

Quantification of PP contamination in recycled PE by TREF analysis for improved the quality and circularity of plastics

Rafael Juan ^{a,b}, Beatriz Paredes ^{a,b}, Rafael A. García-Muñoz ^{a,b,**}, Carlos Domínguez ^{a,b,*}

^a LATEP, Polymer Technology Laboratory, Rey Juan Carlos University, Tulipán St., 28933, Móstoles, Madrid, Spain

^b GIQA, Group of Environmental and Chemical Engineering, ESCET, Rey Juan Carlos University, Tulipán St., 28933, Móstoles, Madrid, Spain

ARTICLE INFO

Keywords:

Recycled high-density polyethylene
Polypropylene
Circular economy
DSC
TREF

ABSTRACT

Polyethylene constitutes more than one-third of the world's plastic and is one of the main components in municipal waste streams. Unfortunately, varying amounts of polypropylene (PP) are usually found in recycled high-density polyethylene (rHDPE), which erodes their mechanical properties and reduces the quality of these recyclates and their possible reuse in the industry. Differential Scanning Calorimetry (DSC) is the technique commonly used to detect and determine the presence of PP in these blends, but intrinsic limitations of this method lead to inaccurate results. Thus, alternative techniques must be employed to solve these drawbacks and help to estimate more accurately the levels of the PP impurities in rHDPE. In this work, crystallization techniques, such as Temperature Rising Elution Fractionation (TREF) is used to fractionate PE and PP blends into their components to obtain quantitative information. Municipal waste samples of rHDPE contaminated with different amounts of PP have been characterized by DSC and TREF. Comparative results of both techniques show an underestimation of PP values when DSC is used as analytical technique. Results prove that TREF analysis irrespective of the crystallization rate used is valid for the identification and quantification of PP impurities in rHDPE samples, even at low PP percentages in the blend lower than 2 wt. %, which could help to control the quality of rHDPE and achieve the priority of reusing and recycling adopted by the European Union for a Circular Economy of Plastics.

1. Introduction

Plastics have rapidly developed into one of the most important materials in our society since its discovery and synthesis in the beginning of the 20th century, experiencing an exponential growth in production and use in the past decades, which will presumably double in the next few years. This vast production of plastics as a result of modern-day lifestyles is eliciting important environmental concerns related to the management of plastics. Last year in European countries, 50.7 million tonnes were used, being packaging (39.6%) and construction (20.4%) the most demanded markets for these plastic resins [1]. As most plastic products proceed from packaging and single-use applications, these causes that tons of plastic waste are generated every year [2]. Thus, plastics' pollution is an important problem for countries that have seen increased social awareness. Management of plastic waste and ways of recover discarded plastics have become priorities for governments and

industries. In recent years, the European Union has set up their own guidelines, through the implementation of its first European strategy for plastics, to facilitate a transition towards a Circular Economy of plastics materials [3]. Notwithstanding these measures, undesired treatments for plastic waste like energy recovery or landfilling are still predominantly used (Fig. 1).

Currently, major progress has already been achieved within the management of plastic waste, such as increased development mechanical and chemical recycling techniques [4–8] and new bio-based plastics [9,10], that help to reduce the amount of plastic waste generated every year or those that are already accumulated in landfills or discarded for energy recovery. Among them, mechanical recycling is still one of the methods most commonly used for plastic recycling, as it is a rapid way to obtain again a material that could be reused to manufacture either the same or new products [6]. However, mechanical recycling also presents some drawbacks, as its dependency on the quality of the plastic waste.

* Corresponding author. LATEP, Polymer Technology Laboratory, Rey Juan Carlos University, Tulipán St., 28933, Móstoles, Madrid, Spain.

** Corresponding author. GIQA, Group of Environmental and Chemical Engineering, ESCET, Rey Juan Carlos University, Tulipán St., 28933, Móstoles, Madrid, Spain.

E-mail addresses: rafael.garcia@urjc.es (R.A. García-Muñoz), carlos.dominguez@urjc.es (C. Domínguez).

<https://doi.org/10.1016/j.polymeresting.2021.107273>

Received 12 April 2021; Received in revised form 17 May 2021; Accepted 11 June 2021

Available online 16 June 2021

0142-9418/© 2021 The Authors.

Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

For this reason, plastics' selection and sorting before mechanical recycling plays a crucial role in the properties of the recyclates obtained through this way of recycling. Another aspect to be considered in mechanical recycling is the degradation and changes suffered by the polymer chains during reprocessing that may affect the performance and application of the recycled plastic materials [11]. Thus, major issues still limit the use of recycled plastics, mainly due to lack of adequate sorting and collection infrastructures, and presence of contaminants in recycled materials [12]. The presence of impurities and other polymers is widespread in recycled plastics, which lowers the quality of recycled resins and makes it hard to compete with their raw plastics.

Nowadays, polyolefins continue to be by far the most demanded plastics material. Within polyolefins, high-density polyethylene (HDPE) is widely used to manufacture products for construction, cosmetic bottles and specially, food packaging applications [1]. On the other hand, polypropylene (PP) is extensively used in packaging for consumer products, plastic components for various sectors, especially automotive and textile industry. Both materials are the most discarded plastics every year [13] and commonly found in municipal solid wastes (MSW), being part of the light fraction obtained from plastic waste streams. The similar density value of both resins makes it difficult to achieve an accurate separation process [14]. For this reason, cross-contamination for recycled polyolefins can be significant, around 4–5 % of HDPE in recycled PP, and 8–10 % of PP in recycled HDPE [12]. The presence of PP is habitual when recycling HDPE products like bottles [15] or caps [16]. As both polymers are immiscible, blends usually have poor mechanical performance, even at low quantities [17–20], restricting its applicability in industry, where key HDPE properties such as slow crack growth (SCG) [21] suffer from cross contamination [22,23].

To solve these issues, compatibilizing agents are often used to improve the mechanical performance for blends of recycled PE/PP, mainly introducing an ethylene-propylene-diene monomer (EPDM) [24, 25] or olefin block copolymers [26]. However, the use of compatibilizers increase the cost of the recycled polymer, being a drawback in the establishment of recycled resins in the plastic market [27]. In this sense, the identification and quantification of impurities is critical to correctly evaluate the quality and purity of recyclates and thus minimize the need of fillers and compatibilizers [15].

Although spectroscopy analysis techniques like Fourier-transform infrared (FTIR) and Nuclear magnetic resonance (NMR) have been historically used for compositional analysis of polymer blends [28,29], thermal analysis represented by differential scanning calorimetry (DSC) has been the preferred technique due to wide availability and its easy-to-use [30]. However, DSC analysis is rather limited for quantitative determination of polymers present in blends, as the results obtained can be influenced by its thermal history [31], crystallization kinetics and

co-crystallization effects [32]. Also, small amounts of sample analysed by DSC could not be representative in heterogeneous blends of recycled polymers. Moreover, the DSC analysis has serious limitations to detect minor components at low concentrations, which are hardly noticeable [33]. These issues highlight the limitation of the technique and therefore the lack of accuracy in the quantification of the components. Other techniques, such as high temperature interaction chromatography, have been investigated to characterize blends of polyethylene and polypropylene in a most efficient way [34]. Furthermore, the analysis of the chemical composition distribution (CCD) by crystallization techniques, mainly temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF). Both techniques separate the polymer chains of a sample with different crystallinity components, although CRYSTAF is preferred as it takes place in a single step and provides the same information as TREF in a shorter time of analysis [35]. On the other hand, although TREF has longer analysis times, its resolution for separation of blends of HDPE/PP is better than CRYSTAF [36].

In this study, several commercial recycled high-density polyethylene (rHDPE) samples with different contamination level of polypropylene have been deeply characterized using thermal analysis (DSC) and crystallization techniques (TREF and CRYSTAF). Calibration curves were obtained for the techniques in order to establish an effective method to identify more precisely the polypropylene content. Besides, different crystallization rates were tested to shorten the analysis times of TREF and study its effect in the resolution of this technique. Quantitative determination of cross-contamination of these materials will help to improve the quality of recycled high-density polyethylene, increasing its value in the industry and helping to compete with virgin resins in applications that require higher technical performance.

2. Experimental

2.1. Materials

Commercial HDPE recyclates contaminated with PP were obtained from several recycling companies in Europe. Additionally, raw commercial resins of HDPE and isotactic PP were used as references for the different tests.

2.2. DSC

Thermal measurements were performed using 10 ± 0.5 mg of sample at a heat rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ 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 and 207 J/g for an ideal PP crystal.

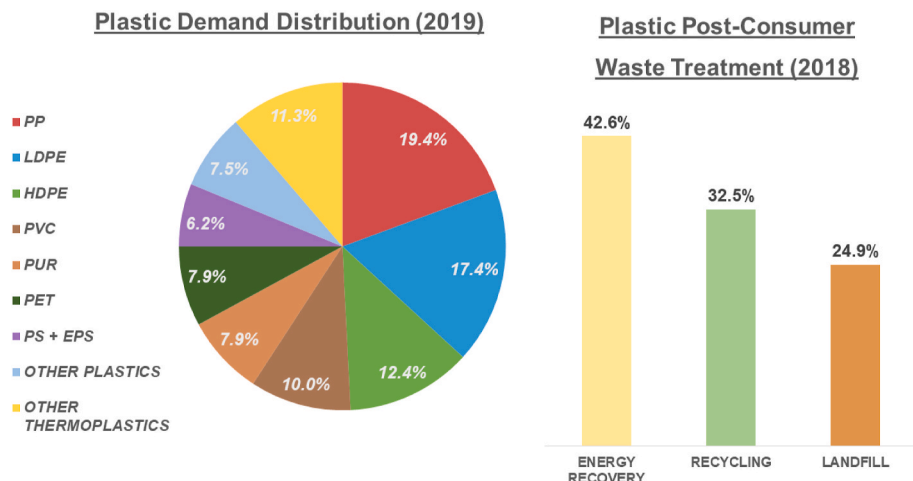


Fig. 1. European data of plastic demand distribution by resin type and plastic consumer waste treatment [1].

2.3. TREF and CRYSTAF

TREF experiments were carried out on a commercial CRYSTAF-TREF instrument model 300 (Polymer Char). 80 ± 0.5 mg of sample was dissolved in 1,2,4-trichlorobenzene (TCB) at 160°C and the solution was stirred. Then the solution was loaded into the column and held at 130°C for 45 min. After the stabilization step, the temperature was reduced to 35°C under a constant cooling rate 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 was used to obtain the crystallization curves. Different cooling rates were evaluated to reduce experimental times and determine the effectiveness of the method for accurate component quantification.

The same CRYSTAF-TREF instrument was also used to perform CRYSTAF experiments. About 20 ± 0.5 mg of sample were dissolved in TCB at 160°C , which was then crystallized at a cooling rate of $0.1^\circ\text{C}\cdot\text{min}^{-1}$. The polymer concentration in solution was analysed by an infrared detector to obtain the first derivative curves.

3. Results and discussion

Several samples of rHDPE contaminated with PP were used in this study. Although the PP impurity content of every sample was not previously known they were selected to cover a contamination range up to approx. 15% wt., the worst-case scenario that would lead to deterioration of the mechanical properties of the HDPE recyclates in packaging industry [12].

3.1. Determination of PP impurities in rHDPE by DSC measurements

Samples were first characterized by differential scanning calorimetry (DSC) analysis to determine the amounts of polypropylene present in rHDPE. DSC is a proper technique for evaluating characterizing the thermal properties of polymeric materials [37–39] and has been widely used to identify, estimate a determine the polymers present in blends based on the enthalpy of melting of both components and due to its ease of use, speed and low cost. Quantification of PE and PP was also reported in the past using the enthalpy of melting (ΔH) of both components [29], since no interactions were observed between them. The different melting temperature (T_m) allows to differentiate PP from HDPE [40]. However, enthalpy determined by DSC has also been questioned as an accurate method to determine the crystallinity of polymers as these measurements are obtained under non-equilibrium conditions [41]. Also, melting transition is dependent on the crystallinity of the samples and thermal history of samples could also affect the analysis [31], which in turn may limit the accuracy of this technique for quantitative analysis.

First, commercial HDPE and isotactic PP resins with similar structures to the recyclates used in this study were tested. The virgin HDPE and PP polymer yielded a single melting transition at 135 and 160°C , respectively, as expected for the 'pure' resins. A calibration curve that establishes a relation between the polyolefin mass and their enthalpy of melting was obtained. Fig. 2 shows a clear linear dependence of the enthalpy of melting as functions of the corresponding polyolefin mass, with a good correlation for both polymers. From this calibration, the content of PP in the rHDPE resins was quantified. Additionally, a second method of PP contaminant measurement based on the direct enthalpy of melting (ΔH) calculation was used.

Then, DSC analysis for all HDPE recyclates were performed 5 times to obtain an average value. The T_m corresponding to the rHDPE appears around 131°C , while a small peak is observed at 163°C for PP impurities in these recyclates (Fig. 3). The smaller temperature melting transition observed in the HDPE recyclate DSC scan compared to the raw HDPE (135°C) is most likely due to the presence of PP. The presence of PP is already observed in all the recyclates studied, being samples 8 and 9 the most contaminated, while samples 1, 2 and 3 exhibit a slight

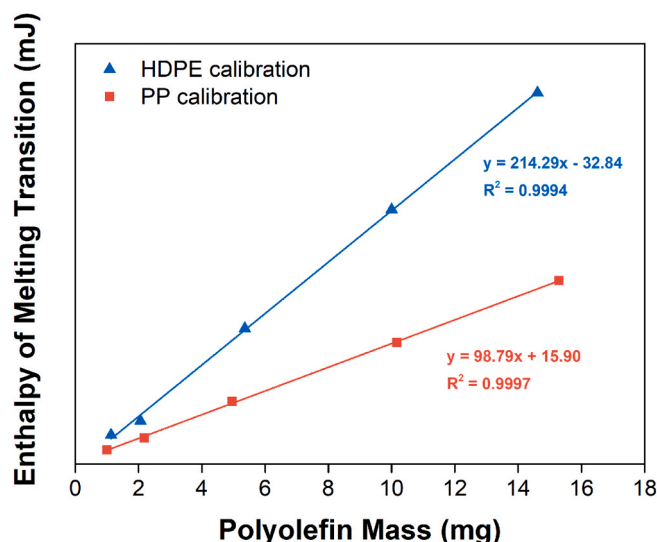


Fig. 2. Heat of fusion of raw resins in function of each polyolefin mass, respectively.

content of PP.

The composition of the HDPE recyclates was estimated through both methods, ΔH and the linear calibration, to determine their effectiveness for PP impurities quantification. Results are summarized in Table 1 and Fig. 4.

Results about the content of PP in rHDPE using the ΔH approach show lower values than those of the linear calibration method, excepting for resins with the lowest PP content (below 2 wt. %). For these latter values, the linear calibration method displays even negative values with large dispersion, which limits the application of the method for samples with PP lower than 2 wt. %. Moreover, difference in crystallinities of both polyolefins could affect the accuracy to determine the PP content when the ΔH method is used, as small overlapping between signals is observed (Fig. 3) [23]. On the other hand, only small amounts of sample (around 10 mg) are analysed by DSC. As it is well known in plastics recycling, it is very common that impurities are not homogeneously distributed along the sample, and therefore the small amount of sample analysed by DSC may result insufficient to obtain a representative value of the whole rHDPE resin, becoming a critical issue that clearly affects the results obtained. This is the reason of the high dispersion of results obtained for some rHDPE resins such as samples 5 and 7. Besides, for samples 8 and 9 that present high impurities content, large discrepancies are observed when both methods are compared. Therefore, the drawbacks of DSC analysis to determine the minority components at low concentrations and the high variability in the measurements at moderate to high concentration makes this technique limited to accurately detect and quantify the presence of PP contaminants, and additional techniques should be employed to solve these drawbacks and help to estimate more accurately the levels of the PP impurities in rHDPE.

3.2. Determination of PP impurities in rHDPE by TREF and CRYSTAF measurements

TREF and CRYSTAF techniques have been widely used in the past to fractionate and characterize the chemical composition distribution of different polymer blends [33,42–44]. In some published examples CRYSTAF has become the preferred technique because the crystallization process takes place in one-single step, unlike TREF which requires a crystallization step follow by an elution step, which considerably increase the analysis time [45,46]. Nevertheless, CRYSTAF is rather limited to quantify the components in blends of HDPE/PP because both crystallization thermal transitions usually appear in a similar range of

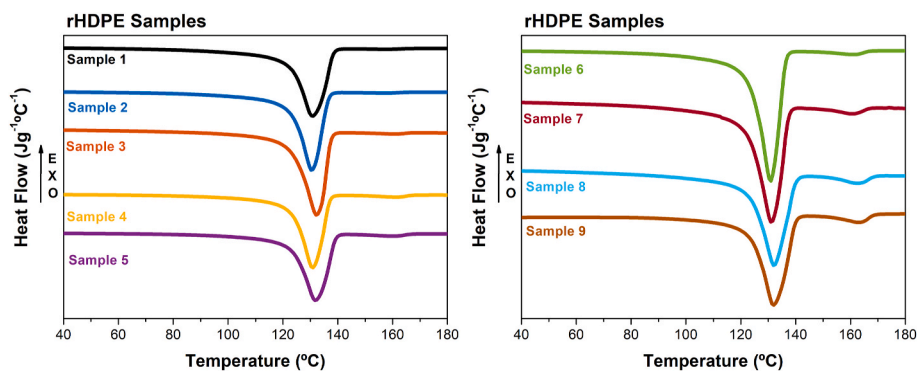


Fig. 3. Comparisons between thermal curves obtained for all rHDPE samples.

Table 1

Percentage of polypropylene obtained by DSC for all the samples of rHDPE.

Sample	Average % PP (ΔH)	% PP (Linear Calibration)
1	0.80 \pm 0.16	-0.25 \pm 0.31
2	0.78 \pm 0.21	-0.31 \pm 0.45
3	1.28 \pm 0.12	0.56 \pm 0.47
4	2.44 \pm 0.08	3.22 \pm 0.18
5	3.23 \pm 0.90	4.78 \pm 1.64
6	2.58 \pm 0.14	3.27 \pm 0.35
7	3.74 \pm 0.72	5.33 \pm 0.86
8	6.51 \pm 0.31	10.8 \pm 0.6
9	6.65 \pm 0.14	11.3 \pm 0.3

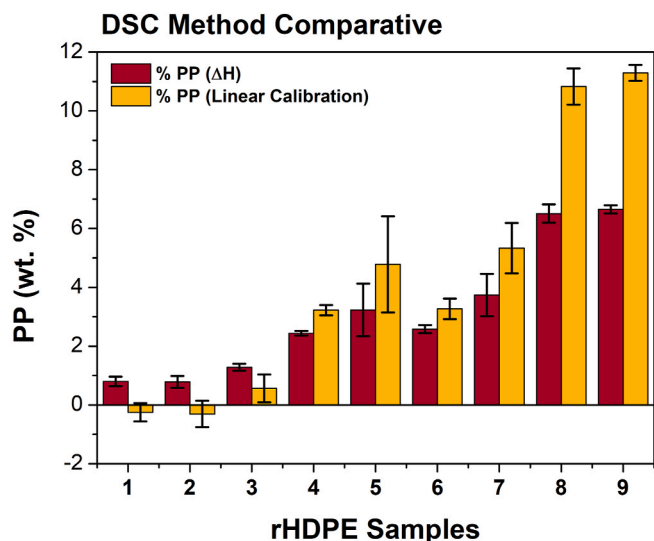


Fig. 4. Comparison between both methodologies used to estimate the % PP by DSC results.

temperatures (80–90 °C) as a result of the undercooling effects [36]. For comparison, Fig. 5 shows the thermograms obtained by CRYSTAF and TREF of the recyclates 1 and 5 with different content of PP impurities. CRYSTAF thermograms display a clear overlapping region for both polymers irrespective of the PP content, which might lead to inaccurate evaluation of the PP content. Unlike, TREF thermograms exhibit two different peaks at 95–100 and 115–120 °C, corresponding to PE and PP moieties, respectively. From these results it is inferred that TREF technique could be valid to detect and estimate the level of PP contaminants in the rHDPE resins from post-consumer and post-industrial recycling.

To gain deeper and more detailed insight in the viability of the TREF approach to determine the presence of PP impurities in rHDPE, calibration curves have been obtained by TREF using the commercial virgin

HDPE and PP as references, with the aim of determining the detection limit and accuracy of the methodology. Virgin resins have been dissolved directly. A usual cooling rate of 0.1 °C.min⁻¹ was chosen to promote separation and reduce co-crystallization effects. Fig. 6 shows a good correlation between experimental and theoretical composition for the entire PP content range, which confirms the robustness and predictive capability of the methodology to estimate the PP cross-contamination in rHDPE resins.

However, a negative aspect that can compromise the viability of TREF as a technique to determine PP impurities in rHDPE is the longer time required for the analysis. Polymer samples are dissolved and then precipitated into a column with an inert support, which allows to fraction different polymer chains as functions of their crystallinity. Then, the elution of polymer chains takes places while increasing the temperature, recording the concentration with an infrared detector [47]. The slowest step of this process is the crystallization one, since usually low cooling rates are used to improve the separation of different components in a polymer blend. Thus, to probe the feasibility of the TREF test at shorter analysis times, different crystallization rates have been tested. In addition to the crystallization rate of 0.1 °C.min⁻¹, which was proven to be adequate for the identification and quantification of PP impurities, as shown in Fig. 6, rHDPE resins were evaluated at 1 and 5 °C.min⁻¹. Higher cooling rates could affect the adequate resolution of the method and were not tested. All the recycled resins were evaluated at this new cooling rates 5 times per sample. Fig. 7 displays the TREF thermograms of rHDPE 5 and 9, as examples of resins with different content of PP, at the three crystallization rates. At the lowest cooling rate of 0.1 °C.min⁻¹, two clear peaks at 100 °C and 118 °C are observed, corresponding to rHDPE and PP, respectively. As the crystallization rate is increased at 1 °C.min⁻¹, the peak corresponding to HDPE becomes wider and a shoulder can be identified. Finally, at 5 °C.min⁻¹, the HDPE signal is split, and two clear peaks are observed at 5 °C.min⁻¹. These results may be accounted for the melting-recrystallization processes of polyethylene chains that take place during the analysis at higher cooling rates. However, the HDPE peak broadening and even splitting hardly affect either the temperature at which the peaks appear or the signals' resolution, allowing a good quantification of both components of the blends, even at the highest cooling rate, without any visible overlapping region.

PP content in rHDPE samples measured by TREF at the three cooling rates tested are summarized in Table 2. Overall, the calculated PP content exhibits very similar values for all the crystallization rates evaluated. rHDPE samples 1, 2 and 3 with the lower amount of PP can be clearly differentiated and show very similar results regardless of the cooling rate used. For resins with PP values in the range of 5–15 wt. %, results appearing in Table 2 indicates that a 5 °C.min⁻¹ the content of PP calculated is slightly lower than those obtained at 0.1 and 1 °C.min⁻¹, although the cooling rates appear to have negligible effect on phase separation. These similar results, irrespective of the cooling rate, can be explained by the fact that in TREF analysis the nucleation step is particularly favoured as the crystallization takes place on a support,

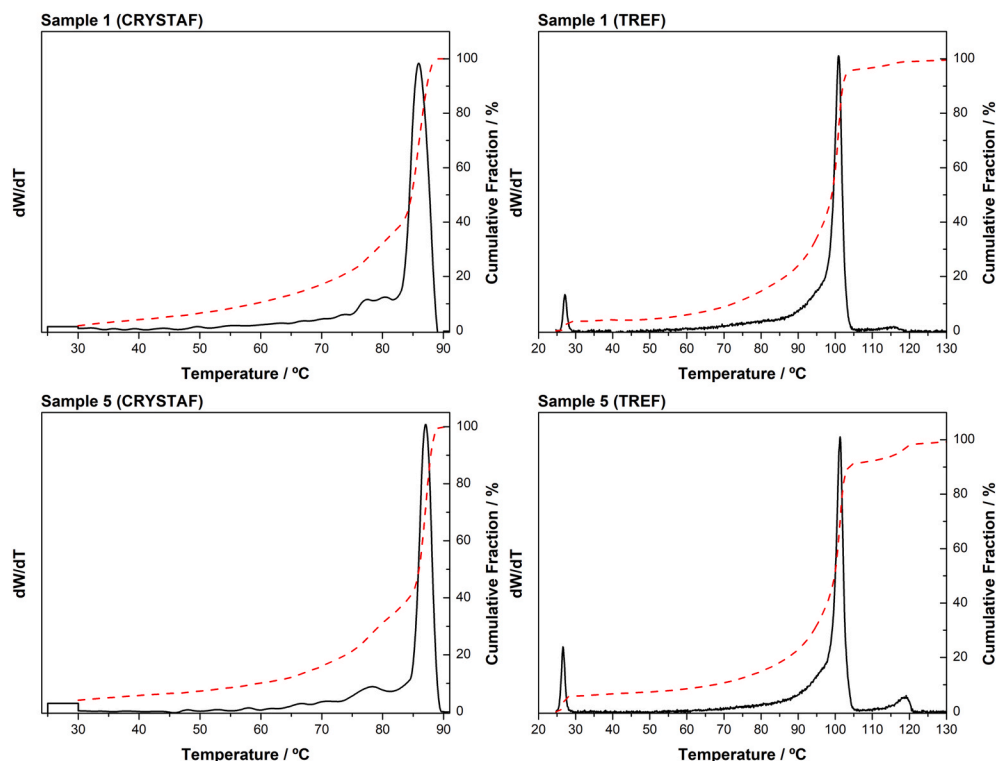


Fig. 5. Comparison of CRYSTAF and TREF curves for samples 1 and 5.

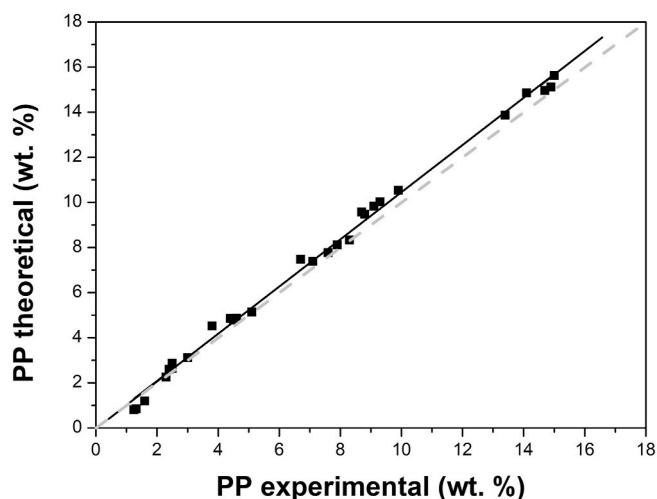


Fig. 6. Comparison of TREF results for reference resins at different PP concentrations.

which makes the analysis less dependent of the crystallization rates as occurs in CRYSTAF measurements, and also the co-crystallization event is avoided among chains with different chemical structure [35].

Fig. 8 compares the PP content measured by TREF with that obtained by DSC considering both approaches, the enthalpy corresponding to melting transition (ΔH) and the linear calibration. The results show that PP wt. % values obtained by DSC using the ΔH method are about half of those obtained by TREF analysis. This trend is observed for all the rHDPE resins analysed regardless of the PP content. Moreover, scattered results have been obtained by calculation of the PP values through the DSC linear calibration approach. Thus, the method provides negative values for rHDPE resins containing values below 2.5 wt. %, while for PP content in the range 5–15 wt. % the obtained values are indistinctly

close to those provided by the TREF technique or the ΔH method, with a broad spread in the measures that leads to large standard deviation pointed out by the error bars in Fig. 8, which highlights the inaccuracy and difficulty to apply this method. These great dispersion in the measures can be explained by the low amount of sample that is analysed by DSC, around eight times lower than TREF technique, and the fact that the impurities are not homogeneously distributed through the resins, which becomes critical in the case of recycled polymers.

Results indicate that the impurities of PP determined by DSC are lower than those using TREF, leading to a clear underestimation of the PP content in the recycled HDPE samples. These results can be explained considering the differences between both techniques. TREF is used as a technique that allows to fractionate semicrystalline polymers according to their solubility-temperature relationship and thus to their molecular structures. TREF is mainly sensitive to differences in polymer crystallinity/solubility and also fractionates polymer chains according to the molecular structure that affects crystallinity/solubility. Overall, TREF is sensitive to and based on the relationship between molecular structure, chain crystallinity and dissolution temperature. In solution the flexible chains of a semicrystalline polymer have a universal behaviour. Also, the polymer-solvent interactions are favoured in dilute solution more than the polymer-polymer ones as in DSC technique, which means that chains behaviour that compose the rHDPE resins can be studied individually by TREF, unlike DSC. Moreover, TREF analysis requires the introduction of an aliquot of the solution in a column packed with an inert support. The fact that chains are separated from each other by solvent implies a better chain relaxation and therefore a faster folding to develop the crystallites. In addition, the nucleation step is more favoured in the directly obtained TREF fraction, as the crystallization takes place on a support, and the co-crystallization phenomenon is therefore avoided among chains with different chemical structure. Moreover, phase separation is improved by an appropriated choice of crystallization rate. Therefore, the importance of using TREF technique lies in its capacity to rank different recycled resins that allows identifying small amounts of any semicrystalline component, even below 2 wt. %. The results show that TREF is an effective and accurate method for quantitative determination of PP

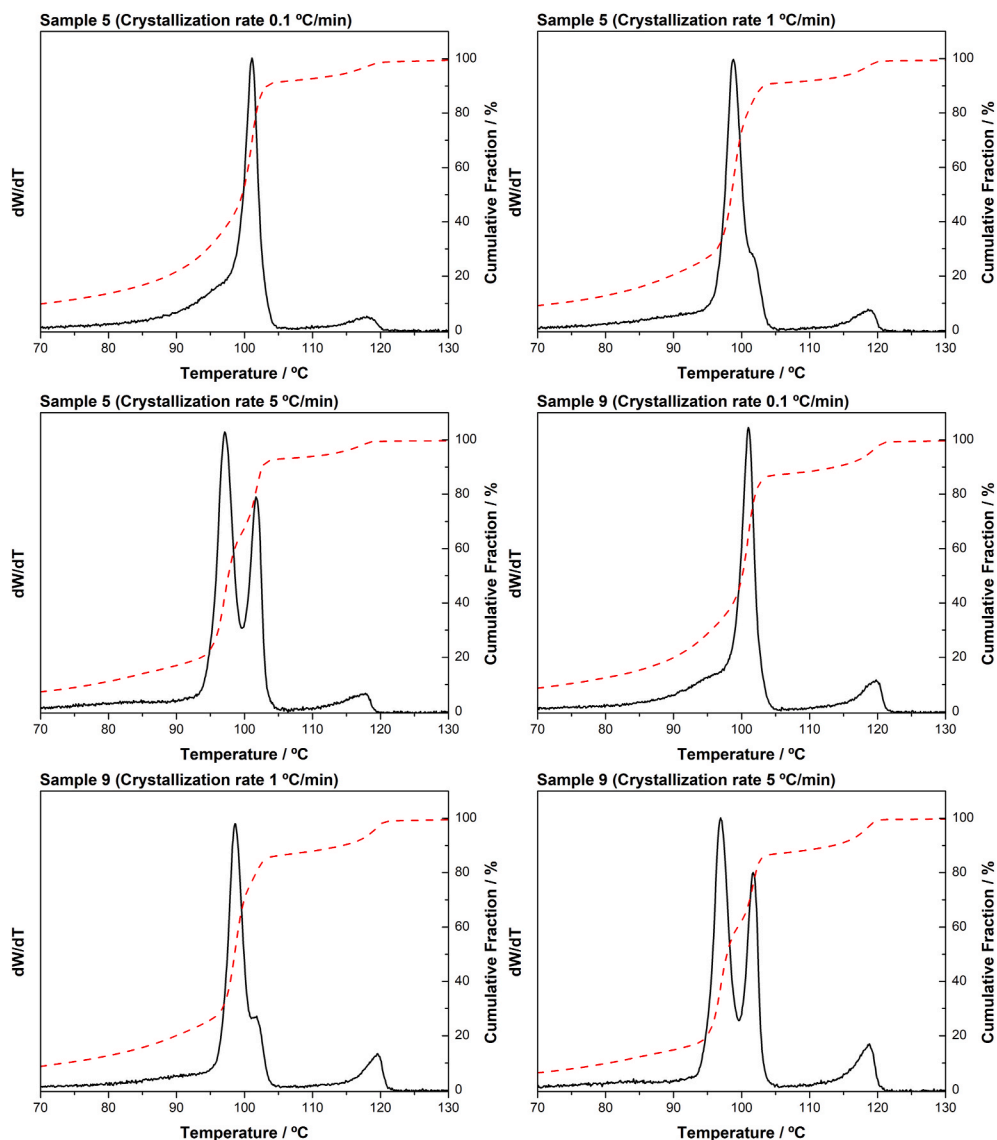


Fig. 7. TREF curves for samples 5 and 9 at different cooling rates.

Table 2
Percentage of polypropylene obtained by TREF for all samples of rHDPE.

Sample	PP wt. % (Cooling rate 5 °C/min)	PP wt. % (Cooling rate 1 °C/min)	PP wt. % (Cooling rate 0.1 °C/min)
1	2.33 ± 0.47	2.38 ± 0.18	2.46 ± 0.29
2	2.16 ± 0.28	2.16 ± 0.42	2.18 ± 0.22
3	3.05 ± 0.28	3.08 ± 0.17	3.20 ± 0.22
4	4.92 ± 0.40	5.32 ± 0.31	5.62 ± 0.25
5	6.40 ± 0.37	7.56 ± 0.53	7.30 ± 0.34
6	5.78 ± 0.16	5.66 ± 0.47	5.90 ± 0.38
7	8.43 ± 0.31	8.57 ± 0.34	8.87 ± 0.42
8	11.8 ± 0.2	10.7 ± 0.5	11.9 ± 0.4
9	12.1 ± 0.4	12.4 ± 0.4	12.6 ± 0.6

content in rHDPE, even at higher crystallization rates that helps to reduce the TREF analysis time by up to 4 times and makes TREF technique a great alternative for the quality control of recycled polyolefins.

4. Conclusions

Cross-contamination of recycled polymers, in particular in HDPE recyclates, is an important factor that limits its applicability, being

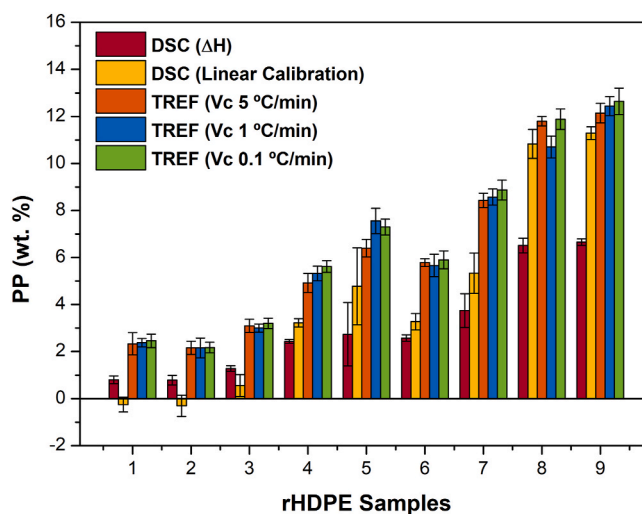


Fig. 8. DSC and TREF results comparison for all rHDPE samples.

necessary to identify and precisely quantify the presence of impurities, mainly PP, for improved the recycled resins and end product quality. DSC has been usually the favourite technique to characterize the HDPE recyclates due to its availability and rapidity. In this work, two different methods based on DSC analysis have been applied to determine the PP content in rHDPE, linear calibration and enthalpy from melting transitions. High spread values were obtained for all the PP range of 1–15 wt. %. The linear calibration method displays negative values for PP content below 2 wt. %, while for a higher PP content shows an important dispersion in the measurements. Discrepancies near to 100% were observed between both methods, which represents a meaningful limitation of the differential scanning calorimetry for the quantitative analysis of polymer blends, especially in the case of HDPE/PP blends, and their incorporation into the virgin polymer feedstock in a polymer production plant.

To solve these problems and to estimate more accurately the real PP content TREF method was deeply analysed in this work as alternative or complement to DSC. In polymer blends and particularly in polymer recycling, small variations of the component amount, between 1 and 5 wt. %, provoke significant changes over the macroscopic properties of the raw blend, and therefore an underestimation of the values could significantly affect the quality of the end product obtained in the recycling plant. Comparative results of both techniques yielded an underestimation of PP values when DSC is used as analytical technique. Results demonstrated that TREF is valid for the identification and quantification of PP impurities in rHDPE samples, even at a very low PP content. Although low crystallization rates are commonly used in TREF analysis, higher cooling rates can be used in order to significantly reduce the analysis times. PP contents for all rHDPE samples were quite similar for all the crystallization rates, even at 5 °C.min⁻¹.

The improvement in accuracy respecting the DSC measurements makes it possible to consider TREF technique enough consistent for analytical quantification and a successful means to characterize rHDPE samples, which makes TREF a great alternative for quality control of recycled polyolefins for subsequently incorporation into the virgin polymer feedstock with the aim of transitioning towards a Circular Economy of plastics.

CRediT authorship contribution statement

Rafael Juan: Investigation, Writing – original draft. **Beatriz Paredes:** Writing – review & editing. **Rafael A. García-Muñoz:** Supervision, Conceptualization, Writing – review & editing, Funding acquisition. **Carlos Domínguez:** Visualization, Conceptualization, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge the technical staff of the Polymer Technology Laboratory (LATEP) for the technical work and support. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- PlasticsEurope, Plastics - the facts 2020, 2020, <https://www.plasticseurope.org/es/resources/publications/4312-plastics-facts-2020>, 2021. (Accessed 12 January 2021).
- Ellen MacArthur Foundation, The new plastics economy: rethinking the future of plastics & catalysing action, 2020, <https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics-catalysing-action>, 2017. (Accessed 20 November 2019).
- European Union, A European strategy for plastics in a circular economy, 2019, <https://publications.europa.eu/s/kIT6>, 2018. (Accessed 28 September 2019).
- A. Rahimi, J.M. García, Chemical recycling of waste plastics for new materials production, *Nat. Rev. Chem.* 1 (2017) 46, <https://doi.org/10.1038/s41570-017-0046>.
- J.C. Worch, A.P. Dove, 100th anniversary of macromolecular science viewpoint: toward catalytic chemical recycling of waste (and future) plastics, *ACS Macro Lett.* 9 (2020) 1494–1506, <https://doi.org/10.1021/acsmacrolett.0c00582>.
- K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, *Waste Manag.* 69 (2017) 24–58, <https://doi.org/10.1016/j.wasman.2017.07.044>.
- J. Maris, S. Bourdon, J.-M. Brossard, L. Cauret, L. Fontaine, V. Montebault, Mechanical recycling: compatibilization of mixed thermoplastic wastes, *Polym. Degrad. Stabil.* 147 (2018) 245–266, <https://doi.org/10.1016/j.polydegradstab.2017.11.001>.
- I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste, *Angew. Chem. Int. Ed.* 59 (2020) 15402–15423, <https://doi.org/10.1002/anie.201915651>.
- H. Karan, C. Funk, M. Grabert, M. Oey, B. Hankamer, Green bioplastics as part of a circular bioeconomy, *Trends Plant Sci.* 24 (2019) 237–249, <https://doi.org/10.1016/j.tplants.2018.11.010>.
- K.W. Meereboer, M. Misra, A.K. Mohanty, Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites, *Green Chem.* 22 (2020) 5519–5558, <https://doi.org/10.1039/D0GC01647K>.
- Z.O.G. Schyns, M.P. Shaver, Mechanical recycling of packaging plastics: a review, *Macromol. Rapid Commun.* 42 (2021) 2000415, <https://doi.org/10.1002/marc.202000415>.
- M. Crippa, B. Wilde, R. Koopmans, J. Leyssens, M. Linder, J. Muncke, A.-C. Ritschkoff, K. V. Doorselaer, C. Velis, M. Wagner, in: *A Circular Economy for Plastics: Insights from Research and Innovation to Inform Policy and Funding Decisions*, 2019.
- R. Geyer, in: T.M. Letcher (Ed.), Chapter 2 - Production, Use, and Fate of Synthetic Polymers, Academic Press, 2020, pp. 13–32, <https://doi.org/10.1016/B978-0-12-817880-5.00002-5>.
- L.A. Utracki, *Commercial Polymer Blends*, Springer US, 1998, <https://doi.org/10.1007/978-1-4615-5789-0>.
- E. Karaagac, T. Koch, V.-M. Archodoulaki, The effect of PP contamination in recycled high-density polyethylene (rPE-HD) from post-consumer bottle waste and their compatibilization with olefin block copolymer (OBC), *Waste Manag.* 119 (2021) 285–294, <https://doi.org/10.1016/j.wasman.2020.10.011>.
- M. Gall, A. Schweighuber, W. Buchberger, R.W. Lang, Plastic bottle cap recycling—characterization of recycle composition and opportunities for design for circularity, *Sustain. Times* 12 (2020), <https://doi.org/10.3390/su122410378>.
- R. Greco, G. Mucciariello, G. Ragosta, E. Martuscelli, Properties of polyethylene-polypropylene blends, *J. Mater. Sci.* 15 (1980) 845–853, <https://doi.org/10.1007/BF00552093>.
- N. Kukaleva, G.P. Simon, E. Kosior, Binary and ternary blends of recycled high-density polyethylene containing polypropylenes, *Polym. Eng. Sci.* 43 (2003) 431–443, <https://doi.org/10.1002/pen.10035>.
- A. Van Belle, R. Demets, N. Mys, K. Van Kets, J. Dewulf, K. Van Geem, S. De Meester, K. Ragaert, Microstructural contributions of recycled polyolefins to the deformation mechanisms of their binary blends, *Polymja* 12 (2020), <https://doi.org/10.3390/polym12051171>.
- M. Gall, G. Steinbichler, R. Lang, Learnings about design from recycling by using post-consumer polypropylene as a core layer in a co-injection molded sandwich structure product, *Mater. Des.* 202 (2021) 109576, <https://doi.org/10.1016/j.matdes.2021.109576>.
- A. Adib, C. Domínguez, J. Rodríguez, C. Martín, R.A. García, The effect of microstructure on the slow crack growth resistance in polyethylene resins, *Polym. Eng. Sci.* 55 (2015) 1018–1023, <https://doi.org/10.1002/pen.23970>.
- R. Juan, C. Domínguez, N. Robledo, B. Paredes, R.A. García-Muñoz, Incorporation of recycled high-density polyethylene to polyethylene pipe grade resins to increase close-loop recycling and Underpin the circular economy, *J. Clean. Prod.* 276 (2020) 124081, <https://doi.org/10.1016/j.jclepro.2020.124081>.
- M. Messiha, A. Frank, T. Koch, F. Arbeiter, G. Pinter, Effect of polyethylene and polypropylene cross-contamination on slow crack growth resistance, *Int. J. Polym. Anal. Char.* 25 (2020) 649–666, <https://doi.org/10.1080/1023666X.2020.1833143>.
- E.G. Hanna, Recycling of waste mixed plastics blends (PE/PP), *J. Eng. Sci. Technol. Rev.* 12 (2019).
- A.A. Al-Juhani, M.A. Suleiman, Study of the effect of EPDM structure on the compatibility of PP/LDPE blends, *Arabian J. Sci. Eng.* 37 (2012) 863–875, <https://doi.org/10.1007/s13369-012-0231-4>.
- S. Vervoort, J. Den Doelder, E. Tocha, J. Genoyer, K.L. Walton, Y. Hu, J. Munro, K. Jeltsch, Compatibilization of polypropylene–polyethylene blends, *Polym. Eng. Sci.* 58 (2018) 460–465, <https://doi.org/10.1002/pen.24661>.
- Z.O.G. Schyns, M.P. Shaver, Mechanical recycling of packaging plastics: a review, *Macromol. Rapid Commun.* n/a, 2020, p. 2000415, <https://doi.org/10.1002/marc.202000415>.
- U. Riaz, S. Ashraf, Characterization of polymer blends with FTIR spectroscopy, in: *Charact. Polym. Blends Miscibility, Morphol. Interfaces*, 2014, pp. 625–678, <https://doi.org/10.1002/9783527645602.ch20>.

- [29] Å.G. Larsen, K. Olafsen, B. Alcock, Determining the PE fraction in recycled PP, *Polym. Test.* 96 (2021) 107058, <https://doi.org/10.1016/j.polymertesting.2021.107058>.
- [30] W. Camacho, S. Karlsson, NIR, DSC, and FTIR as quantitative methods for compositional analysis of blends of polymers obtained from recycled mixed plastic waste, *Polym. Eng. Sci.* 41 (2001) 1626–1635, <https://doi.org/10.1002/pen.10860>.
- [31] H. Pasch, R. Brüll, U. Wahner, B. Monrabal, Analysis of polyolefin blends by crystallization analysis fractionation, *Macromol. Mater. Eng.* 279 (2000) 46–51, [https://doi.org/10.1002/1439-2054\(20000601\)279:1<46::aid-mame46>3.0.co;2-1](https://doi.org/10.1002/1439-2054(20000601)279:1<46::aid-mame46>3.0.co;2-1).
- [32] C. Aumnate, N. Rudolph, M. Sarmadi, Recycling of polypropylene/polyethylene blends: effect of chain structure on the crystallization behaviors, *Polymers* 11 (2019) 1456, <https://doi.org/10.3390/polym11091456>.
- [33] A. Fernández, M.T. Expósito, B. Peña, R. Berger, J. Shu, R. Graf, H.W. Spiess, R. A. García-Muñoz, Molecular structure and local dynamic in impact polypropylene copolymers studied by preparative TREF, solid state NMR spectroscopy, and SFM microscopy, *Polymer* 61 (2015) 87–98, <https://doi.org/10.1016/j.polymer.2015.01.079>.
- [34] H. Pasch, M. Malik, Advanced separation techniques for polyolefins. <https://doi.org/10.1007/978-3-319-08632-3>, 2014.
- [35] S. Anantawaraskul, J.B.P. Soares, P.M. Wood-Adams, Effect of operation parameters on temperature rising elution fractionation and crystallization analysis fractionation, *J. Polym. Sci., Part B: Polym. Phys.* 41 (2003) 1762–1778, <https://doi.org/10.1002/polb.10537>.
- [36] B. Monrabal, Temperature rising elution fractionation and crystallization analysis fractionation, in: *Encycl. Anal. Chem.*, American Cancer Society, 2006, <https://doi.org/10.1002/9780470027318.a2035>.
- [37] C. Schick, Differential scanning calorimetry (DSC) of semicrystalline polymers, *Anal. Bioanal. Chem.* 395 (2009) 1589, <https://doi.org/10.1007/s00216-009-3169-y>.
- [38] J.D. Menczel, R.B. Prime, *Thermal Analysis of Polymers*, 2009.
- [39] Y. Kong, J.N. Hay, The measurement of the crystallinity of polymers by DSC, *Polymer* 43 (2002) 3873–3878, [https://doi.org/10.1016/s0032-3861\(02\)00235-5](https://doi.org/10.1016/s0032-3861(02)00235-5).
- [40] A. Manivannan, M. Seehra, Identification and quantification of polymers in waste plastics using differential scanning calorimetry, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 42 (1997).
- [41] Y. Kong, J.N. Hay, The enthalpy of fusion and degree of crystallinity of polymers as measured by DSC, *Eur. Polym. J.* 39 (2003) 1721–1727, [https://doi.org/10.1016/s0014-3057\(03\)00054-5](https://doi.org/10.1016/s0014-3057(03)00054-5).
- [42] B. Monrabal, P. del Hierro, Characterization of polypropylene–polyethylene blends by temperature rising elution and crystallization analysis fractionation, *Anal. Bioanal. Chem.* 399 (2011) 1557–1561, <https://doi.org/10.1007/s00216-010-4061-5>.
- [43] S. Anantawaraskul, J.B.P. Soares, P.M. Wood-Adams, Fractionation of semicrystalline polymers by crystallization analysis fractionation and temperature rising elution fractionation, in: *Polym. Anal. Polym. Theory*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, pp. 1–54, <https://doi.org/10.1007/b135559>.
- [44] R.A. García, B. Coto, M.-T. Expósito, I. Suarez, A. Fernández-Fernández, S. Caveda, Molecular characterization of polypropylene heterophasic copolymers by fractionation techniques, *Macromol. Res.* 19 (2011) 778–788, <https://doi.org/10.1007/s13233-011-0811-2>.
- [45] H. Pasch, Recent developments in polyolefin characterization, *Macromol. Symp.* 165 (2001) 91–98, [https://doi.org/10.1002/1521-3900\(200103\)165:1<91::aid-masy91>3.0.co;2-2](https://doi.org/10.1002/1521-3900(200103)165:1<91::aid-masy91>3.0.co;2-2).
- [46] R. Brüll, V. Grumel, H. Pasch, H.G. Raubenheimer, R. Sanderson, U.M. Wahner, Analysis of polyolefin blends by CRYSTAF, *Macromol. Symp.* 178 (2002) 81–92, [https://doi.org/10.1002/1521-3900\(200202\)178:1<81::aid-masy81>3.0.co;2-z](https://doi.org/10.1002/1521-3900(200202)178:1<81::aid-masy81>3.0.co;2-z).
- [47] E.C. Kelusky, C.T. Elston, R.E. Murray, Characterizing polyethylene-based blends with temperature rising elution fractionation (TREF) techniques, *Polym. Eng. Sci.* 27 (1987) 1562–1571, <https://doi.org/10.1002/pen.760272011>.