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Qualitative and quantitative contaminants assessment in recycled pellets from post-consumer plastic waste by means of spectroscopic and thermal characterization

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Abstract

The complexity of any plastic recycling initiative lies in the heterogeneous nature of the post-consumer commingled plastic waste stream: recycling treatments are challenging without prior reliable sorting. A suitable identification system should be able to recognize different plastics and blends. Nowadays, the main technique used as quality control in plastic waste sorting centers is differential scanning calorimetry, whose result can be purely qualitative or semi-quantitative, since only the crystalline fraction is evaluated. Moreover, the time required for data acquisition is relatively long. Infrared spectroscopy is an alternative, faster technique extensively used in applied research, but not widely utilized in industry. In this work, the cross-use of infrared spectroscopy and calorimetry is tested in a real, practical case: the quality control of recycled pellets (namely composed of polyolefins only), which represent the output of a commingled plastic recycling plant and are used as secondary raw materials for different applications. Appropriate infrared spectroscopy calibration curves were built to allow the quantitative analysis with respect to the most common polymers found in the commingled plastic waste stream; the composition and contaminants in the recycled pellets were thereby determined and tracked through different production batches through the cross-use of the two techniques outlined above.

KEYWORDS
DSC, FTIR, plastic waste, recycling

1 | INTRODUCTION

The use of plastic objects has dramatically boosted during the last decades and is nowadays widespread in everyday life, leading to an expansion in plastic production worldwide.[1,2] Since most of these objects are designed to be single-use or disposable parts, the increase in their use was inevitably followed by a growth in the amount of generated plastic waste, which is leading to well-known and serious environmental consequences.[3] Plastic reusing and recycling are thus becoming nowadays issues of paramount importance.[1,2,4] Unfortunately, only 30% of the collected plastic waste was effectively recycled in the EU in 2018, while the remaining share is simply lost to

landfill (25%) or incinerated (43%).[5,6] The main challenge ahead of any recycling initiative lies in the fact that post-consumer commingled plastic waste is a uniquely miscellaneous, heterogeneous stream that includes both high and low-quality materials.[7] The different compositions, properties, and melting points of different polymers hinder a simple physical recycling treatment without a prior upstream reliable sorting.[2,4,7,8] For an effective separation, correct identification of different types of post-consumer plastic materials is critical: a suitable identification system should be able to recognize among dozens of different polymers and blends.[4,9] The greatest fraction (40%) of plastic waste comes from packaging, with the largest share (50%) consisting of polyethylene (PE) and polypropylene (PP), followed by polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), and polyamides (PA).[5,10] The effectiveness of a precise plastic waste separation poses serious challenges to the recycling process: ideally, each waste stream should be divided into homogeneous polymer types, grades, and structures (i.e., high density or low density polyethylene—HDPE or LDPE).[9] Generally, sorting processes follow several steps.[8,11–14] The waste stream is initially sorted by size passing through progressively narrower physical filters (rotating sieves). Small (bottle caps-HDPE) and large pieces (films and bags-usually LDPE) are removed at this initial stage. Rotating drums and ballistic separators are useful to remove heavy objects such as rocks, metals, and pieces of glass; "float-sink" separators are used to separate materials with density lower than that of water (such as PE and PP, which float) from PET, PS, and PVC (which instead sink). Further steps usually consist of magnetic and eddy current separators to remove residual ferrous and non-ferrous metal debris and wind sifters to remove bags and light films. Final steps are optical sorting (infrared and color) and manual selection. Nowadays, the main characterization technique used for quality control in waste plastic sorting centers is differential scanning calorimetry (DSC). This technique evaluates the difference in heat transfer between a specimen and a reference as a function of temperature and time. The result is reported in a graph called "thermogram." The measurement is carried out using a calorimeter and takes a certain amount of time (approximately one or two hours). It is able to detect effectively the melting points and enthalpies of the different components, but this implies that they must be composed of a semi-crystalline fraction (as it happens, for example, in PE, PP or PET). Amorphous plastics (such as PS) do not show any distinctive melting peaks, but only a glass transition temperature (Tg), which is not always easily detectable, especially if overlapped with other transitions featured in the thermogram. In addition, the Tg may be

dependent not only on composition, but also on other factors including sample thermal history and molecular mass. Moreover, Tg is not a univocal fingerprint for identifying different types of plastics. Therefore, DSC can only be used to recognize an unknown plastic sample if there are distinct transitions shown in the thermogram. The main problems in using this technique are mainly: (i) the data acquisition time, which can be long; (ii) the fact that it can only be used effectively to detect plastics having a semi-crystalline fraction (clear melting peaks). In the latter situation, it is also possible to determine the degree of crystallinity, as the ratio between the melting enthalpy (heat) and a reference value of a completely crystalline specimen.

Other techniques, widely used in academia or applied research, but not widely utilized in industry, are Raman Spectroscopy[15–17] and the Fourier transform infrared spectroscopy (FT-IR).[18,19] These techniques, which belong to the wider family of vibrational spectroscopies, are non-destructive measurements that allow to recognize the functional groups found in the sample through the analysis of characteristic vibrational bands. The measurement time is short (from 30 s to a few minutes), especially if compared with the DSC. With the measurement of an FT-IR spectrum on an unknown sample, it is possible to univocally identify the various plastic compounds through the comparison of the acquired spectrum with reference vibrational bands, used as real "fingerprints" of the main commercial polymers. The technique, unlike DSC, works perfectly on either amorphous or semi-crystalline polymers, even on thin material layers. Quantitative analysis with this technique is possible as long as adequate calibration curves are available. Calibration curves for the determination of PE content in recycled PP and vice-versa have been already reported[18,19]; to the authors' knowledge, no calibration curves have been reported so far for PET and PS content determination in recycled PE. In this study, the cross-use of FTIR and DSC was tested in a real, practical case: the quality control of recycled plastics pellets, which were the output of a commingled post-consumer plastic waste recycling plant. Different commingled plastics were sorted before pellet production process, with the goal of maximizing the recycled polyolefin fraction (PE and PP). Since these recycled pellets are used as secondary raw materials suitable for different applications, (such as bitumen modifiers for the production of insulating membranes, additives for the production of high-performance asphalts or the production of materials for industry, logistics, and automotive sector, as well for the production of composite panels for the urban and residential furnishing sector) the control in their composition and contaminants is a primary goal.

TABLE 1 Composition of blends used for calibration curves.

Blend	PE/PP	PE/PET	PE/PS
Composition 1	98/2	98/2	98/2
Composition 2	96/4	96/4	96/4
Composition 3	94/6	94/6	94/6
Composition 4	92/0	92/8	92/8
Composition 5	90/10		

Namely, these pellets are mainly composed of polyolefins, with a declared PE content of 90%–95%. The objective of this study was to identify and quantify the different plastic contaminants in the composition of the pellets and to track their variation in different production batches, by means of the cross-use of the two techniques described above.

2 | MATERIALS AND METHODS

2.1 | Materials

Recycled polyolefin pellets were obtained from a recycling plant in north-eastern Italy. Reference materials were gathered from relevant post-consumer plastic waste, such as single-use water bottles (PET), plastic bags and caps (LDPE and HDPE), food containers (PP) and plastic dishes (PS).

Model blends for calibration curves were obtained by solvent blending (up to 100 mg of polymer in 10 mL of solvent, in 25-ml glass beckers) in boiling xylene (reagent grade, mixture of isomers) for PE/PP and PE/PS blends or boiling 1,2-dichlorobenzene (reagent grade) for PE/PET blends. Dissolution time was 10 min. PE/PP blends were prepared in the following compositions: (% wt PE/PP): 98/2, 96/4, 94/6, 92/8, 90/10, 75/25, 50/50, 25/75, 10/90; PS/PE and PET/PE in the following compositions (% wt.): 98/2, 96/4, 94/6, 92/8. Blend compositions are reported in Table 1. Solutions were drop cast on glass slides to obtain blend reference samples.

2.2 | Fourier transform infrared spectroscopy and compositional analysis

Fourier transform infrared spectroscopy (FT-IR) spectra were measured by a Thermo-Nicolet Nexus 470 spectrometer equipped with a diamond crystal attenuated total reflection (ATR) accessory. Spectra were acquired at resolution of 2 cm^{-1} over a spectral range from 600 to 4000 cm^{-1}; for each sample, five spectra from different location were acquired, with 16 spectral accumulation per measurement. Wavelength-dependent penetration depth was corrected by the ATR correction routine from the Omnic software. The spectra were analyzed using hyperSpec package[20] of the R software for statistical analysis; data were converted into absorbance and baseline were subtracted with a polynomial fitting.

In order to identify the different polymers in the recycled pellets, distinctive absorption bands were chosen as "fingerprints".[21–24] The band at 1376 cm^{-1} (CH$_3$ deformation) was chosen as the distinctive absorption band for PP, the band at 697 cm^{-1} (CH deformation in aromatic ring) for PS, and the band at 1120–1100 cm^{-1} (C-O stretch) for PET.[25–27] Following the principles reported by the ASTM standard D7399[28] and by procedures previously reported in other works,[18,19] ad-hoc calibration lines were constructed to determine the quantitative composition (PP, PET, and PS content in recycled PE). FT-IR spectra of model blends were acquired, and heights of distinctive absorption bands were recorded. The ratios between the heights of these distinctive bands and the height of a suitable reference band were plotted as a function of the model blend composition to obtain the calibration lines. The vibrational band at ≈ 2920 cm^{-1} (CH$_2$ stretching) was chosen as a suitable reference band.

The same distinctive bands heights were then measured on recycled pellets; the ratios between the measured band height and the reference band were used to assess their composition through the calibration lines.

2.3 | Differential scanning calorimetry

DSC measures were carried out by means of a Netzsch DSC 200 F3 Maia in Argon atmosphere. The thermal cycle was set as follows: initial stand-by at −50°C for 10 min; first heating from −50°C to 190°C at 10 K/min; isothermal stand-by at 190°C for 5 min; cooling down to −140°C at 10 K/min; and second heating from −140°C to 190°C at 10 K/min. The degree of crystallinity K for each component was calculated by the following equation:

$$K = \frac{\Delta H_m}{\Delta H_0}$$

where ΔH_m is the measured heat of fusion, and ΔH_0 is the heat of fusion of 100% crystalline polymer. After the first scan, a second DSC measure was acquired, as the first is generally considered to be biased by the previous thermal history of the sample.
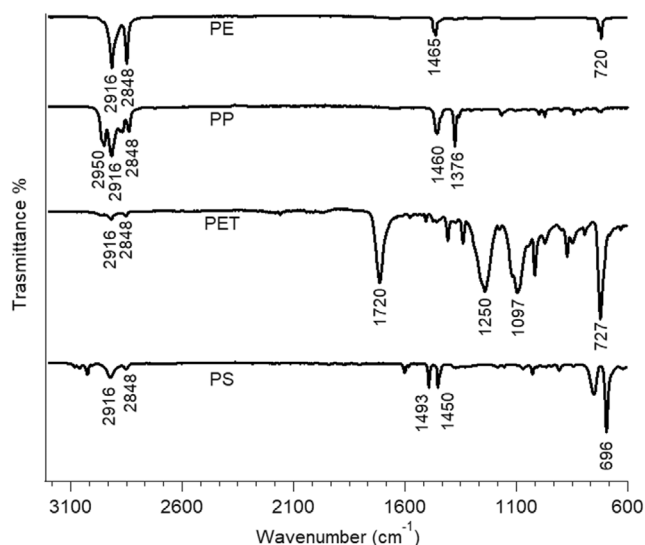
FIGURE 1 FT-IR spectra of post-consumer waste plastics: LDPE bag (blue curve), PP food container (green curve), PET (orange curve), and PS (red curve).
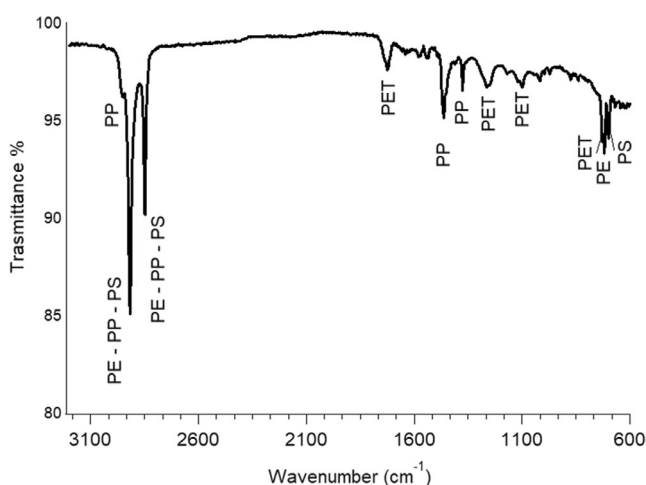

FIGURE 2 FT-IR spectrum of recycled pellet: each characteristic band has been associated with the corresponding polymer functional group.

3 | RESULTS AND DISCUSSION

3.1 | Qualitative composition via FT-IR and DSC

Reference FT-IR spectra collected on post-consumer plastic waste are shown in Figure 1, while the FT-IR spectrum of a recycled pellet is shown in Figure 2. The spectrum of the recycled material is similar to that of PE, as evidenced by the peaks associated with the vibrations of the CH_2 group, in particular stretching (2916–2848 cm^{-1}), deformation (1460–1470 cm^{-1}), and rocking (720 cm^{-1}). The other bands identified, such as CH_3 group deformation

(1376 cm^{-1}), CH bond deformation in the aromatic ring (696 cm^{-1}), and stretching of C=O (1720 cm^{-1}) and C-O (1250 cm^{-1}), were attributed to the presence of contaminants such as PP, PS, and PET, respectively.[21,22,26] Therefore, FT-IR spectroscopy confirms the presence of PE as the primary constituent in the recycled pellets, with the secondary presence of PP, PS, and PET

DSC first and second heating traces of a recycled pellet are shown in Figure 3. The first heating trace (red curve)—which is commonly considered to be flawed by the previous thermal history of the sample—shows three endothermic events: the first one has two distinct peaks consistent with LDPE (110°C) and HDPE (126°C) melting[18,19,29]; the third endothermic peak at 162°C is attributable to PP melting.[30–32] A glass transitions is visible at 85°C, ascribable to PET.[33,34] Since the presence of PS was highlighted in FT-IR spectroscopy but not detected in thermograms, it can be speculated that the glass transition of PS (100°C) contributes to the first endothermic phenomenon, even if it is hidden by the event itself.

The second heating trace (blue curve) shows the same three melting peaks recorded during the first heating, at 112°C (LDPE), 126°C (HDPE), and 162°C (PP). In this case, the glass transition of PET does not arise: the absence of these phenomena is reasonably attributable to a higher degree of crystallinity reached by the polymers during cooling at controlled speed.

3.2 | Quantitative composition based on FT-IR spectroscopy calibration lines

Normalized vibrational band heights of recycled pellets were used to determine their composition through calibration curves. Calibration curves are shown in Figure 4; curve parameters are shown in Table 2. A quantitative analysis of recycled pellets from five different batches is shown in Table 3.

It can be noticed that the amount of contaminants varies among the different batches: PP is between 4.8% and 6.0%, PS does not exceed 2.0%, while PET varies between 1.5% and 3.0%. We can suppose that this variation can be due to the heterogeneity of the plastic waste stream as a function of different times of the year; for instance, after the increase in the usage of plastic bottles, containers, and tableware during holidays and particular events. According to the sorting center management, some input streams are, therefore, richer in PS or PET with respect to others, and thus their final purity can be affected. This can reflect on contaminant variation across different batches. The PE content, calculated by subtracting the values of the contaminants, is about 90%, which is in line with the content declared by the manufacturer.

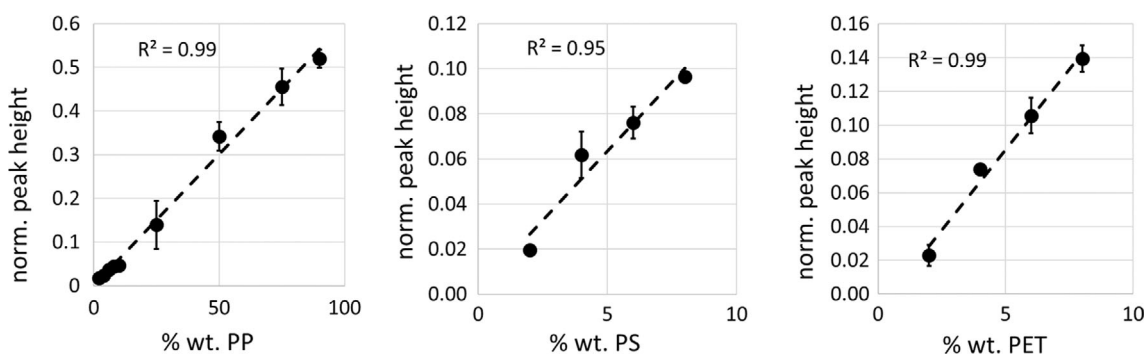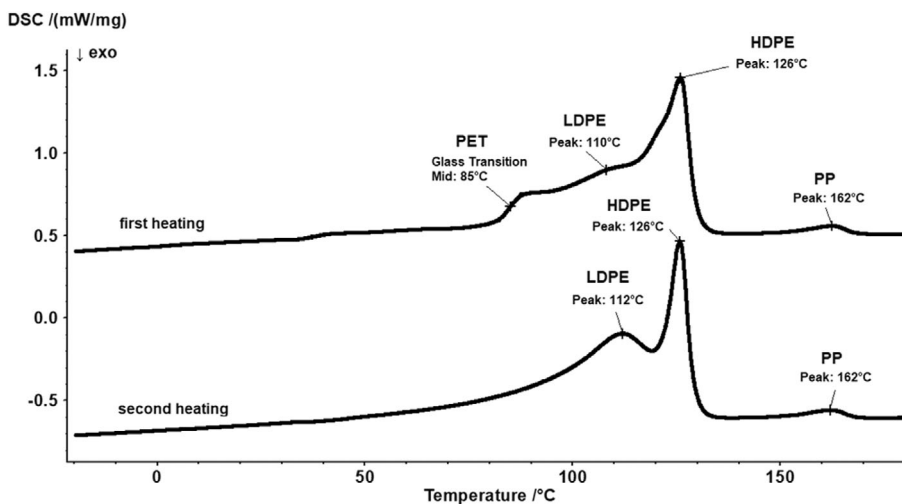**FIGURE 3** DSC first and second heating traces of recycled pellet.

FIGURE 4 Calibration lines obtained by FT-IR for PE/PP, PE/PE, and PE/PET blends.

TABLE 2 Calibration lines parameters.

Calibration line ($y = ax + b$)	a	b	R^2
PP/PE	6.0×10^{-3}	5.3×10^{-4}	0.99
PS/PE	1.2×10^{-2}	2.2×10^{-3}	0.95
PET/PE	1.9×10^{-2}	-9.8×10^{-3}	0.99

TABLE 3 Concentration (% wt.) of PP, PS, and PET in different batches.

Batch nr.	PP % wt.	PS % wt.	PET % wt.	PE % wt. (rem.)
1	5.8 ± 0.2	1.9 ± 0.4	1.9 ± 0.3	89.5–91.2
2	4.8 ± 0.3	2.0 ± 0.2	1.7 ± 0.3	90.8–92.2
3	6.0 ± 0.5	1.9 ± 0.2	3.0 ± 0.7	87.8–90.4
4	5.1 ± 0.1	1.5 ± 0.2	2.8 ± 0.4	90.0–91.4
5	4.9 ± 0.1	1.8 ± 0.3	1.5 ± 0.1	91.3–92.3

3.3 | Semi-quantitative composition based on DSC melting enthalpies

Quantitative results deriving from DSC analysis of recycled pellets from five different batches is shown in Table 4. The area under the melting peak of a DSC thermogram reflects the degree of crystallinity of the material.

The melting enthalpy associated with PP (endothermic peak around 162°C) was related to the reference melting enthalpy of 100% crystalline isotactic PP (182.6 J/g[29]) to estimate the PP crystalline fraction. It is worth remembering that only the crystalline fraction contributes to this melting endotherm; therefore, amorphous PP content was not taken into account. Similarly, the melting enthalpy

TABLE 4 Concentration (% wt.) of crystalline PP and PE in different batches.

Batch nr.	Peak 162 area (J/g)	Crystalline PP % wt.	Peak 110–140 area (J/g)	Crystalline PE % wt.
1	4.61	2.5%	110.20	38.3%
2	4.98	2.7%	109.30	38.0%
3	4.86	2.7%	116.20	40.3%
4	5.48	3.0%	118.60	41.2%
5	5.10	2.8%	114.40	44.9%

associated with PE (endothermic peak around 110–140°C) was divided by the reference melting enthalpy of a 100% crystalline PE (288 J/g[29]) to estimate the crystalline PE content. As previously discussed, DSC does not provide an accurate quantitative investigation, since the area underlying the melting peaks (which is a function of the melting enthalpy) is proportional to the crystalline fraction of the polymer only. The amorphous fraction, which also contributes to the actual content of the blend, is not taken into account. Moreover, completely amorphous polymers (such as PS) would be completely excluded from the count. PS is mostly commercialized in the atactic form,[15–17] whose random styrene group positioning hinders the chain regularity and the possibility to crystallize. PET has the ability to crystallize,[18,19] particularly via strain-induced crystallization, that is, in the stretch blow molding process (bottles production). It is likely that the semi-crystalline PET objects (bottles) were effectively removed during the initial manual waste sorting phase, while the non-crystalline PET (food containers, film - more easily mistaken for PS or PE) were left in the commingled plastics that were used later for pellets production. In any case, given the low amount of PET recorded by FTIR (about 2% wt.), a hypothetical crystallization exothermic peak (around 129°C) is likely well hidden by the melting endothermic peaks of LDPE and HDPE, and, therefore, not noticeable in the first heating traces of recycled pellets. Even during the second heating, a hypothetical melting peak could be barely noticed due to the low amount of PET in the pellets. As an example, the composition of sample 1 calculated with DSC data would underestimate the amount of PP (2.3%) and completely neglect the amount of PS and PET, thus overestimating PE content (97.7%).

On average (five batches), the crystalline PP content determined by melting enthalpies was 2.7 ± 0.2%, while the crystalline PE content was 40.5.3 ± 2.%. These values are lower than those estimated by FTIR spectroscopy; this is in line with the fact that only the crystalline fraction was computed by evaluating the DSC peak areas, while FTIR collected information on the overall chemistry. It can be noticed that the average PP content estimated by DSC (2.7 wt.) was about

51% of that estimated by FTIR (5.3% wt.), while the average PE content estimated by DSC (40.5 wt.) was about 45% of that computed by FTIR (90.7% wt.). Hence, a slightly higher crystalline fraction in PP with respect to that in PE in the post-consumer commingled plastics could be speculated. No information regarding other contaminants (PS and PET) was obtained by DSC.

4 | CONCLUSIONS

FT-IR spectroscopy and DSC have proven to be appropriate techniques to identify the different polymers inside recycled plastic pellets. DSC could be suitable only for blends in which melting peaks, crystallization peaks, or other features (e.g., glass transitions) associated with the polymeric components are adequately distinct to enable identification. However, DSC results can be purely qualitative or semi-quantitative, since only the crystalline fraction is evaluated through the peak areas. Thus, the use of DSC is only effective under specific circumstances and when performed in parallel with FT-IR measurements. On the other hand, DSC has proved to be useful to assess the presence of different grades of PE (LDPE and HDPE): this information is not easily accessible with FT-IR spectroscopy. FT-IR spectroscopy, on the contrary, is able to detect also the amorphous signal; moreover, FTIR is faster (1–2 min acquisition time vs. 60–120 min for DSC) and non-destructive, and should be regarded as the preferred technique for quality control or to correctly determine the quantitative chemical composition of the recycled blends. Finally, the construction of ad-hoc calibration curves allows to assess the pellet composition with respect to some selected polymers (PP, PS and PET), which represent the most common contaminants in this PE-based recycled material. Fourier transform infrared spectroscopy, which is extensively used in academia but not so common in the plastics recycling industry, can, therefore, find a wider use in this field as a fast and reliable characterization technique.

CONFLICT OF INTEREST STATEMENT

The authors have no relevant financial or non-financial interests to disclose.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

[1] K. Hamad, M. Kaseem, F. Deri, *Polym. Degrad. Stab.* **2013**, *98*, 2801.

[2] N. Singh, D. Hui, R. Singh, I. P. S. Ahuja, L. Feo, F. Fraternali, *Compos. Part B* **2017**, *115*, 409.

[3] United Nations Environment Programme. Beat Plastic Pollution n.d.

[4] M. N. Siddiqui, M. A. Gondal, H. H. Redhwi, *J. Environ. Sci. Health A* **2008**, *43*, 1303.

[5] PlasticsEurope. Plastics - The Facts 2019. **2019**.

[6] PlasticsEurope. Plastics post-consumer waste treatment in the European Union (EU-28) in 2006 and 2018. **2019**.

[7] M. K. Eriksen, A. Damgaard, A. Boldrin, T. F. Astrup, *J. Ind. Ecol.* **2019**, *23*, 156.

[8] K. Ragaert, L. Delva, K. Van Geem, *Waste Manag.* **2017**, *69*, 24.

[9] L. Cafiero, D. Fabbri, E. Trinca, R. Tuffi, C. S. Vecchio, *J. Therm. Anal. Calorim.* **2015**, *121*, 1111.

[10] K. Kaiser, M. Schmid, M. Schlummer, *Recycling* **2017**, *3*, 1.

[11] M. Jansen, A. Feil, T. Pretz, *Waste Management, Volume 3 - Recycling and Recovering*, Thomé-Kozmiensky Verlag GmbH, Neuruppin, Germany **2012**.

[12] Jansen M, van Velzen EUT, Ferreira B, Pretz T. Recovery of plastics from municipal solid refuse waste in Europe in materials recovery facilities. 14th International Waste Management and Landfill Symposium 2013.

[13] C. Cimpan, A. Maul, M. Jansen, T. Pretz, H. Wenzel, *J. Environ. Manag.* **2015**, *156*, 181.

[14] A. Mio, S. Bertagna, L. Cozzarini, E. Laurini, V. Bucci, A. Marinò, M. Fermeglia, *Mater. Technol.* **2021**, *29*, 29.

[15] H. Sato, M. Shimoyama, T. Kamiya, T. Amari, S. Šašic, T. Ninomiya, et al., *J. Appl. Polym. Sci.* **2002**, *86*, 443.

[16] D. J. da Silva, D. F. Parra, H. Wiebeck, *Chem. Eng. J.* **2021**, *426*, 131344.

[17] M. L. Henriksen, C. B. Karlsen, P. Klarskov, M. Hinge, *Vib. Spectrosc.* **2022**, *118*, 103329.

[18] W. Camacho, S. Karlsson, *Polym. Eng. Sci.* **2001**, *41*, 1626.

[19] Å. G. Larsen, K. Olafsen, B. Alcock, *Polym. Test.* **2021**, *96*, 107058.

[20] Beleites C. hyperSpec 2015. Accessed December 6, 2022. https://hyperspec.r-forge.r-project.org/

[21] M. R. Jung, F. D. Horgen, S. V. Orski, C. V. Rodriguez, K. L. Beers, G. H. Balazs, et al., *Mar. Pollut. Bull.* **2018**, *127*, 704.

[22] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed. Wiley-VCH Verlag, Weinheim, Germany **2004**.

[23] P. Larkin, *Infrared and Raman Spectroscopy - 1st Edition*, 1st ed., Elsevier, Amsterdam, the Netherlands **2011**.

[24] A. Kumar, D. Naumenko, L. Cozzarini, L. Barba, A. Cassetta, M. Pedio, *J. Raman Spectrosc.* **2018**, *49*, 1015.

[25] I. Noda, A. E. Dowrey, J. L. Haynes, C. Marcott, in *Physical Properties of Polymers Handbook* (Ed: J. E. Mark), Springer, New York, NY **2007**, p. 395. https://doi.org/10.1007/978-0-387-69002-5_22

[26] J. P. Luongo, *J. Appl. Polym. Sci.* **1960**, *3*, 302.

[27] S. Krimm, C. Y. Liang, G. B. B. M. Sutherland, *J. Chem. Phys.* **1956**, *25*, 549.

[28] ASTM International. *ASTM D7399 Standard Test Method for Determination of the Amount of Polypropylene in Polypropylene/Low Density Polyethylene Mixtures Using Infrared Spectrophotometry*, West Conshohocken, Pennsylvania, United States of America **2018**.

[29] I. Borovanska, T. Dobreva, R. Benavente, S. Djoumaliisky, G. Kotzev, *J. Elastomers Plast.* **2012**, *44*, 479.

[30] A. C.-Y. Wong, F. Lam, *Polym. Test.* **2002**, *21*, 691.

[31] M. Majewsky, H. Bitter, E. Eiche, H. Horn, *Sci. Total Environ.* **2016**, *568*, 507.

[32] M. Windt, D. Meier, R. Lehnen, *Holzforschung* **2011**, *65*, 65.

[33] A. Manivannan, M. Seehra, *Prepr. Symp. Div. Fuel Chem. Am. Chem. Soc.* **1997**, *42*, 1028.

[34] S. A. Jabarin, *J. Appl. Polym. Sci.* **1987**, *34*, 85.