due to the higher molecular weight and polydispersities than those blends containing Rec-*A* and –*B* samples, which help to maintain the toughness of the raw resin. These results indicate that the resistance to RCP measured by means of PSIE test is a key parameter that needs to be considered to control the effect of the amount of recycling PE added to the blends.
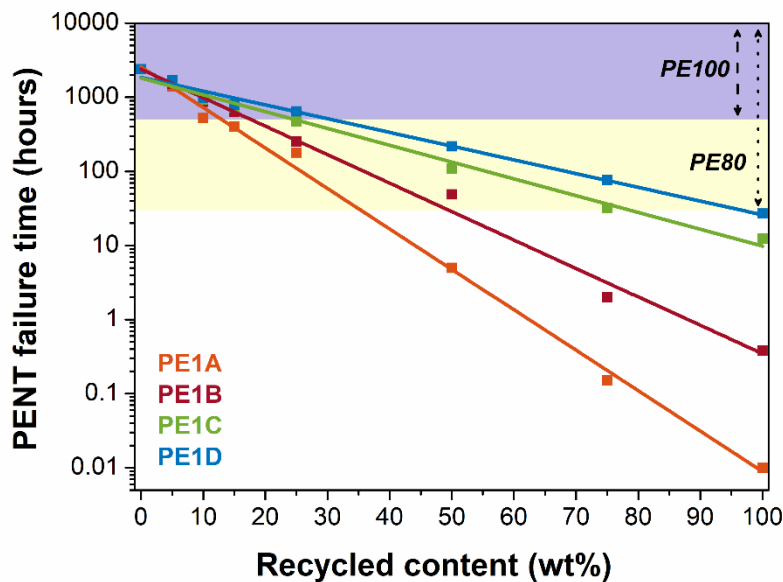

Figure 8. PSIE values vs. recycled content for all blends.

3.3. Long-term mechanical properties

For PE, the SCG resistance is highly dependent on physical parameters like load stress, temperature, test specimen and presence of a notch. Also, molecular architecture plays a key role, particularly molecular weight, branching, crystallinity and tie molecules (Cheng, 2008; Huang and Brown, 1988). In the case of rHDPE, the presence of contaminants of different shapes and sizes could also affect the SCG resistance, acting as a stress concentration point that leads to craze opening and propagation.

The long-term performance for all blends has been studied through the PENT test that allows evaluating the SCG resistance. Figure 9 shows that PENT failure time exponentially decrease with the content of recycled material for all blends. It is well accepted that failure times for PE80 / PE2708 and PE100 / PE4710 pipe grades are above 30 and 500 hours (ASTM-D3350-14, 2014), respectively, which represents a limitation on the recycled content added to the blends. To fulfill the SCG requirements for PE100 pipe grades to overcome 500 hours before the specimen breaks, incorporation of Rec-*A* and –*B* in blends cannot exceed values of 12 and 18 wt%, respectively. Unlike, blends incorporating Rec-*C* and -*D* show better SCG performance, reaching values of 25 and 32 wt% of Rec-*C* and –*D*, respectively, to satisfy with the PE 100 pipe grades specifications. This outcome can be explained by the presence of heterogeneous materials and more contaminants in the recyclates obtained from MSW, Rec-*A* and –*B*, than those obtained selectively from industrial containers and fuel tanks, Rec-*C* and -*D*. This indicates that it is possible to correlate the PENT failure time with the recycled content in the blend, also in accordance with the PE homopolymer-copolymer blend systems results previously reported by our research group (García et al., 2011a). This outstanding result is a good predictor of the amount of recycled material that it is possible to incorporate prior to physically blending, to meet the required specification.

Figure 9. PENT failure time vs. recycled content for all blends.

Furthermore, to assess that SCG governs the main failure mechanism relative to long-term fracture for all blends studied, SEM microscopy of the blends fracture surface is performed. Figure 10 shows SEM images of the fracture surface for all blends containing 25 wt% of recycled materials, Rec-*A*, -*B*, -*C* and –*D*. All samples exhibit homogeneous fractures

morphology with fibrillar structure and smooth surfaces that clearly confirms the brittle SCG process that each sample has suffered.
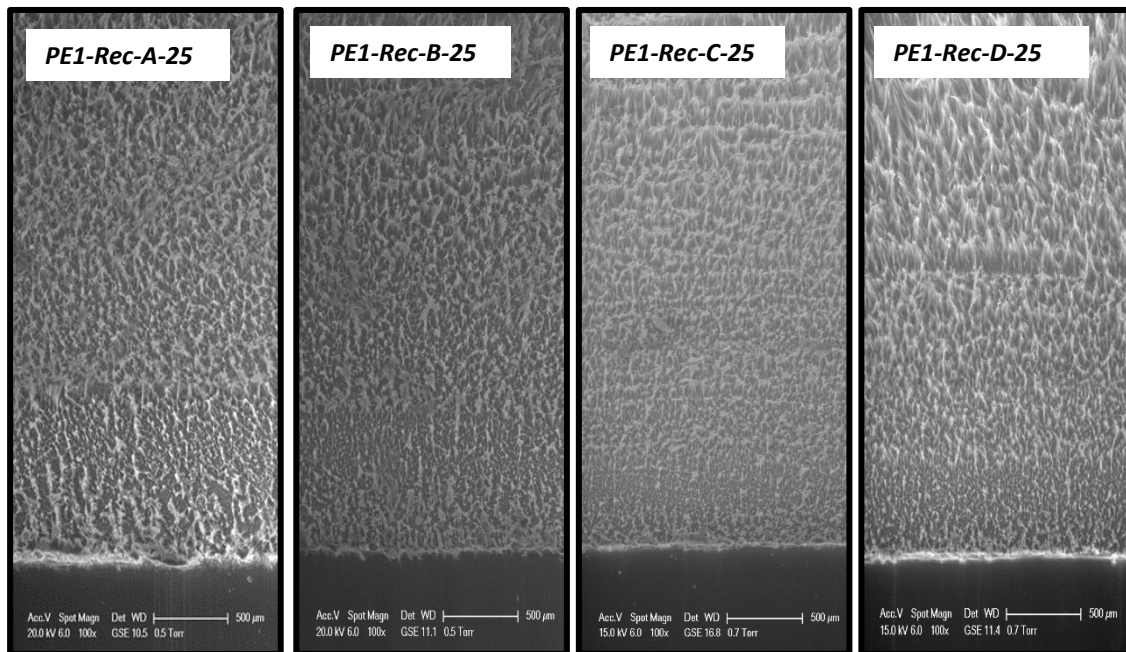
Figure 10. SEM images of fracture surface for blends containing 25 wt% of recycled materials.

3.4.   Application interval on pipes

The analysis of short- and long- term mechanical properties allows concluding that both RCP and SCG resistances are key factors that limit the possible content of recycled resin in blends. However, several differences are observed among all resin blends that are related to the recyclates used, since the limiting factor to satisfy the requirements of both RCP and SCG varies for each one.

First, for blends incorporating recycled polyethylene obtained from MSW, Rec-*A* and –*B*, the influence of the resistance to RCP, and not the SCG, is the driven force that limits the recyclate content in blends. Figure 11.a and b shows the interval of application to satisfy the requirements of pipe grades for PE1-Rec-*A* and PE1-Rec-*B* blend systems. Thus, to meet the requirements of PE80 pipe grade the maximum recyclate incorporation can be 23 and 37 wt% of Rec-*A* and –*B*, respectively, while to achieve the PE100 pipe grade requirements, the maximum recycled content decreases up to 5 and 9 wt% of Rec-*A* and –*B*, respectively. These differences between both blends may be attributed to the higher molecular weight and the presence of lower impurities of Rec-*B* in contrast with Rec-*A*. On the other hand, Figure 11.c and d also shows the interval of application of the PE1-Rec-*C* and PE1-Rec-*D* blend systems. For these recyclates, the limiting step to their application in pipes appears to be the SCG

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resistance, in contrast with the resistance to RCP for recyclates Rec-*A* and –*B*. Rec-*C* and –*D* recycled plastics possess both a higher molecular weight and an origin from more homogeneous waste source than MSW Rec-*A* and –*B*, which makes possible a clearly enhancement of short and long-term mechanical properties. Nevertheless, it is noteworthy to point out that when used up to 50 wt% of Rec-*C* in blends, PSIE values remain almost constant and enough above the limited established to not compromise the performance of these blends for pipe applications. From 50 wt% onwards of the content of recycled material, a dramatic decrease of PSIE values is noticed, which consequently restricts its application for pipes. Otherwise, when used Rec-*D* in blends all PSIE values are well above the limit of 0.85J, fitted as the minimum requirement to behave as PE100 pipe, which means that the resistance to RCP is not an impediment, and the SCG resistance is the only property that restricts the content of the recyclates in blends to be used for high pressure polyethylene pipe application. Table 3 summarizes the intervals of recycled materials than can be used for these blends considering each pipe grade. The percentage of recycled resin Rec-*C* and –*D* that could be used is higher than those of the Rec-*A* and-*B* proceeding from MSW recycled resins. Considering the limitations of PE100 grades, the incorporation of Rec-*C* and –*D* recycled resins in blends increases up to 25 and 31 % (purple surface in Figure 11-c and -d), respectively, which allows including a higher recycled amount in blends than recyclates obtained from common MSW plastic, Rec-*A* and -*B*. Based on this investigation, it is concluded that an improvement in the sorting and recycling process of the plastic wastes would allow increasing the recycled PE content related to raw HDPE materials in blends, but fulfilling with the high requirements and specifications for PE80 and 100 pipe grades, without compromising its performance and definitely aligned with the aims of the circular economy.
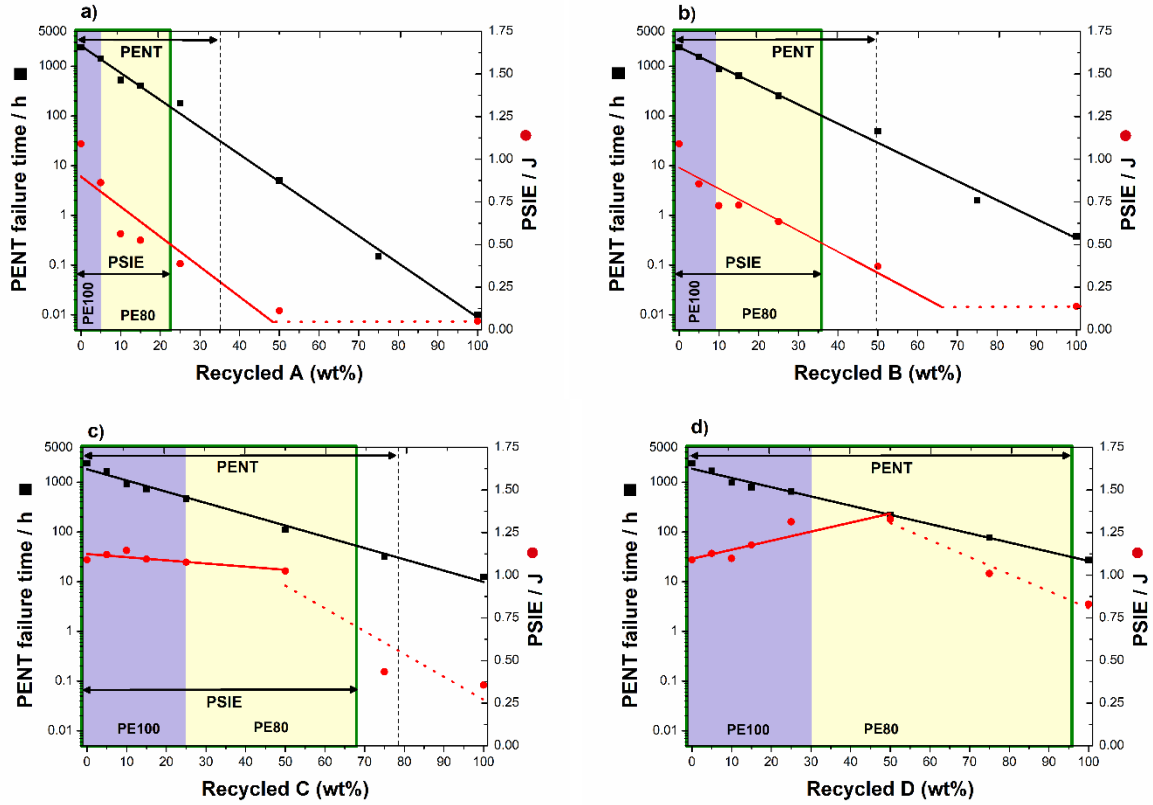
Figure 11. *Interval of application on common pipe grades for a) PE1-Rec-A, b) PE1-Rec-B, c) PE1-Rec-C and d) PE1-Rec-D blend systems.*

Table 3. *Percentage of recycled HDPE allowed for each blend system and corresponding pipe grade.*

Blend	% Recycled Content	Pipe Grade
PE1A	0 - 5	*PE100*
	5 - 23	*PE80*
PE1B	0 - 9	*PE100*
	9 - 37	*PE80*
PE1C	0 - 25	*PE100*
	25 - 68	*PE80*
PE1D	0 - 31	*PE100*
	31 - 96	*PE80*

4. Conclusions

Although recycled HDPE is currently used for non-pressure pipes, the lack of development and restriction by policies, due to the high structural and loading requirements that must be met, limit the incorporation of recycled materials to pressure pipes. In this work, different recycled materials from injection products such as industrial crates and caps (A), blow moulding goods

(B), industrial containers (C) and automobile fuel tanks (D) have been mixed with a raw pipe grade PE100 resin to study the incorporation of the end-of-life post-consumer PE waste and its feasibility to integrate in the manufacture of polyethylene pressure pipes to increase their recycling rates. The blending process was performed by a twin-screw extruder system. Conclusions are summarized as follows:

- The blend compatibility was evaluated by GPC and DSC. MWD curves of blends exhibited intermediate distribution between the raw and recycled PEs, while all DSC were characterized by thermograms with one single peak.

- TREF analysis of the blends also confirmed the intermediate behavior derived from the composition of the blends. These results demonstrated the effective degree of intimacy and good compatibility of the blends.

- The short-term properties, tensile strength at yield, elongation at break and flexural modulus for all blends rendered values above the minimum required for PE100 grades, so these properties do not represent any limitation related to the potential application of using recycled PE materials for pressure pipe manufacture.

- The resistance to rapid crack propagation (RCP), a particular short-term parameter for PE pipes, and the SCG resistance, the main long-term failure in PE pipelines, are greatly affected by the source and origin of recycled HDPE. Thus, both properties resulted critical to control the origin of the plastic waste and the incorporation of recycled PE into pipelines.

- A dual correlation of RCP and SCG resistances with the content of PE recyclate in blends is established, so we conclude that this method can be used to predict the amount of recycled PE that guarantees the high requirements and specifications for pipe applications.

The results are really promising and would allow incorporating recycled polyethylene to pressure pipe application. A remarkable conclusion of this work is that recycled PE for pipe applications is largely dependent on their quality and, therefore mixtures of high-quality PE waste with other plastic materials of lower quality cause contamination. In this particular case, a better sorting of HDPE recovered from waste would reduce the degree of contamination. Investment in technology that sorts HDPE would be justified, especially when there is an important market for these materials, such as the plastic pipe industry and, therefore it is possible to establish a way in which a cooperative relationship between recyclers and manufacturing industries could constitute an important innovation that would make sense from economic and environmental point of view.

Our work paves the way to reduce the consumption of raw polyethylene and giving to the plastic waste a new cycle for closing HDPE loops, and moreover the basis for the recycling of huge amount of post-consumer high density polyethylene pipe at its end-life, after 50 years in service.

Acknowledgments

**5.	References**

Alzerreca, M., Paris, M., Boyron, O., Orditz, D., Louarn, G., Correc, O., 2015. Mechanical properties and molecular structures of virgin and recycled HDPE polymers used in gravity sewer systems. Polym. Test. 46, 1–8. https://doi.org/https://doi.org/10.1016/j.polymertesting.2015.06.012

ASTM-D2513-19, 2019. Standard Specification for Polyethylene (PE) Gas Pressure Pipe, Tubing, and Fittings. ASTM International. https://doi.org/10.1520/D2513-19

ASTM-D3350-14, 2014. Standard Specification for Polyethylene Plastics Pipe and Fittings Materials. ASTM International. https://doi.org/10.1520/D3350-14

ASTM-F1473-18, 2018. Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins. ASTM International. https://doi.org/10.1520/F1473-18

ASTM-F2231-02, 2019. Standard Test Method for Charpy Impact Test on Thin Specimens of Polyethylene Used in Pressurized Pipes. ASTM International. https://doi.org/10.1520/F2231-02R19

Board, T.R., National Academies of Sciences, E., Medicine, 2018. Field Performance of Corrugated Pipe Manufactured with Recycled Polyethylene Content. The National Academies Press, Washington, DC. https://doi.org/doi:10.17226/24934

Brown, N., Bhattacharya, S.K., 1985. The initiation of slow crack growth in linear polyethylene under single edge notch tension and plane strain. J. Mater. Sci. 20, 4553–4560. https://doi.org/10.1007/BF00559346

Brown, N., Lu, X., 2001. The dependence of rapid crack propagation in polyethylene pipes on the plane stress fracture energy of the resin. Polym. Eng. Sci. 41, 1140–1145. https://doi.org/10.1002/pen.10815

Cheng, J.J., 2008. Mechanical and Chemical Properties of High Density Polyethylene: Effects of Microstructure on Creep Characteristics (Doctoral dissertation). Waterloo Univ. UWSpace.

Domínguez, C., 2009. Estudio del Proceso de Crecimiento Lento de Grieta en el Polietileno de Alta Densidad para su Aplicación en Tubería (Doctoral dissertation). Universidad Rey Juan Carlos.

Domínguez, C., García, R.A., Aroca, M., Carrero, A., 2012. Study of the PENT test conditions for reducing failure times in high-resistance polyethylene resins for pipe applications. Mech. Time-Dependent Mater. 16, 105–115. https://doi.org/10.1007/s11043-011-9151-z

Ellen MacArthur Foundation, 2017. The new plastics economy: Rethinking the future of plastics & catalysing action [WWW Document]. URL https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics-catalysing-action (accessed 11.20.19).

European Union, 2018. A European Strategy for Plastics in a Circular Economy [WWW Document]. URL https://publications.europa.eu/s/kIT6 (accessed 9.28.19).

Fávaro, S., 2010. Chemical, morphological and mechanical analysis of sisal fiber-reinforced recycled high-density polyethylene composites. Express Polym. Lett. - EXPRESS POLYM LETT 4, 465–473.

https://doi.org/10.3144/expresspolymlett.2010.59

Fernández, A., Expósito, M.T., Peña, B., Berger, R., Shu, J., Graf, R., Spiess, H.W., García-Muñoz, R.A., 2015. Molecular structure and local dynamic in impact polypropylene copolymers studied by preparative TREF, solid state NMR spectroscopy, and SFM microscopy. Polymer (Guildf). 61, 87–98. https://doi.org/https://doi.org/10.1016/j.polymer.2015.01.079

Fonseca, C.A., Harrison, I.R., 1997. Fractionation of HDPE on quench cooling. J. Therm. Anal. 49, 417–424. https://doi.org/10.1007/bf01987465

Gama, D.A., Yan, Y., Rodrigues, J.K.G., Roque, R., 2018. Optimizing the use of reactive terpolymer, polyphosphoric acid and high-density polyethylene to achieve asphalt binders with superior performance. Constr. Build. Mater. 169, 522–529. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2018.02.206

García, R., Carrero, A., Aroca, M., Prieto, O., Domínguez, C., 2008. Slow crack growth resistance in resin blends of chromium and metallocene catalyzed ethylene-hexene copolymers for pipe applications. Polym. Eng. Sci. 48, 925–933. https://doi.org/10.1002/pen.21038

García, R.A., Carrero, A., Martín, C., Domínguez, C., 2011a. Effects of the structural components on slow crack growth process in polyethylene blends. Composition intervals prediction for pipe applications. J. Appl. Polym. Sci. 121, 3269–3276. https://doi.org/10.1002/app.33911

García, R.A., Coto, B., Expósito, M.-T., Suarez, I., Fernández-Fernández, A., Caveda, S., 2011b. Molecular characterization of polypropylene heterophasic copolymers by fractionation techniques. Macromol. Res. 19, 778–788. https://doi.org/10.1007/s13233-011-0811-2

Geyer, R., 2020. Chapter 2 - Production, use, and fate of synthetic polymers, in: Letcher, T.M.B.T.-P.W. and R. (Ed.), . Academic Press, pp. 13–32. https://doi.org/https://doi.org/10.1016/B978-0-12-817880-5.00002-5

Gooch, J.W., 2011. Law of Mixtures, in: Gooch, J.W. (Ed.), Encyclopedic Dictionary of Polymers. Springer New York, New York, NY, p. 421. https://doi.org/10.1007/978-1-4419-6247-8_6810

Graziano, A., Jaffer, S., Sain, M., 2018. Review on modification strategies of polyethylene/polypropylene immiscible thermoplastic polymer blends for enhancing their mechanical behavior. J. Elastomers Plast. 51, 291–336. https://doi.org/10.1177/0095244318783806

Hope, P.S., 1998. Compatibilizers for recycled polyethylene, in: Pritchard, G. (Ed.), Plastics Additives: An A-Z Reference. Springer Netherlands, Dordrecht, pp. 162–169. https://doi.org/10.1007/978-94-011-5862-6_19

Huang, Y.L., Brown, N., 1988. The effect of molecular weight on slow crack growth in linear polyethylene homopolymers. J. Mater. Sci. 23, 3648–3655. https://doi.org/10.1007/BF00540508

Ignatyev, I., Thielemans, W., Vanderbeke, B., 2014. Recycling of Polymers: A Review 7, 1579–1593. https://doi.org/10.1002/cssc.201300898

Krishnaswamy, R.K., Lamborn, M.J., Sukhadia, A.M., Register, D.F., Maeger, P.L., Leevers, P.S., 2006. Rapid crack propagation failures in HDPE pipes: Structure–property investigations. Polym. Eng. Sci. 46, 1358–1362. https://doi.org/10.1002/pen.20582

Lei, Y., Wu, Q., Yao, F., Xu, Y., 2007. Preparation and properties of recycled HDPE/natural fiber composites. Compos. Part A Appl. Sci. Manuf. 38, 1664–1674. https://doi.org/https://doi.org/10.1016/j.compositesa.2007.02.001

Lustiger, A., Corneliussen, R.D., 1987. The role of crazes in the crack growth of polyethylene. J. Mater. Sci. 22, 2470–2476. https://doi.org/10.1007/BF01082132

Mantia, F.P. La, 1999. Mechanical properties of recycled polymers. Macromol. Symp. 147, 167–172. https://doi.org/10.1002/masy.19991470116

Maris, J., Bourdon, S., Brossard, J.-M., Cauret, L., Fontaine, L., Montembault, V., 2018. Mechanical recycling: Compatibilization of mixed thermoplastic wastes. Polym. Degrad. Stab. 147, 245–266. https://doi.org/https://doi.org/10.1016/j.polymdegradstab.2017.11.001

Mount, E.M., 2017. 12 - Extrusion Processes, in: Kutz, M. (Ed.), Applied Plastics Engineering Handbook (Second Edition). William Andrew Publishing, pp. 217–264. https://doi.org/https://doi.org/10.1016/B978-0-323-39040-8.00012-2

Pasch, H., Brüll, R., Wahner, U., Monrabal, B., 2000. Analysis of polyolefin blends by crystallization analysis fractionation. Macromol. Mater. Eng. 279, 46–51. https://doi.org/10.1002/1439-2054(20000601)279:1<46::AID-MAME46>3.0.CO;2-1

Pasch, H., Malik, M.I., 2014. Crystallization-Based Fractionation Techniques, in: Pasch, H., Malik, M.I. (Eds.), Advanced Separation Techniques for Polyolefins. Springer International Publishing, Cham, pp. 11–73. https://doi.org/10.1007/978-

3-319-08632-3_2

PE100+ Association, 2020. HDPE Pipe Technical Guidance [WWW Document]. URL https://www.pe100plus.com/PE-Pipes/Technical-guidance/model/r203.html (accessed 3.5.20).

PlasticsEurope, 2019. Plastics - the Facts 2019 [WWW Document]. URL https://www.plasticseurope.org/es/resources/publications/1804-plastics-facts-2019 (accessed 1.12.20).

Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. Waste Manag. 69, 24–58. https://doi.org/https://doi.org/10.1016/j.wasman.2017.07.044

Satapathy, S., 2018. Development of value-added composites from recycled high-density polyethylene, jute fiber and flyash cenospheres: Mechanical, dynamic mechanical and thermal properties. Int. J. Plast. Technol. 22, 386–405. https://doi.org/10.1007/s12588-018-9211-1

Šindelář, P., Nezbedová, E., Šimková, P., Buráň, Z., Bohatý, P., 2005. Effect of structural parameters on rapid crack propagation and slow crack growth in high density polyethylene pipeline materials. Plast. Rubber Compos. 34, 329–333. https://doi.org/10.1179/174328905X59827

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. https://doi.org/https://doi.org/10.1016/j.compositesb.2016.09.013

The Plastics Pipe Institute, 2008. 3 - Material Properties, in: The Plastics Pipe Institute: Handbook of Polyethylene Pipe. The Plastics Pipe Institute, pp. 43–103.

Yayla, P., Leevers, P.S., 1992. Rapid crack propagation in pressurised plastic pipe—II. Critical pressures for polyethylene pipe. Eng. Fract. Mech. 42, 675–682. https://doi.org/https://doi.org/10.1016/0013-7944(92)90049-K