



Assessment of plastic packaging waste: Material origin, methods, properties



Benny Luijsterburg^{a,b}, Han Goossens^{b,*}

^a Top Institute Food and Nutrition, P.O. Box 557, 6700 AN Wageningen, The Netherlands

^b Laboratory of Polymer Materials, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT

The global plastics production has increased annually and a substantial part is used for packaging (in Europe 39%). Most plastic packages are discarded after a relatively short service life and the resulting plastic packaging waste is subsequently landfilled, incinerated or recycled. Laws of several European and Asian countries require that plastic packaging waste collected from households has to be sorted, reprocessed, compounded and reused. These recycling schemes typically produce milled goods of poly(ethylene terephthalate) (PET), poly(ethylene) (PE), isotactic poly(propylene) (PP), mixed plastics, and agglomerates from film material. The present study documents the composition and properties of post-consumer polyolefin recyclates originating from both source separation and mechanical recovery from municipal solid refuse waste (MSRW). The overall composition by Fourier transform-infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC) were determined and compared with the sorting results of the sorted fractions prior to the reprocessing into milled goods. This study shows that the collection method for the plastic packaging waste has hardly any influence on the final quality of the recyclate; however, the sorting and reprocessing steps influence the final quality of the recyclate. Although the mechanical properties of recyclate are clearly different than those of virgin polymers, changes to the sorting and reprocessing steps can improve the quality.

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1. Introduction

Today, plastic waste is considered a serious social problem. The market for plastics has increased exponentially to an estimated annual production of 280 million tons in 2011 (Plastics, 2011), of which approx. 18.5 million tons, i.e. 39% of the European plastics demand, is used for packaging in Europe. After a short service life, the packaging plastics are disposed of either as landfill, incinerated or reused. The reuse can be done via chemical or mechanical recycling. In chemical recycling, the plastics are depolymerized to their respective monomers and subsequently re-polymerized (Kiran Ciliz et al., 2004) or to other valuable chemicals (Brems et al., 2012). In mechanical recycling, the plastics are sorted, melt compounded and shaped into new products. Mechanical recycling is presently the preferred treatment option for post-consumer plastic waste.

Post-consumer plastic waste can be collected via different schemes. In the Netherlands, this is done either via source separation (SS) or commingled collection (CC) with municipal solid

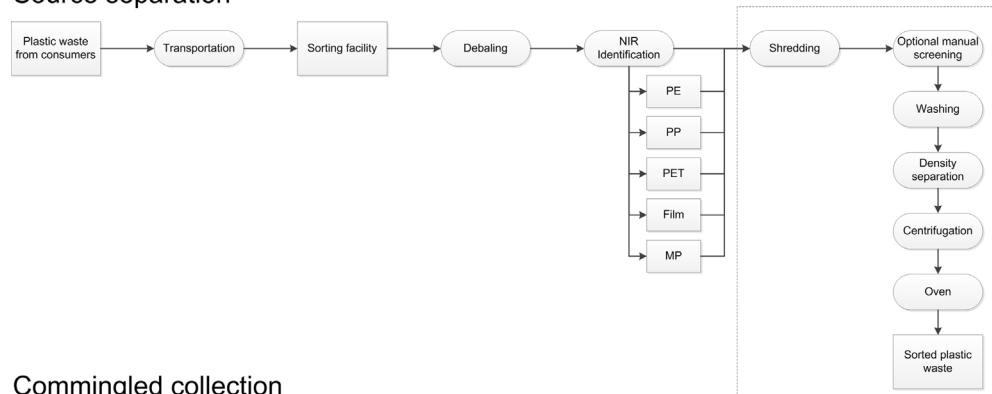
refuse waste (MSRW) and subsequent mechanical recovery. In the SS scheme, plastic packaging waste (PPW) is separated by the consumer and offered to curbside collection services or drop-off containers. The collected PPW is subsequently transferred to sorting facilities, which yield the following fractions: poly(ethylene terephthalate) (PET), poly(ethylene) (PE), isotactic poly(propylene) (*i*-PP), film, mixed plastics (MP) and rest. The sorting facilities use near-infrared (NIR) spectroscopy sorting machines, ballistic separators, wind sifters and drum sieves. Depending on the sorting facility, plastics sorting is done in different steps or sequence. Examples of the separation procedure of the sorting facilities related to this research are depicted in Fig. 1. A more detailed description about the sorting and reprocessing procedure of the samples is given elsewhere (Jansen et al., 2012).

Sorting technologies have developed substantially in the last decade and, as a result, the sorted plastics contain only small amounts of other plastics. One intrinsic limit of the sorting efficiency is that many plastic products consist of multiple polymers used to improve their properties, e.g. the mechanical, barrier and/or optical. Examples are multilayer films and blends. Therefore, some polymer contamination will always be present that will affect the ultimate properties of the recyclates.

* Corresponding author. Tel.: +31 40 247 3899.

E-mail address: j.g.goossens@tue.nl (H. Goossens).

Source separation



Commingled collection

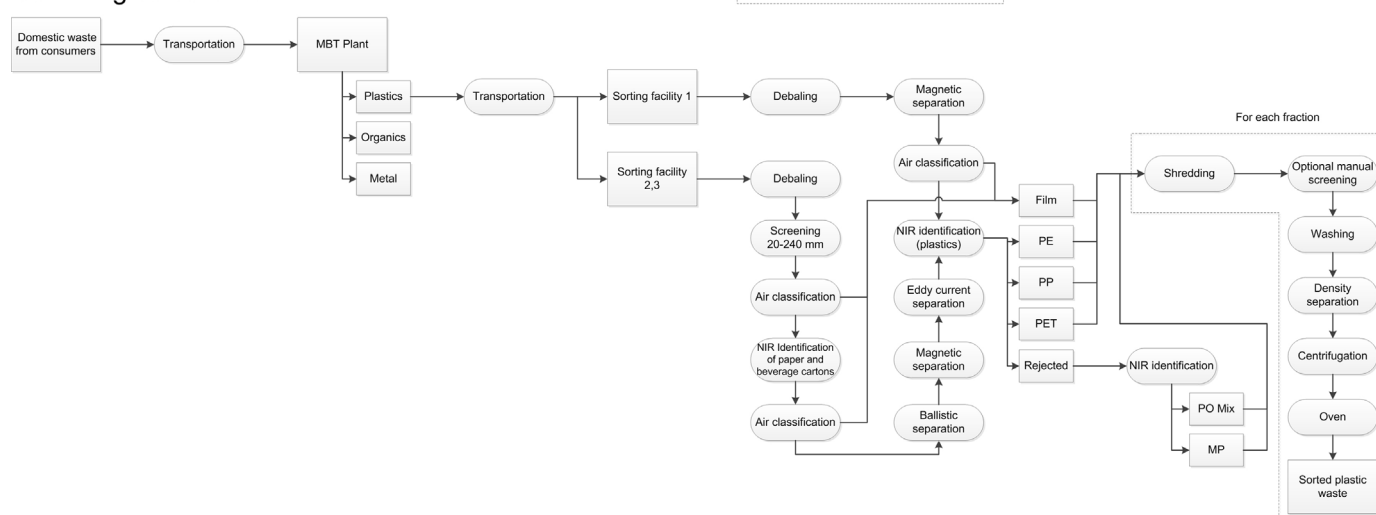


Fig. 1. Treatment of samples from source separation (SS) and commingled collection (CC) in the Netherlands.

After the sorting step, the residual fraction is incinerated, while the other fractions are reprocessed into so-called milled goods and agglomerates. The various reprocessing industries involved in this mechanical recycling typically use shredders, washing drums, flotation separators, centrifuges and tumble dryers. In the CC scheme, the PPW is collected together with the MSRW and transported to material recovery facilities, which produce a few types of plastic concentrates, i.e. so-called rigids and flexibles. Subsequently, these concentrates are sent to the abovementioned sorting facilities.

The sorting and reprocessing are two subsequent steps in the chain of material recycling and are often performed by different companies. It is unknown how the quality of recyclates depends on the different sorting and reprocessing technologies. This study aims to understand the relationship between the quality of the produced milled goods, as provided by the reprocessing industry, and the origin of the post-consumer PPW (SS vs. CC). The material quality can be assessed via an analysis of the composition and mechanical performance, which are correlated, as reviewed by Karlsson (2004). They developed (semi-)quantitative methods for the compositional analysis of polymer blends, which were obtained from recycled mixed plastic waste (Camacho and Karlsson, 2001b), by using DSC, near- and mid-infrared spectroscopy for the compositional analysis with detecting limits of approx. 1 wt%. NIR was found to be fast and precise over a large compositional range and can be used in-line. However, a drawback of NIR is that it cannot detect black materials, unlike Mid-IR. In their research, only transparent materials were used. According to the authors, attenuated

total reflection (ATR) spectroscopy can be a suitable method to provide information of thick materials, but quantitative analysis of non-homogeneous materials can be difficult due to the limited penetration depth of the evanescent wave ($\approx 2\text{--}3\ \mu\text{m}$). Therefore, good sample preparation is critical (Camacho and Karlsson, 2001b). Besides the polymers other chemical components are present, i.e. additives and contaminants, in plastic packaging waste. The quality of recyclates can also be assessed by the determination of these components via extraction techniques (Camacho and Karlsson, 2001a). A large variety of low molecular weight contaminants was identified in recycled high-density PE (HDPE) and PP, such as alcohols, esters, and ketones. The majority of these compounds were not present in the virgin plastics.

The mechanical performance of plastics is often characterized by tensile testing. Earlier studies reported on the influence of blend composition of polyolefins in relation to the mechanical properties. Teh et al. (1994) published an extensive review on PE/PP blends and the role of compatibilization and the mechanical performance in relation to the composition of post-consumer plastics, of which the majority consists of polyolefins. The morphology that governs the mechanical properties is highly dependent on the blend composition and processing/compounding conditions (Bartlett et al., 1982). Therefore, the mechanical properties of PE/PP blends are not easy to predict. Tensile specimens can be prepared via compression or injection molding. Generally, the properties from samples produced via injection molding are better, i.e. improved necking and higher strain at break (Nolley et al., 1980) in the flow direction, than via compression molding. This can be explained by the influence

of flow-induced crystallization in injection molding which leads to anisotropic properties. For a fair comparison, it is better to use compression molding to avoid flow effects.

A number of publications report about synergism or antagonism in virgin PE/PP blends (Camacho and Karlsson, 2001b; Teh et al., 1994; Flaris and Stachurski, 1992; Mehrabzadeh and Farahmand, 2001; Nolley et al., 1980; Shan et al., 2007). As mentioned before, whether synergy exists, depends on a great number of parameters, which hinders a good comparison. Little is reported about actual plastic waste. In simulating a ternary commingled waste blend, Engelmann et al. (1992) blended either virgin or recycled PE, PP and poly(styrene) (PS) in various compositions and determined tensile and impact strengths at different extruder screw speeds. For all virgin blends, negative deviations from the rule of mixtures were observed with the best results for low screw speeds, when little shear degradation occurred. For post-industrial recycled blends, additional negative effects for PE/PP and PE/PS were found, which were attributed to extensive delamination. For post-consumer blends, which were more contaminated, the rule of mixtures was obeyed for PE/PS blends. Another paper described the role of compatibilization on the mechanical properties of blends of post-consumer waste in comparison to virgin PP/HDPE blends (Blom et al., 1998). The addition of small amounts of recycle to virgin PP yielded a material with improved impact properties. However, the addition of recycle to virgin HDPE resulted in a material with poor impact and tensile properties. Compatibilization improved the results to some extent.

For all the studies on mechanical properties of recycled polyolefin blends reported so far, no detailed information about the sorting or reprocessing technologies has been given. In this paper, two analytical techniques (DSC and IR) were used for the analysis of the composition of recycled polyolefin fractions of different origin by using a calibration set of virgin PE/PP blends. The mechanical properties for the same recycle samples are related to the origin of the recycles.

2. Material and methods

2.1. Materials

The model blends of virgin materials were prepared in different ratios from HDPE (Sabic M40060S), *i*-PP (DSM Stamylan P 1UM10), and LDPE (LyondellBasell Lupolen 3020F). All materials were in pellet form and used as received.

Several milled goods originating from Dutch household waste – both SS and CC – were examined. The CC samples were collected and transported to industrial sorting facilities in the Netherlands and Germany (see Fig. 1). Big bag-sized samples were further reprocessed at the sorting and reprocessing facilities at the Wageningen UR Food & Biobased Research. An overview of the samples is given in Table 1. In general, the following steps were applied: manual NIR identification, shredding, manual screening (PE 5, Film 4, PP 5), cold washing, density separation, centrifugation, and drying at 90 °C. The recycle samples were divided in five groups, i.e. film, PE, PP, PO mix, and mixed plastics (MP). The film samples were separated by air classification of film fragments >240 mm. The PE and PP samples were taken from the fractions of the first NIR identification step. The recognized polyolefins from the second NIR identification step with higher sensitivity are classified as PO, which was subdivided as rigid (PO 1,4,6) or flexible (PO 2,3,5). PO 3 differs from PO 2 by an extra centrifugation step. PO 2, 3, and 4 were cold washed, while PO 5 and 6 were hot washed (50–60 °C). The mixed plastics (MP) samples were collected from the float fraction of the density-separated remainder of the plastics, being not identified by NIR sorting lines. Kilogram-sized samples were transported to

the laboratories at Eindhoven University of Technology for further compounding and analysis.

2.2. Compounding

The model blends were extruded in ratios PE/PP 100/0, 97/3, 94/6, 90/10, 80/20, 60/40, 50/50, 20/80, 10/90, 6/94, 3/97, and 0/100 in a Prism twin screw extruder (25 L/D) at 200 °C. The extrudate was pelletized and compression molded (dimensions 15 cm × 12 cm × 0.1 cm) at 200 °C and 100 bar for 3 min.

A representative sample of 50 g was taken from a bag (200–2000 g) of milled goods. It was mixed in a Haake batch mixer equipped with roller rotors, operating at a temperature of 200 °C for 10 min at a speed of 50 rpm. Prior to mixing, the chamber was purged with nitrogen to minimize oxidative degradation. After discharging the material from the mixing chamber, the material was compression molded as described above. The plaques obtained were used for further characterization.

2.3. Characterization

2.3.1. Fourier transform-infrared spectroscopy (FT-IR)

The blend compositions were studied by FT-IR spectroscopy. Spectra were obtained by placing the blends on the diamond crystal of a Specac Golden Gate attenuated total reflection (ATR) setup placed in a Varian FTS 6000 IR spectrometer. Fifty spectra at a spectral resolution of 1 cm⁻¹ over a spectral range from 650 to 4000 cm⁻¹ with a scan speed of 5 kHz were signal-averaged and the resulting spectra were analyzed using the BioRad Merlin 3.0 software. For each calculation at least 3 spectra were used, obtained from different locations on the samples.

2.3.2. Differential scanning calorimetry (DSC)

A TA Instruments Q1000 DSC was used to record heat exchange during heating and cooling of the samples. The melting and crystallization behavior was used for compositional analysis. The samples with a mass between 3 and 10 mg were heated from 30 to 220 °C, kept isothermal for 5 min to remove the thermal history, cooled down to 30 °C, kept isothermal for 5 min, and heated up again to 220 °C. For these experiments, a rate of 10 °C min⁻¹ and Tzero hermetic DSC pans were used. The second heating run was used for analysis.

2.3.3. Tensile testing

A Zwick Z100 tensile tester with a 100 N load cell was used to determine the mechanical properties of all samples. A crosshead speed of 50 mm min⁻¹ was used at a gauge length of 20 mm. A preload of 0.2 N was applied. Eight tensile specimens per sample were prepared according to ISO 527 (5B).

3. Results and discussion

First, a compositional analysis is discussed by using DSC to derive a calibration line for virgin model blends, after which recycled materials are analyzed to determine the composition of these blends. Secondly, a similar procedure is discussed for the FT-IR spectroscopy results. A comparison between the composition from these methods to sorting data is given. Finally, an overview of the mechanical properties of recycled materials is presented and correlated with the origin of the recycles.

3.1. Compositional analysis

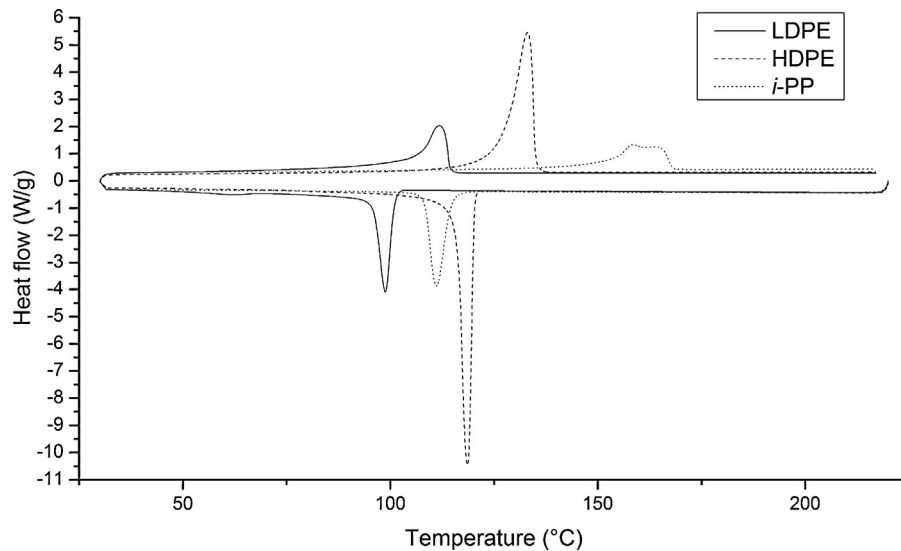
3.1.1. Compositional analysis based on thermal analysis

In DSC, phase transitions of semi-crystalline polymers can be measured as a function of temperature. Glass transitions will result

Table 1

Overview of the recycled samples used in this study.

Code	Source	Origin	Main plastic type	Additional separation steps
PE 1	CC	Collector 1, Facility 1	PE	
PE 2	CC	Collector 2, Facility 2	PE	
PE 3	CC	Collector 3, Facility 3	PE	
PE 4	SS	Collector 4	PE	
PE 5	SS	Collector 5	PE	Manual screening
PE 6	SS	Collector 5	PE	
Film 1	CC	Collector 1, Facility 1	PE	Extensive hand-NIR sorting
Film 2	CC	Collector 3, Facility 3	PE	
Film 3	SS	Collector 4	PE	
Film 4	SS	Collector 5	PE	Manual screening
Film 5	SS	Collector 5	PE	
PP 1	CC	Collector 1, Facility 1	PP	
PP 2	CC	Collector 2, Facility 2	PP	
PP 3	CC	Collector 3, Facility 3	PP	
PP 4	SS	Collector 4	PP	
PP 5	SS	Collector 5	PP	Manual screening
PP 6	SS	Collector 5	PP	
PO 1	CC	Collector 1, Facility 1	PE, PP (rigids)	
PO 2	CC	Collector 3, Facility 3	PE, PP (flexibles)	
PO 3	CC	Collector 3, Facility 3	PE, PP (flexibles)	Centrifugation
PO 4	CC	Collector 3, Facility 3	PE, PP (rigids)	
PO 5	CC	Collector 3, Facility 3	PE, PP (flexibles)	Hot water washing
PO 6	CC	Collector 3, Facility 3	PE, PP (rigids)	Hot water washing
MP 1	CC	Collector 1, Facility 1	PE, PP, PET	
MP 2	CC	Collector 2, Facility 2	PE, PP, PET	
MP 3	CC	Collector 3, Facility 3	PE, PP, PET	
MP 4	SS	Collector 4	PE, PP, PET	

**Fig. 2.** DSC thermograms of LDPE (solid line), HDPE (dashed line) and *i*-PP (dotted line) (exo down).

in a step-wise increase of the heat capacity in the thermogram. Endothermic melting peaks and exothermic crystallization peaks are visible either sharp or broad depending on the lamellar thickness distribution. In Fig. 2, the melting and crystallization peaks for LDPE, HDPE and *i*-PP are displayed. It can be observed that the pure components show a distinctive behavior with respect to the

melting temperature (T_m) and melting enthalpy, which correlates with the degree of crystallinity, which enables the semi-quantitative characterization of the polyolefin blends. The degree of crystallinity can be calculated by the ratio of the melting enthalpy and the melting enthalpy of the 100% crystalline material, which can be found in the ATHAS Data Bank (Pyda, 2005). An overview of

Table 2

Transition temperatures in polyolefins and their blends.

Material	Ratio	T_m (°C)	Type of peak	T_c (°C)	Type of peak
LDPE		112	Sharp	99	Sharp
HDPE		132	Sharp	120	Sharp
PP		158, 164	Broad	112	Sharp
LDPE/HDPE	70/30	109, 126	Overlapping	101, 115	Irregular
HDPE/ <i>i</i> -PP	50/50	132, 159	Sharp, broad	119	Sharp, shoulder
LDPE/ <i>i</i> -PP	50/50	112, 158	Sharp, broad	102, 112	Sharp

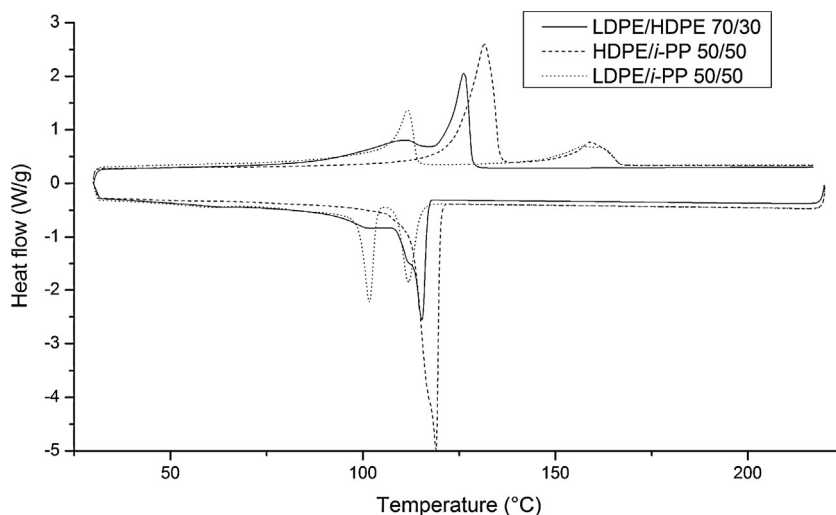


Fig. 3. DSC thermograms of a 70/30 LDPE/HDPE blend (solid line), a 50/50 HDPE/*i*-PP blend (dashed line) and a 50/50 LDPE/*i*-PP (dotted line) (exo down).

the melting and crystallization temperatures (T_c) is given in Table 2. It has to be taken into account that melting temperature depression may occur with polyolefin blends due to a high compatibility that often coincides with a lower degree of crystallinity. As can be observed in Fig. 3 and Table 2, for LDPE/HDPE blends the melting endotherms show overlap, because the melting temperatures of LDPE/HDPE shift a few degrees compared to the homopolymers to the above mentioned melting temperature depression. For the HDPE/*i*-PP blends, separated melting endotherms are observed.

In designing a method to characterize the composition of recycled polyolefin blends, the melting enthalpy has to be used, while the melting temperature, i.e. maximum of the peak, can be used to discriminate between the polymers. Severe peak overlap due to strong compatibility and/or similar chain microstructure may complicate the quantification. Therefore, this approach is not suitable for characterizing LDPE/HDPE blends or even worse linear-low density PE (LLDPE)/HDPE blends.

For LDPE/*i*-PP and HDPE/*i*-PP, model blends with known ratios of the virgin polymers were pre-mixed, compounded and characterized by using DSC. The melting enthalpies were calculated using a linear peak integration and the results are shown in Fig. 4. Linear trend lines were fitted. The statistical analysis on these lines showed that the residual sum of squares for the melting temperature of PP is lowest and the adjusted R^2 value (0.99454) is comparable to the other peaks. Therefore, in HDPE/*i*-PP blends, the enthalpy of melting of PP is most indicative for the compositional analysis.

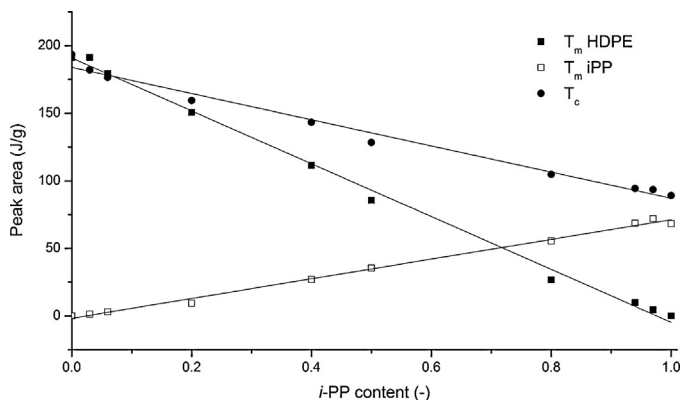


Fig. 4. DSC peak areas for the HDPE/*i*-PP model blends.

The composition of sorted household plastic waste was determined by using the DSC thermograms of the recyclates and the obtained calibration line from the model blend analysis. The results are shown in Fig. 5. From this graph, it can be observed that the T_c calibration line gives an overshoot and no reliable composition data can be obtained. While the T_m HDPE calibration line predicts PP contents up to 30% in sorted PE samples, the T_m PP calibration line shows up to 10% PP contamination. Furthermore, film samples (LDPE) are predicted to contain high amounts of PP according to the T_m HDPE calibration line, compared to other PE samples, because of peak overlap in the DSC traces. In conclusion, the calibration line based on the T_m of PP can preferably be used for compositional analysis of recyclates with DSC.

3.1.2. Compositional analysis based on vibrational spectroscopy

In FT-IR spectroscopy, energy in the form of light is used to track molecular translations, rotations, vibrations and electronic energy. Since the absorbed energy is specific for each chemical bond, a spectrum is obtained which is polymer specific and, therefore, can be used as a fingerprint to identify polymers. The spectra of the different polyolefins are given in Fig. 6. In this figure, it can be seen that there are distinctive peaks for both PE and *i*-PP. LDPE and HDPE yield similar spectra due to their identical chemical nature. A clear distinction between the types of polyethylene can therefore not be made based on peak position. An overview of the peaks and their nature is given in Table 3. Some of the PE and PP peaks are overlapping, while others are discriminative. The relative intensities of the absorption bands depend on penetration depth of the evanescent wave, which is sensitive to contact pressure applied during mounting the samples for the ATR measurements. Before comparing spectra, they should be normalized with a reference peak, present in spectra of both polymers. The methylene asymmetric stretch peak at 2915 cm^{-1} is suitable as reference. Furthermore, all peaks have their own specific extinction coefficient, which causes differences between relative peak heights and the concomitant peak areas. It is important to take this into account when characterizing polyolefin blends.

The relative heights of several distinctive peaks were monitored as a function of blend composition. The results are displayed in Fig. 7. From the data of the model blends, calibration lines were constructed by using linear regression. The statistic analysis of these lines is presented in Table 4. A good calibration line shows a low residual sum of squares and a high slope value, indicating an observable peak change with composition. The peak calibration

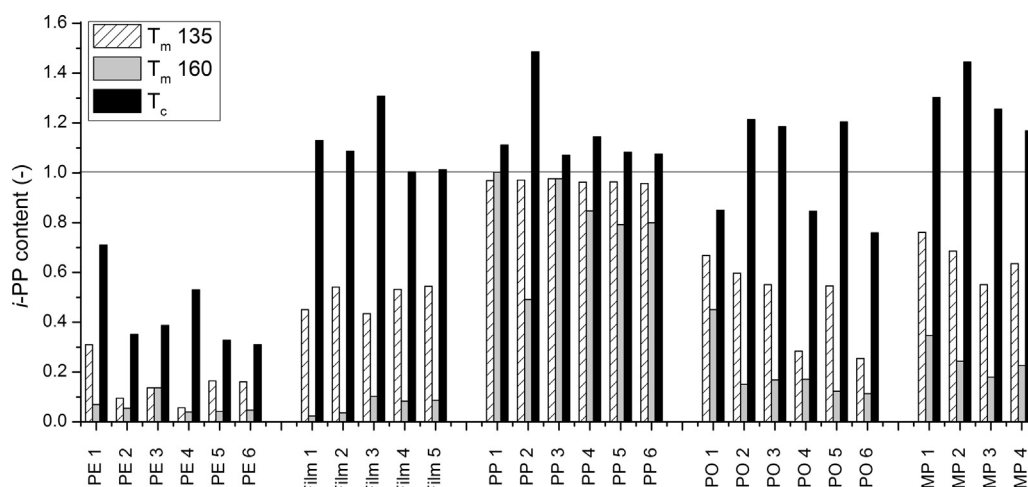


Fig. 5. Calculated *i*-PP content based on the calibration lines of HDPE (T_m 135) and *i*-PP (T_m 160) melting enthalpies and crystallization peak areas (T_c) in the used waste plastics (see Table 1).

Table 3

Characteristic peaks in FT-IR spectroscopy of PE and PP.

PE wave number (cm^{-1})	Origin	Amorphous/crystalline	PP wave number (cm^{-1})	Origin	Amorphous/crystalline
2935–2915	Methylene asym. stretch	A	2970–2950	Methyl C–H asym. stretch	A
2865–2845	Methylene sym. stretch	A + C	2880–2860	Methyl C–H sym. stretch	A
1485–1445	Methylene C–H bend	A + C	2935–2915	Methylene asym. stretch	A
750–720	Methylene rocking	A	2865–2845	Methylene sym. stretch	A
			1485–1445	Methylene C–H bend	A
			1470–1430	Methyl C–H asym. bend	C
			1380–1370	Methyl C–H sym. bend	A + C
			1300–700	Skeletal C–C vibrations	C

lines of PE at 2868 cm^{-1} and PE at 1463 cm^{-1} show a low sum of squares, while the slope is also relatively low. The PE peak at 2848 cm^{-1} shows a somewhat higher residual sum of squares, but also an increased slope. As a result, the adjusted R^2 is higher. This value describes the fraction of the data that can be described by the calibration line. For the model blends, the PE peak at 2848 cm^{-1} and the PP peak at 1376 cm^{-1} are most suitable.

Several recycled samples were examined for their composition (PE/PP) using these calibration lines. Spectra of each sample were averaged from 50 scans, recorded with a spectral resolution of 1 cm^{-1} and at least measured in duplicate. The composition was determined as the average of the calculated composition from each calibration line (Fig. 8). Since some methods resulted in different

compositions, the calibration lines yielding the highest and lowest composition were discarded. Sometimes, these values exceeded the physical limits, i.e. an *i*-PP content below zero or above 1. The results based on the three remaining calibration lines are plotted in Fig. 8 and are considered more reliable. On average, the calibration lines of PP at 2951 cm^{-1} and especially the PP at 1376 cm^{-1} yielded the most reliable results.

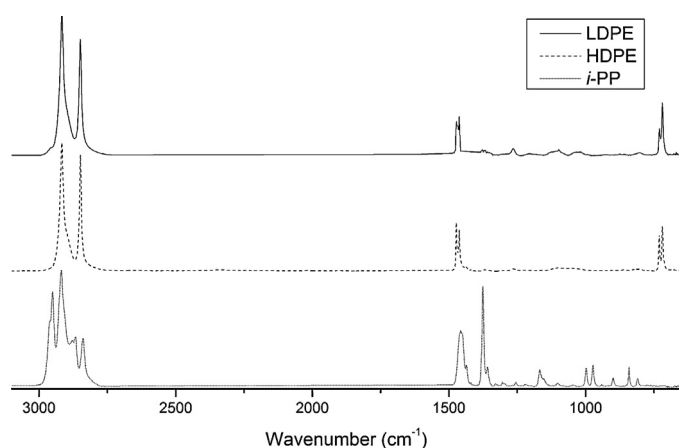


Fig. 6. FT-IR spectra of LDPE (solid line), HDPE (dashed line) and *i*-PP (dotted line). The spectra are vertically shifted for clarity.

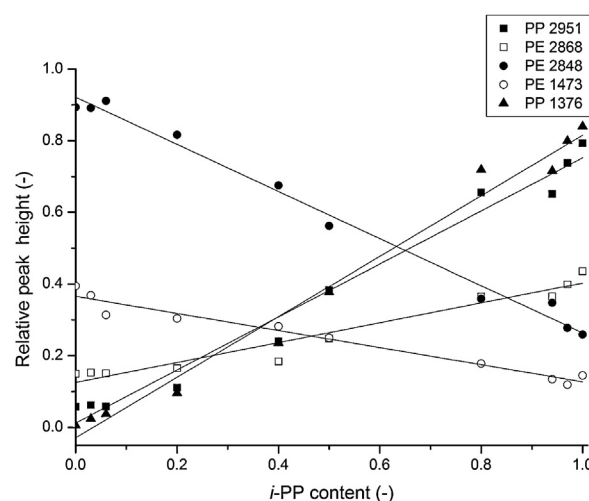


Fig. 7. FT-IR calibration lines based on PP peaks at 2951 cm^{-1} (black square) and at 1376 cm^{-1} (black triangle), and on PE peaks at 2868 cm^{-1} (white square) and at 1473 cm^{-1} (white circle).

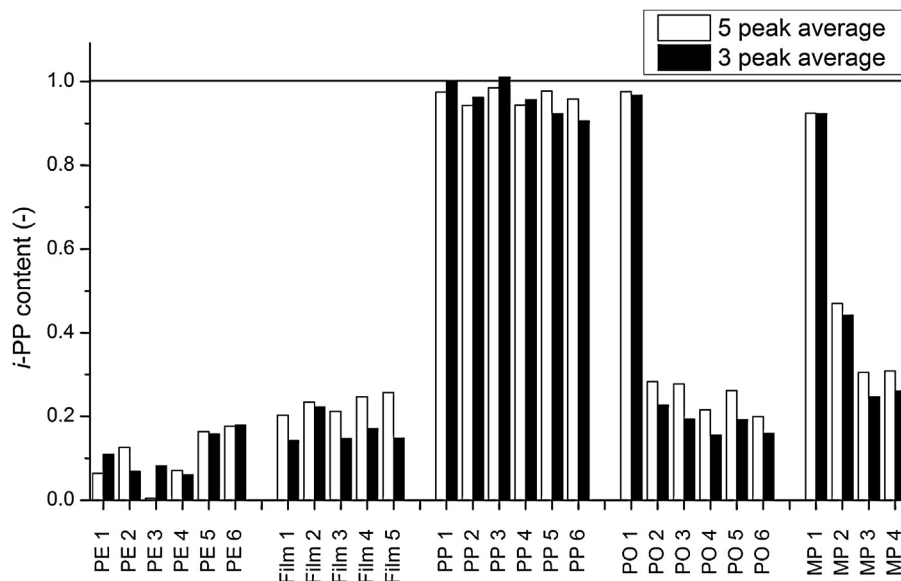


Fig. 8. PP content calculated from the FT-IR calibration lines. Results presented are based on five or three calibration lines.

3.1.3. Comparison between analysis methods

In the previous section, the PE/PP calibration lines were constructed by DSC and FT-IR spectroscopy of virgin model blends and the quality of these trend lines was discussed by measuring recyclates. The actual quality of recyclates is discussed in this section. The recyclate composition calculated by FT-IR was compared to the results from DSC. These compositions were compared to the results from the NIR sorting. The samples were weighed, from which a macroscopic composition could be calculated. An overview of these results is given in Table 5.

The class of rigid PE samples contains on average 5–10% PP, whereas for films the PP content is a few percent higher. The amount of PET, as determined from the sorting experiments, is higher in films than in rigid PE samples. The PE samples are quite consistent in composition. The most pure PE samples, from both analyses, are PE 2 and 4. Film samples 1 and 3 were found to be purest in their category. Here, the spread in results is somewhat larger. Pure samples come both from CC and SS for PE and Film. In SS, collector 4 seems most effective in delivering pure PE recyclates.

The PP samples investigated were quite pure and consistent in composition, containing approx. 96% PP. The contamination of PET is similar to the contamination of PET in the PE samples. From the analytical compositional calculations, the amount of PP is in good agreement with the sorting composition and the differences between samples are little. The sorted PP waste contains a few percent less polymer contamination than the sorted PE waste. PP 3 is the purest sample, which was obtained via CC.

The PO mix samples were not identified by the first NIR line, but classified as polyolefin in a second line. This stream contains both rigid and flexible materials, which were manually sorted in

a subsequent step. In terms of sorting and analytical composition, these samples consist mainly for 80% out of PP, 20% PE and some residual PET. The spread in results of extensive manually sorted PO samples is rather low. An exception is PO 1, which predominantly consists out of PP. The output composition originates from the difference in sorting processes of the sorting facility of PO 1.

Mixed plastics (MP) are a rest stream and have a large variation in composition, which is different for each sorting facility. Mixed plastics contain a significant amount of PET that was not filtered out. This could also be seen by visual inspection. At first sight, the sorting and analytical compositions do not seem to match. Since the presence of PET is significant, the amounts of PE and PP sorting compositions are low. In comparison to the laboratory analysis, PET should be left out of consideration. In this way, the calculated PP contents are more alike, but a large spread between techniques and samples remains.

3.1.4. Compositions of source separation vs. commingled collection

The analysis did not reveal significant differences in composition between SS and CC samples. The sorting process can handle both streams, although some additional separation steps may be necessary, such as a manual screening. The composition of the plastic waste streams does not depend on the collection scheme. It has to be noted that this is valid for the quality of the sorted plastics, but not for the yield as described in a paper by Jansen et al. (2012). Manual screening was done after determining the composition from sorting experiments. Visible improperly sorted plastics were manually picked out of a sorted stream and put in its designated stream.

Table 4
Fitting of FT-IR calibration lines.

	PP 2951	PE 2868	PE 2848	PE 1463	PP 1376
Residual sum of squares	0.018	0.006	0.007	0.003	0.018
Pearson's <i>r</i>	0.990	0.975	−0.995	−0.981	0.992
Adj. <i>R</i> -square	0.977	0.944	0.988	0.959	0.982
$y = a + b \cdot x$					
Intercept	0.012	0.125	0.921	0.365	−0.029
Intercept standard error	0.024	0.014	0.015	0.010	0.024
Slope	0.740	0.277	−0.658	−0.238	0.845
Slope standard error	0.038	0.022	0.024	0.016	0.039

Table 5Comparison of calculated *i*-PP content from sorting data and analyzing techniques.

	Source	Composition after sorting			Composition after compounding	
		PP content (–)			PP content (–)	
		PE	PP	PET	IR	DSC
PE 1	CC	0.84	0.10	0.05	0.11	0.07
PE 2	CC	0.98	0.01	0.01	0.07	0.06
PE 3	CC	0.96	0.02	0.02	0.08	0.14
PE 4	SS	0.97	0.02	0.01	0.06	0.04
PE 5	SS	0.91	0.07	0.02	0.16	0.04
PE 6	SS	0.91	0.07	0.02	0.18	0.05
PE average		0.93	0.05	0.02	0.11	0.10
Film 1	CC	0.90	0.10	0.00	0.14	0.02
Film 2	CC	0.89	0.06	0.05	0.22	0.04
Film 3	SS	0.94	0.06	0.00	0.15	0.10
Film 4	SS	0.89	0.05	0.06	0.17	0.08
Film 5	SS	0.89	0.05	0.06	0.15	0.09
Film average		0.90	0.07	0.04	0.17	0.07
PP 1	CC	0.02	0.96	0.02	1.00	0.97
PP 2	CC	0.01	0.93	0.06	0.96	0.97
PP 3	CC	0.02	0.98	0.00	1.00	0.98
PP 4	SS	0.02	0.95	0.03	0.96	0.96
PP 5	SS	0.01	0.98	0.01	0.92	0.96
PP 6	SS	0.01	0.98	0.01	0.91	0.96
PP average		0.02	0.96	0.02	0.96	0.97
PO 1	CC	0.47	0.48	0.04	0.97	0.67
PO 2	CC	0.85	0.13	0.01	0.23	0.15
PO 3	CC	0.85	0.13	0.01	0.19	0.17
PO 4	CC	0.80	0.18	0.02	0.16	0.17
PO 5	CC	0.79	0.20	0.02	0.19	0.12
PO 6	CC	0.82	0.15	0.02	0.16	0.11
PO average		0.76	0.21	0.02	0.32	0.20
MP 1	CC	0.11	0.13	0.76	0.92	0.76
MP 2	CC	0.15	0.14	0.70	0.44	0.24
MP 3	CC	0.27	0.04	0.69	0.25	0.18
MP 4	SS	0.44	0.28	0.29	0.26	0.23
MP average		0.24	0.15	0.61	0.47	0.40

Screening of material (PE 5 vs. PE 6, film 4 vs. film 5, PP 5 vs. PP 6) does not seem to result in significant changes in composition as can be observed from Table 5.

Comparing the results of both analysis techniques, it can be observed that the PP content after compounding is generally higher than sorting. This is probably due to the presence of multi-plastic products. With NIR sorting, products get identified by the dominant type of plastic. In the case of for example a shampoo bottle, NIR will identify it as PE, since the flask comprises the majority of the product. The cap is often made from *i*-PP, which will also end up in a sorted PE fraction. The weight of the cap is substantial, therefore resulting in an increased amount of measured PP from the laboratory analysis.

In general, the PP content estimated by DSC is lower than the PP content estimated by FT-IR spectroscopy. This holds for all sample categories and might be due to migration of PP to the surface during compression molding. It was found that migration of PP to the surface is higher than HDPE and LDPE (Teh et al., 1994). As a result, a surface characterization technique such as ATR FT-IR will overestimate the PP content. DSC renders information of the complete volume rather than just the surface, although the total volume is low. Exceptions are PE 3, PP 2, and PO 4. Furthermore, it is seen that for the HDPE and LDPE samples, similar PP contaminations are found. In PP-rich samples, an overshoot may occur, which might be due to the fact that just one grade of PP was used in the model blends. Therefore, the value obtained is set as 100%, while a different PP with different crystallinity or molecular weight may result in different data. For this reason, the results presented should be treated semi-quantitatively, to relate between the samples examined. Some large discrepancies between techniques are seen in calculated PP content, e.g. for PO 1.

Since the DSC measurements were performed with approx. 10 mg of material, one could argue whether a representative sample was taken. Some samples were measured in duplicate or triplicate, which resulted in similar outcomes. Therefore, the samples can be considered as homogeneous in terms of composition. In addition, the results obtained for composition calculation show significant changes between sample categories. The used methodology is suitable to determine the composition of a recycled polymer blend in a semi-quantitative fashion.

3.2. Mechanical properties

The mechanical performance of the recyclates was determined via testing in tensile mode. In terms of tensile strength, some differences are seen between SS and CC, although no clear trends are visible. For all categories, the tensile strengths of SS materials are similar, while for CC the results deviate significantly from the average. The different fractions and the effect of additional sorting steps on the mechanical properties will now be discussed (Table 6).

The tensile strength of post-consumer rigid PE is in general quite consistent, although the properties of the virgin materials cannot be reached. Manual screening of material (PE 5 vs. 6) leads to more reproducible results, as demonstrated by the reduced standard deviations (SD). However, an opposite trend is found for the strain at break. This may be related to a somewhat higher measured PP content in the unscreened PE 6. Less PP contaminated samples, such as PE 2, 3, and 4, give higher strains at break, since less stress concentration zones of the contaminants are present. The standard deviation for strains at break does not vary substantially. The highest strains at break within the PE category samples were observed for PE 2, which was obtained via commingled collection.

Table 6
Mechanical properties of PPW.

	Source	Tensile strength (MPa)	SD (MPa)	Strain at break (%)	SD (%)
PE 1	CC	21.80	1.56	75.94	95.06
PE 2	CC	26.00	1.00	522.22	80.40
PE 3	CC	24.11	2.53	189.92	233.89
PE 4	SS	25.23	0.75	314.20	224.77
PE 5	SS	25.12	0.18	147.76	202.29
PE 6	SS	25.94	0.38	430.39	150.50
PE average		24.70	1.07	280.07	164.49
Film 1	CC	19.51	3.67	530.75	101.11
Film 2	CC	10.67	1.80	36.10	18.21
Film 3	SS	15.56	0.32	137.13	111.85
Film 4	SS	12.40	1.91	127.49	172.49
Film 5	SS	12.47	2.61	19.56	8.16
Film average		14.12	2.06	170.21	82.36
PP 1	CC	25.88	0.41	17.75	11.12
PP 2	CC	6.06	1.87	2.65	1.00
PP 3	CC	30.21	0.93	13.17	6.14
PP 4	SS	25.04	1.50	13.13	9.94
PP 5	SS	24.31	4.30	8.04	5.04
PP 6	SS	26.49	1.61	14.31	7.69
PP average		23.00	1.77	11.51	6.82
PO 1	CC	17.86	1.25	7.91	2.89
PO 2	CC	13.08	1.23	95.81	107.33
PO 3	CC	14.71	0.90	175.71	147.81
PO 4	CC	21.75	3.88	15.04	7.12
PO 5	CC	11.96	0.59	56.89	55.31
PO 6	CC	20.22	3.41	230.07	204.08
PO average		16.60	1.88	96.91	87.42
MP 1	CC	4.82	2.49	2.28	1.17
MP 2	CC	15.07	2.42	4.88	1.21
MP 3	CC	11.86	3.07	15.43	5.49
MP 4	SS	10.87	2.57	31.49	6.27
MP average		10.65	2.64	13.52	3.54

Within the film category, Film 1 showed a high tensile strength in combination with a high strain at break. This material was additionally NIR sorted, while the other films were not. Manual screening of the film fractions (Film 4 vs. Film 5) improved the tensile strength and the strain at break; furthermore, lower standard deviations were obtained, although these results are not directly related to sample purity.

Although the measured purity was high, very low strains at break (~30%) were observed for recycled PP samples in comparison to the strains at break of virgin PP samples (approx. 800%). This difference originates from degradation of the PP samples by β -scission, while in PE both chain cleavage and crosslinking reactions may occur. PP 3 showed a high tensile strength and was obtained via commingled collection. PP 2 has inferior properties, which are a logical result from the presence of PET, i.e. a low strain at break and a low tensile strength.

The spread in tensile strength and strain at break for the PO mix samples is larger between samples than for the earlier discussed sample categories. In general, the mechanical properties are inferior and the samples are not homogeneous, which can be deduced from the large deviations in strain at break. PO 4 and PO 6 were purest and showed the highest tensile strength. PO 6 showed a high strain at break, but compared to PE it has low uniformity. Hot washing of PO mix samples (5 and 6) and centrifugation (PO 3) have a positive influence on the mechanical properties.

The performance of mixed plastic (MP) samples is the lowest of all categories. Since these samples were very inhomogeneous and contained a significant amount of PET due to deficiencies in density separation, these were impossible to measure in tensile mode.

4. Conclusions

DSC and FT-IR are demonstrated here as suitable techniques for compositional analysis of polyolefin blends. The melting enthalpy

of *i*-PP is a reliable parameter to characterize HDPE–PP blends composition with DSC. For DSC analysis it is important to use a homogeneous, representative sample of the blend. In FT-IR analysis of PE–PP blends, the PE peak at 2848 cm^{-1} and the PP peak at 1376 cm^{-1} are most suitable for characterization, since these peaks are abundant and non-overlapping. Both characterization methods can be applied to calculate the composition of a polyolefin blend with unknown composition. To eliminate the effect of differences in crystallinity, FT-IR is the preferred method since it also takes amorphous signals into account. Furthermore, this method is rapid and non-destructive.

It can be concluded that extensive sorting leads to purer waste fractions with better mechanical properties. Typically, the post-consumer PP recycle samples were most pure and contained about 96% PP. The post-consumer PE recycles contained about 90% PE and the post-consumer film samples contained 80–85% PE. No quality differences between source-separated and commingled-collected PPW were observed. Applying a hot washing step, additional manual screening and centrifugation showed to improve the purity and mechanical properties of the recycle. Recycled materials with improved purity and mechanical properties allow for new compounding technologies to be designed to develop potentially higher value applications from these recycles.

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