A differential scanning calorimetry (DSC) approach for assessing the quality of polyethylene terephthalate (PET) waste for physical recycling: a proof-of-concept study

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Abstract

Physical recycling of plastics is among the most important approaches of circular economy. The efficiency of the recycling is influenced by many factors including the number of recycling cycles, composition of plastics, chemical modifications, additives and others. Currently, however, there are no methods enabling to distinguish the quality of plastics for recycling. In this work, we address this issue and suggest a new method based on the correlation of solely thermophysical properties of polyethylene terephthalate (PET) waste obtained using differential scanning calorimetry (DSC) during repeated heating and cooling. The combination of results of differential scanning calorimetry and advanced statistical methods enabled to separate 76 PET samples into six groups according to their origin, chemical modification, degradation and suitability for recycling. The discriminant analysis enabled to suggest a model which uses for the discrimination a combination of temperatures and enthalpies of melting and crystallization. The approach illustrates that thermophysical properties, which can be obtained using a single DSC experiment, can be used to distinguish the polymers of various origin and quality.

Keywords Polyethylene terephthalate · PET · PET-G · DSC · Recycling · Model

Introduction

Polymers found their application in industry, agriculture, science and daily products due to their resistance and durability, low production costs, easy manufacturing and adaptation to the required product. An important application is food packaging, which accounts for 41% of the plastic production in OECD countries [1]. Among the most used polymers is polyethylene terephthalate (PET), which is the main packaging component of soft drinks, water, milk, beer, as well as detergents and other substances used for technical purposes. Importantly, PET packaging is usually classified as disposable waste materials, i.e. for single use only [3–5].

In OECD countries, the amount of plastic produced annually per person is around 69 kg. Out of that, in EU countries, PET represents around 8.4% of this waste [1]. Such a considerable amount of PET waste demands a wide range of suitable approaches for its further processing or reuse. Different types of chemical and mechanical recycling are currently applied. For PET, physical (or mechanical) recycling appeared as an ideal economical solution with a low environmental burden. Yet, however, there are still several limitations of this approach [6–8].

Physical recycling of polymers is among the most prominent and important strategies of circular economy. For this reason, it has been implemented into EU legislation, which stipulates the maximum allowed content of recycled polymers in new products. For PET, this limit is planned to be 25% [9–12].

The methods of physical recycling of PET are relatively simple, they include separation of waste plastics, shredding and washing (mostly bottles to flakes). The resulting PET materials (PET flakes) are then extruded and regranulated into recycled PET (rPET) regranulates [3]. The main disadvantage of physical recycling is the deterioration of product properties and quality in each recycling cycle. In

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addition, the products made of physically recycled PET may not always be appropriate to produce food-contact materials. This is caused by the composition of PET waste that includes different types of PET containing various additives and also potentially toxic/unsuitable substances [7, 13–15]. The PET waste includes products such as recycled PET, bottles with additives, preforms, regranulates or virgin PET, but also other PET products such as food containers, fibres, straps and other. Therefore, the key problem for successful recycling and regranulation is distinguishing the PET quality, which reflects the PET history and chemistry. Each of the PET waste types may have different chemical and physicochemical properties that affect their suitability for the recycling process.

State-of-the-art sorting devices separate PET from other plastics with more than 99% efficiency [15, 16], but it does not sort PET materials according to their aforementioned quality (e.g. distinguishing PET from bottles and from trays which have different properties). This is an important issue as the recycled PET for food applications (food grade) should not contain more than 5% of PET originating from the packaging of household chemicals [13]. Therefore, there is a need for a methodology that helps to separate the PET waste of different quality to fulfil these criteria.

In particular, PET bottles are not always made of virgin PET. As a result, PET flakes originating from the multiple or repeatedly recycled PET are known for "greying" caused by admixtures of other plastics during the regranulation [17–19]. Therefore, the critical point is to identify the types of recycled PET and estimate at what stage of the recycling process they currently are in order to choose the best recycling method for each PET fraction [20]. However, those methods are currently missing.

Another challenge is related to method inaccuracy to anticipate the PET degradation during recycling. In fact, most studies reported solely the deterioration of PET sample after repeated extrusion [21–26]. It was suggested that thermo-mechanical treatment influences negatively properties by changing the PET microstructure [24]. Other studies have reported that deteriorating quality of degraded PET can be used for some applications, due to its easy crystallization and processing [22, 23].

The industrial regranulation process includes a number of purification and polymerization steps which can deteriorate or improve the quality of the final product. The processing of certain types of PET waste requires specific recycling technology. Thus, it is necessary to assess prior to recycling which products are already too degraded to be recycled and which can still undergo the physical recycling. Similarly, as with other semi-crystalline polymers, the physical and mechanical properties of PET depend on its microstructure and are therefore determined by crystallization rate, the degree and quality of crystallinity [22, 27]. Correlations

between the molecular weight distribution, type and ratio of comonomers on the morphology and thermophysical parameters of PET crystals and crystallization kinetics are well establish and were published in many studies [28–30] It has been confirmed that temperature, strain rate, elongation and molecular weight are the most important variables, which alter the final mechanical and physical properties of PET [31].

PET is a semicrystalline material, having crystalline regions dispersed into an amorphous phase. PET properties and used feedstock are reflected in fundamental thermophysical parameters such as glass transition, crystallization and melting enthalpy, which can be easily determined using differential scanning calorimetry (DSC) [19, 32–34]. The combination of these properties can also be used for chemical identification purposes [35].

In this proof-of-concept study, we present a DSC-based method useful for identification of PET suitability for recycling. The method is based on the working hypothesis that the thermophysical parameters and their combination are unique for specific groups of PET and may therefore be used for PET identification. The method uses simple parameters obtained from DSC runs such as temperatures and enthalpies of melting, crystallization, and glass transitions of the first, second heating and cooling cycles. The parameters are used as primary parameters for simple and advanced statistical analyses, which allow to distinguish the samples into groups according to their history and properties. This is a base to design a simple and relatively quick method for identification of unknown PET samples. Because the entire cycle of re-use of PET is quite complex (re-granulation, different levels of contamination, etc.), we would also like to answer the question, whether only repeated regranulation can be a suitable method for simulating the whole recycling process of PET.

Experimental

Methods

Thermal properties of PET were analysed using a DSC TA Instruments DSC 2500 equipped with a RCS90 module. Approximately 10 mg of sample was weighed into an open pan (Tzero Aluminium) and transferred to the DSC instrument. The measurement was performed under a 50 mL min^{-1} nitrogen flow (5.0 grade). The following temperature programme was used: heating at 5 K min^{-1} to 320 °C, cooling to 0 °C at 5 K min^{-1}, heating at 5 K min^{-1} to 320 °C and cooling again to 0 °C at 5 K min^{-1}.

The obtained records were evaluated using TRIOS software (TA Instruments). The analysed parameters included glass transition (parameters: temperature, change and delta

Cp) and melting temperature (parameters: temperature, enthalpy and onset) for first and second heating, from the cooling run was extracted the crystallization point (parameters: temperature, enthalpy and onset). In total 18 parameters were obtained and used for further evaluation.

Statistical evaluation of DSC parameters

In a first step, glass transition, melting temperature and enthalpy were used for correlation analysis using linear regression in Microsoft Excel®. In a second step, all parameters of cooling, first and second heating were analysed by principal component analysis (PCA) and hierarchical cluster analysis (HCA) using STATISTICA version 13.3.0. For a better distribution of the samples, the preservation of the distance between the points was used, as we analysed the same type of samples that differed only in some parameters [36].

For HCA, Ward's method was used with Euclidean distance (i.e. the square root of the sum of the square differences). In general, clustering methods use different metrics to determine the distance between vectors, and Ward's method uses a combination of all vectors of the considered sets as well as representative vectors [36].

Analysed samples

Samples for a preliminary study

To test our hypothesis, we used the DSC parameters of 14 PET samples from the PET physical recycling loop. Samples were divided into 7 groups depending on degree of recycling and origin (Figure S1). As a control sample, virgin PET from one of the manufacturers (PET_1) is considered here as Group 1. Other samples can be divided into following units: Group 2 includes PET_2, 3, 4 and 5. Thus, a preform and PET bottles of different composition (30% bioPET) or utilization (food grade/non-food grade). Group 3 contains two samples, PET_6 and 7. PET_6 is recyclate from physical recycling by wet route. PET_7 is a recycled product that has a significant change in colour, i.e. greying. It is assumed that greying was caused by degradation caused by repeated recycling (multiple physical recycling). Group 4 contains the direct products from the recyclate PET_6, i.e. PET_8 and 9 (fibre and binding tape, respectively). They were included here for studying how their specific use affects their thermophysical properties. Group 5 comprises of regranulates made from recyclate PET_6. The samples are produced with different technologies and with varying purity of the final product (food grade/non-food grade). Group 6 is the PET samples from food containers (PET_12 and 13) because they are food grade, it is assumed that they are made of regranulates.

Samples for model development

For the development of the model, we used 76 PET samples (the set included the samples from preliminary study). Samples differed in the types of PET according to their commercial and domestic uses or according to materials of different origin and recycling degree. Selected samples cover the largest possible area of the recycling cycle and as many different types of PET as possible (Table 1).

Samples, in general, fall into 4 groups.

(1) Virgin PET, preforms, PET-G and products from PET and rPET
(2) PET regranulate and degraded samples (virgin, flakes and regranulates)
(3) PET bottles (bottles from virgin PET, with additives and with a certain amount of rPET and/or bioPET)
(4) PET flakes (pure, modified, dry recycling)

PET standard: In the industry, there is no universal PET standard used. Available materials vary according to the method of production and specific requirements for the final product. Therefore, one virgin sample was used as a standard, i.e. control sample. Preforms for PET bottles come from different manufacturers and differ especially in colour (clear, green, blue, red, silver and white). As a standard for PET-G 2 products for 3D printing (filaments) were used (Sigma-Aldrich, Gembird). PET products category consists of two groups. In the first group are products made of PET flakes for non-food use (fibre and binding tape). In the second group are food containers (trays for fruits and vegetables). Regranulates were made of PET flakes from sample PET_6. They were produced with different technologies and with varying purity of the final product (food grade/non-food grade). PET bottles consists of 3 groups. According to their composition were analysed bottles made entirely of virgin PET, bottles containing additives, bottles containing a certain amount of recycled material, i.e. rPET and PET made from natural sources (bioPET). PET flakes are products of mechanical recycling and fall into 3 groups: PET flakes, manipulated PET flakes, and PET from dry recycling (they were only crushed without washing).

Samples for degradation study

For degradation, 5 different samples of PET were studied— virgin (PET_1), flakes (PET_6) and regranulates (PET_10, 11 and 14). Samples underwent controlled degradation at 200 °C for 25, 35 and 45 h (Figure S2) in a laboratory oven. In this study, they are labelled as follows: PET original sample_heating time. For example, PET_1_35 comes from a PET_1 sample that has been exposed to 200 °C for 35 h

Table 1 Groups of samples PET

Groups		Amount	Samples	Description
1. aPET	Pure PET	2	PET_1, 15	Virgin material
	PET preforms	11	PET_2, 34–43	Preforms and crushed preforms from PET bottles of various colours
	PET-G	2	PET_47, 48	Samples used as three-dimensional ink printers declared as "PET-G"
	PET product	2 + 2	PET_8, 9	Products from recycled PET other that bottles
			PET_12,13	Food container and PET-G food container
2. rPET	PET regranulate	3	PET_10, 11, 14	Regranulated PET for food and non-food purposes
	PET degraded	15	PET_1_25-14_45	Samples PET_1, 6, 10, 11, 14, exposed to controlled degradation
3. PET bottles	PET bottles	6	PET_3,4, 49,50, B_13,14	PET bottles from virgin material
	PET with additives	12	B_1-B12	Bottles confirmed by other analysis for the presence of additives
	PET bottles—100% recycled	6 + 1	PET_19-25	Bottles declared as "100% from recycled material", refill bottle
	PET bottles—% bio, recycled	4	PET_5,16–18	Bottles declared as "to contain a certain percentage of bioPET and/or rPET"
4. PET flakes	PET flakes	5	PET_6,7,31–33	PET recycled from bottles
	PET flakes modified	3	PET_28-30	PET flakes for which manipulation was confirmed by another analysis
	PET flakes dry recycling	2	PET_26,27	Dry recycling (only crushed)

or PET_10 25 stands for the sample PET_10 exposed for 25 min to 200 °C.

FTIR analysis

FTIR analysis was conducted in order to test some of hypotheses suggested in the text further below. Bruker ALPHA spectrometer with ATR module with a diamond crystal was used, the resolution was set to 4 cm^{-1}, and number of repetitions to get better S/N ratio was 128. The OPUS software was used to analyse the data.

Results and discussion

DSC records

The exemplary DSC record of sample PET_1 is reported in Fig. 1. In particular, first heating run in a DSC record reflects the PET thermal history (blue curve). The subsequent cooling run indicates the PET physical parameters with erased thermal history. The cooling process was investigated especially because in industrial processing the crystallization quantities are an important parameter directly defining further use (green and dark red curve). The second heating run provides parameters of PET with erased thermal history. The second heating run is thus defined by controlled conditions and more indicative for the morphological properties of the

sample (red curve). As it can be seen the erasing thermal history shifted slightly some of the measured parameters, i.e. melting enthalpy from 33.4 to 29.4 J g^{-1}.

Within the measurement, sample PET_47 (PET-G) showed exceptional behaviour as it had only a glass transition while melting observed in Fig. 1 was missing (Fig. 2). This observation is discussed further below.

Preliminary study

In the preliminary study, we examined 14 samples from different stages of the PET recycling loop. The first task was to determine whether the parameters of DSC record are indicative for different origin of the PET samples. As an exemplary, Fig. 3 compares the crystallization of samples from 3 groups, first PET_7, second PET_1 and 14, and third — PET_8. The records differ in peak temperatures, enthalpy of crystallization and onset temperatures. As it can be seen from Fig. 3, these groups differ in peak temperature by 20 °C (first and second) and 10 °C (second and third). In terms of enthalpy, the observed different values between the groups are approximately 5 J g^{-1}. The onset of the first group is approximately at 140 °C, for the second beginning can be observed the around 150 °C and for the third, up to 185 °C. Therefore, a simple comparison of DSC records can be used to identify some differences between groups of samples. The differences were evident also for other phase transitions.

Fig. 1 DSC record of sample with establish parameters. Down lines: blue—first heating, red—second heating. Up lines: green—first cooling, dark red—second cooling. (Color figure online)
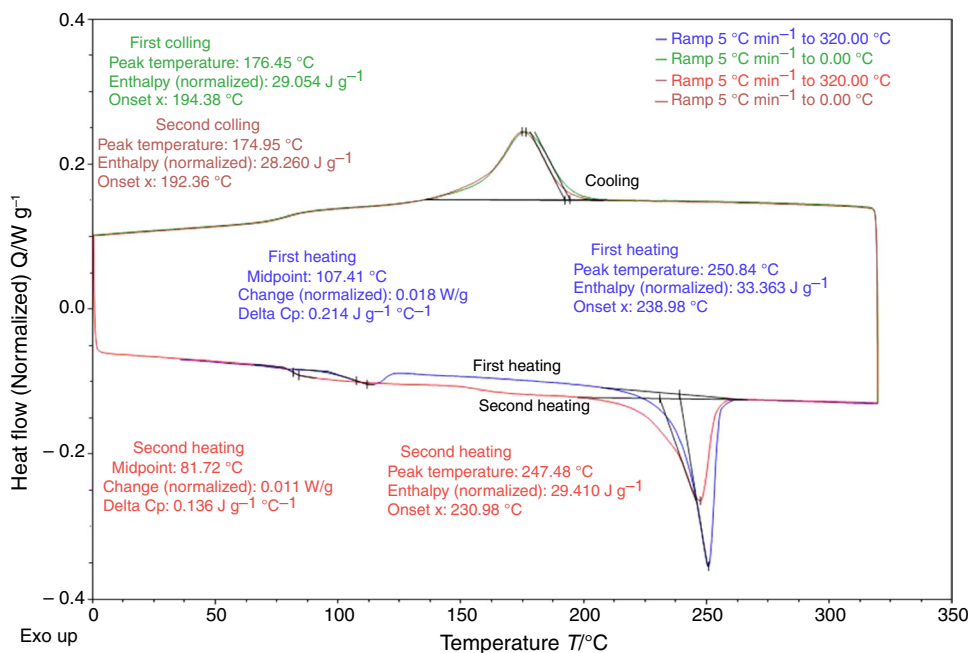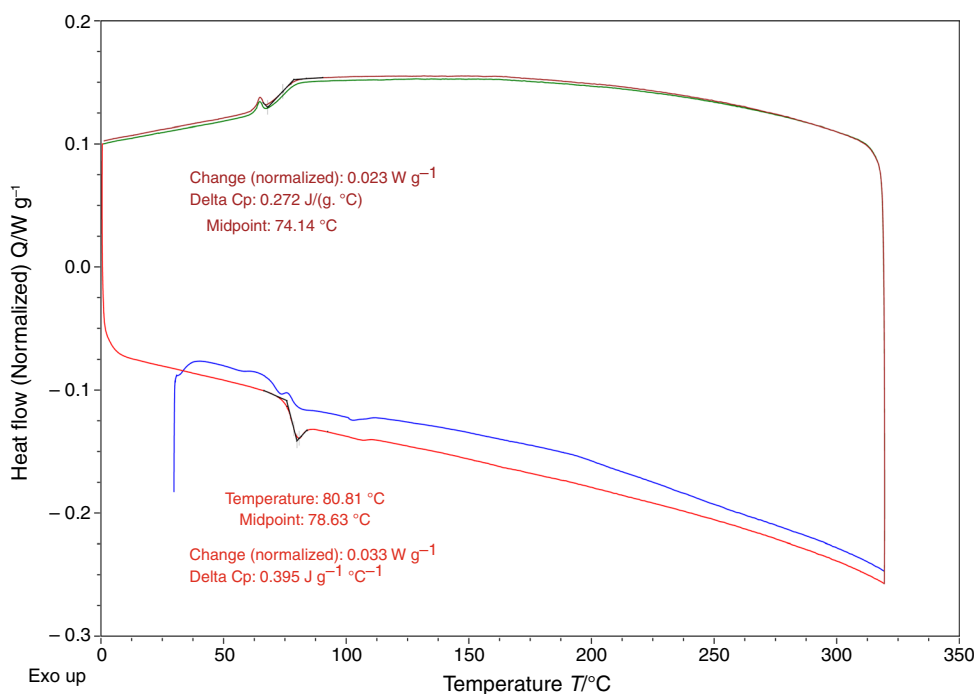

Fig. 2 DSC record of PET_47 (PET-G)

Correlation between obtained parameters

After determining the physicochemical parameters, their mutual relationships were investigated by linear regression. Exemplary results are reported in Fig. 4 which shows linear correlation between enthalpy of crystallization and its temperature T_{peak}. The correlation shows that the samples can be divided into 3 groups, i.e. first—bottles and flakes (PET_2-7), second—virgin, container and

regranulates (PET_1, 11–14), and third—PET products (PET_8 and 9).

When using parameters of second heating (enthalpy and T_{peak} of melting) it is also possible to divide the samples into to the groups to which they belong (Figure S3). As it can be observed, virgin PET is easily identifiable due to its position in the graph. The position of PET_13 can be explained by its properties, which are different from all the others (food container from PETG). This is also confirmed

Fig. 3 An example of DSC record of PET cooling with marked crystallization parameters (samples from 3 groups—first—PET_7, second—PET_1 and 14, and third—PET_8)
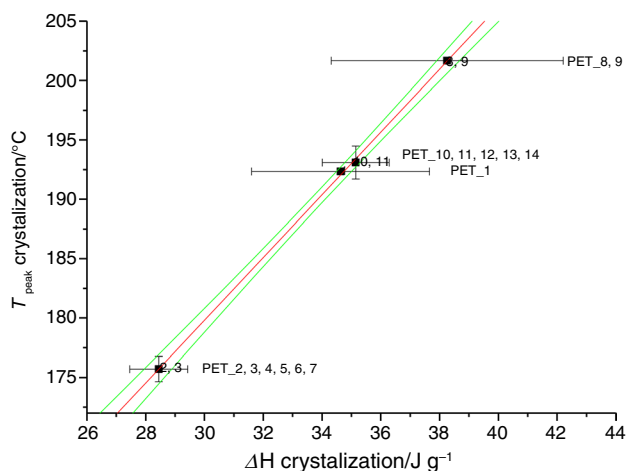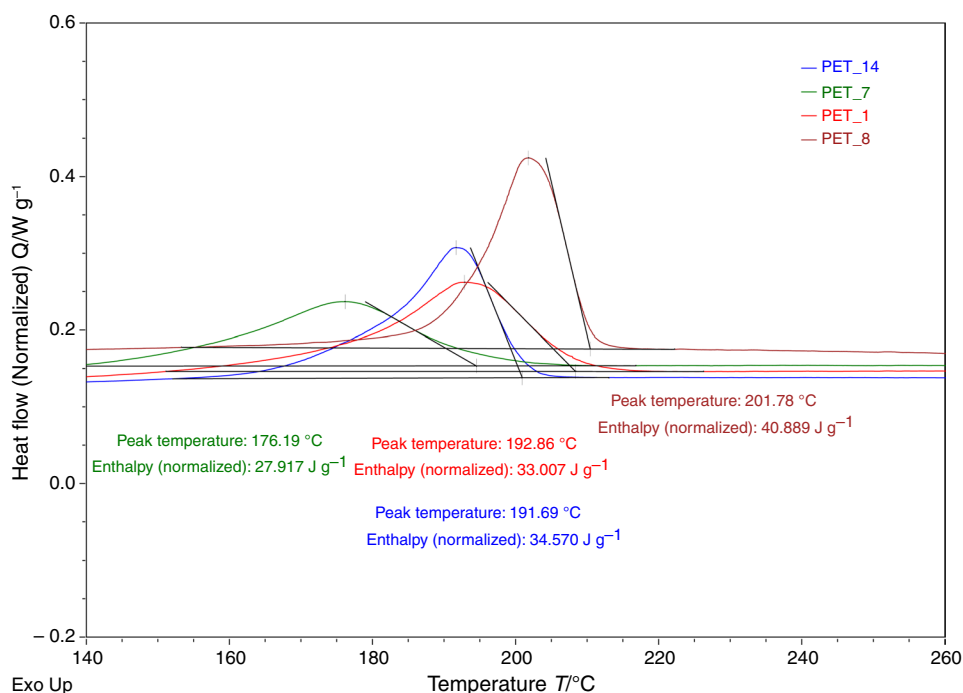

Fig. 4 Correlation between enthalpy of crystallization and its T_{peak} (divided into 3 groups—first—bottles and flakes (PET_2–7), second—virgin, container and regranulates (PET_1, 11–14), and third—PET products (PET_8 and 9)

by Group 4—PET products. For groups 2, 3 and 5, 6, it can be observed a shift in the properties due to the process in the recycling cycle (Figure S1).

The correlation between various physicochemical parameters of polymers and the influence of external factors on those parameters are already known [37]. For example, the thermophysical properties of the PET crystals depend on the intrinsic PET properties such as molecular weight and its distribution, type and ratio of the comonomers and PET history which includes cooling rate, pressure, crystallization

temperature, nucleating agents and others [37]. This supports our primary working hypothesis that the properties are interrelated, which can be used for PET identification.

The preliminary results reported here suggest that the correlation of only two parameters can already help to distinguish some samples in different stages of recycling loop. For this purpose, parameters such as specific heat capacity, enthalpy of melting and melting temperature were found of particular applicability. However, the approach is not sensitive enough to clearly discriminate each PET group, e.g. groups 2 from 3 or 5 from 6. Therefore, more complex approach combining the correlations of large number parameters is needed.

PCA results

To obtain a more sensitive model, all the thermophysical parameters were treated using PCA. The individual thermophysical PET properties extracted from DSC record were used as primary parameters for the analysis. Figure 5 shows PCA projection and the first component explains 58.58% of the variation, and the second component 26.01%. Importantly, PCA requires independent variables, but as it can be seen in the text, although some DSC parameters correlate, they are not dependent on each other.

Figure 5 reports the results of PCA. Groups 1–6 can be distinguished from each other by using all the measured parameters of the first, second heating and cooling. PET_1 differs significantly and is located in a single quadrant
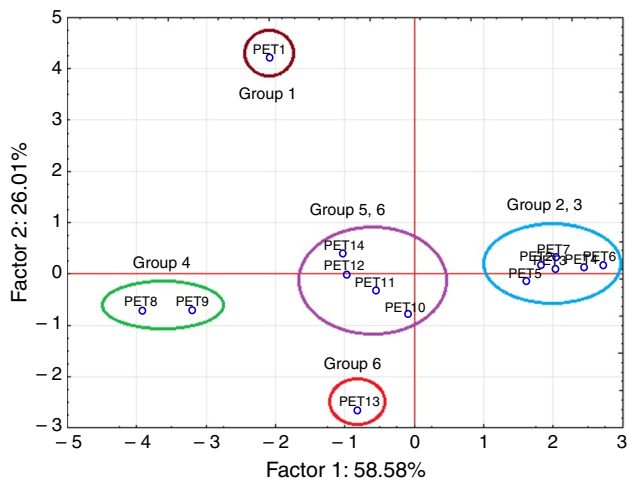
Fig. 5 PCA analysis of groups 1–6. Parameters from the first, second heating and cooling

(upper, left), which we attributed to its purity (the absence of additives, fillers, pigments, etc.)

Group 2 and 3 (PET bottles and recycled flakes) are located in the upper right quadrant. Group 4 (PET products, non-food) is placed on the left downside of the projection. Group 5 and 6 (regranulates and products) are in the middle. Their parallel position with the groups 2, 3 and 4 confirms that the recycled materials show different DSC properties comparing to virgin material. Also, the specific treatment of the material shows different DSC properties which is directly displayed at the position in the PCA.

PET_13, a food container from PET-G, which is generally perceived in the industry as unsuitable for recycling together with PET bottles, can be easily distinguished from other samples due to its position. This confirms that PET-G has significantly different properties than the other PET samples.

Model development

Principal component analysis (PCA)

The verification of the concept showed that PCA represents as suitable method to separate the PET samples based on the combination of their thermophysical properties. For this reason, the number of samples was increased to a total of 76 samples of different types of PET. The samples were selected to cover all types of PET on the market and in the recycling loop (Table 1).

PCA results for those 76 samples are reported in Fig. 6. For better orientation, individual quadrants were named A, B, C and D. The individual groups were also marked to indicate where are located the samples belonging to individual groups. At the first sight, it is clear that PCA visualization sorted specific groups to various quadrants.

Virgin material is projected into quadrant A. It is easily distinguishable material from others. Degraded samples, food containers and bottles with additives can be observed in the B quadrant and partially also in A quadrant. Those are materials with high degree of influence of processing, either due to the high temperature or due to the addition of other substances. Quadrant C contains rPET, bioPET and PET-G

Fig. 6 PCA of all 76 samples marked according on which groups are belonging
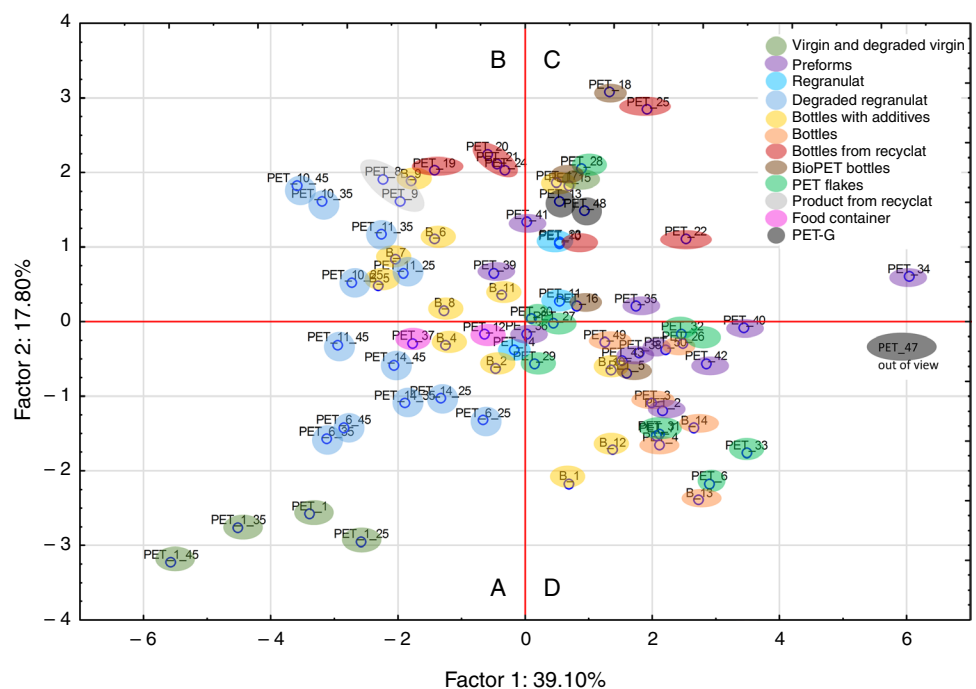
products. Therefore, in this quadrant are projected products from chemically modified or chemically different PETs. Quadrant D contains preforms, bottles and flakes and thus can be assigned to the PET bottle production and recycling process. Therefore, the PCA showed a potential to separate the PET materials based on their origin and properties, and however, several groups are still overlapping. Therefore, it was necessary to employ an additional approach.

Hierarchical cluster analysis (HCA)

In addition to PCA, HCA (Fig. 7) was used to separate better those sample close to each other in PCA projection. For better orientation, the individual branches of the tree diagram were highlighted with dividing lines and marked with letters and numbers (A1–A6, B1–B5). At the first sight, there are differences between the samples due to the distance they take.

In line A can be found virgin as first alone, degraded material (A1 and A2), regranulate (A2 and A4) and recycled bottles (A3 and A6) together with products (A3). Bottles with additives belong mostly in A4 and A6. Line B contains bottles, flakes and preforms mixed in different groups. PET-G can be found alone in B5.

Discussion on statistical results

Comparison of results of PCA and HCA

In PCA results (Fig. 6), the virgin PET dominates the quadrant A, even in its degraded form. The HCA results (Fig. 7) confirmed that the degraded PET_1 is most similar

to the original PET_1 (section A1). As aforementioned, there is no virgin PET standard in the industry, the available materials vary according to the method of production and specific requirements for the final product. Nevertheless, all the virgin PET materials fall into quadrant A and can be considered as the highest quality PETs.

Using PCA, most PET preforms belong to quadrant D. However, the differences can be seen in samples PET_38, 39 and 41. That is the preforms white, silver and dark green. Their position overlaps with the regranulates, which suggests that they are at least partially made of rPET. This would also confirm their distinctive coloration, which is a commonly used technique to cover highly degraded material that acquires a grey colour or mask yellowing [19, 38]. Therefore, most likely they are made of recycled materials with significant addition of additives to achieve the desired colour. This hypothesis is supported by the HCA. In fact, within the HCA, most samples of preforms belong to sections B3 and B4. PET_41 (dark green) even belongs to section A6—samples with partial content of rPET/bioPET. PET_39 (silver) belongs to section A4—with additives.

In quadrant A (Fig. 6) can also be observed the rPET food container (PET_12) and the crumb from the rPET food container (PET_37). However, as we attributed quadrant A to a PET with the highest quality, this may put into question if the rPET was really used in those products. Nevertheless, in PCA projection are these materials close to the regranulates, which confirms that the recycling processes (including the addition of suitable substances and treatment of the recycled polymer) can increase the quality of PET for further processing [39–41]. This is in accordance with the HCA, because PET_12 is located in section

Fig. 7 The dendrogram of HCA of all samples (Ward´s method, Euclidean distances)
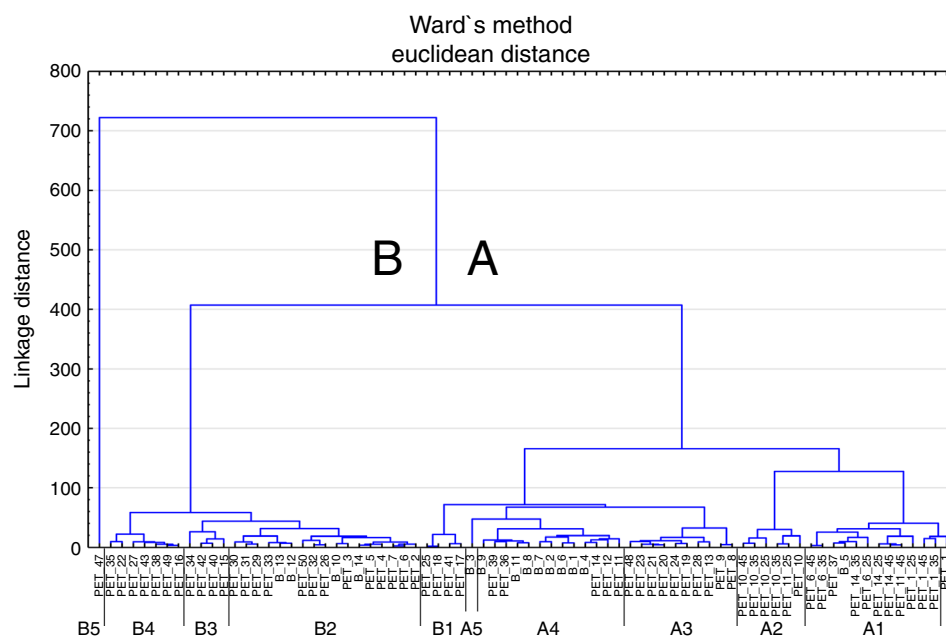
A4, right next to the regranulate and PET_37 is even in section A1.

Products for non-food use are in quadrant B (Fig. 6). In the HCA they are located in section A3, which corresponds to rPET. They are represented by products made of lower rPET quality, i.e. contaminated PET, which influences the DSC results. In addition, this PET is often modified by addition of additives to achieve better performance and/or desired properties. Therefore, these are materials from the downcycling process.

Most PET flakes and PET bottles are in quadrant D. This suggests that wet recycling (without regranulation, i.e. extrusion process (crushing and hot washing) has no significant effect on the thermophysical properties of the samples. Samples in quadrant D may thus be classified as suitable for recycling. Within the HCA, most samples belong to sections B1 and B2. There are only two differences: PET_27 belongs to section B4 (materials with dyes), and PET_28 belongs to section A3 together with recycled bottles. Sample PET_28 should be with manipulated samples. However, as it appears from the shift towards quadrant D, it may also contain modified PET. The samples PET_27, 29 and 30 are shifted to the left from the others. These samples were suspected of being previously manipulated, i.e. these samples were heated to make contaminants more visible, which is a common approach in industry laboratories [42]. Based on this practice, contaminants could be removed, and the quality of the sample could be artificially improved. If we consider the shift to quadrant B as an indicator of controlled degradation (see the discussion further below) the probability of sample manipulation is very likely. A complementary FTIR-ATR analysis confirmed our assumption about the manipulation with the samples, because their spectra show characteristic peaks in area 1600–1515 cm^{-1} (Figure S4) which correspond to degraded material PET_625. Importantly, these peaks are characteristic of degraded materials and did not occur in FTIR records of any other group of samples. These findings are very useful when evaluating the samples from various suppliers, because this manipulation can lead to the acceptance of poorer quality material from physical recycling than what is determined in the sample.

The regranulates are in the centre of the PCA diagram (Fig. 6). PET_14 is the only sample projected in the quadrant A. The closest to its position is the food container, preform and PET flakes. This may reflect the use of specific food technology, which improves properties of material and eliminates the effects of recycling. However, between PET_14 and PET_1 (virgin), are all its degraded samples. This could indicate that regranulation can result in high product quality (food container, preform), but certain degradation processes still occur. PET_10 (non-food technology) and PET_11 (food technology) showed a higher effect of material structure because they are located in quadrant C,

which is dominant for rPET. But still PET_11 is closer in its properties to PET flakes and bioPET bottle, thus has higher quality. On the contrary PET_10 coincides with position of PET_23—recycled bottle, thus has lower quality. This corresponds to the type of technology of their production and the intended use.

In the HCA, PET_10 on the contrary to PCA is in section A2 along with its degraded samples. This may correspond to a significant shift of its degraded samples to quadrant B. In contrast, PET_11 and 14 are in section A4 together with PET_12 (food container) and bottles with blockers, which can also be seen in PCA analysis and indicate applications for food use.

Controlled degradation of PET

As it can be seen in PCA (Fig. 6), controlled degraded samples are located in quadrants A and B. According to results of HCA (Fig. 7), all degraded samples are in section A1. The only exception is PET_10 and its degradation products, all of which are located in section A2.

In PCA projection, the original regranulation samples and PET flakes are all located more on the middle-left side. In the case of controlled degradation (Fig. 8), there is a shift to the right in all samples (indicated by arrows).

All samples of controlled degradation show the same shift regardless whether they are PET flakes, regranulates for food or non-food use. Samples PET_1 and PET_14 show only a small shift, which could indicate their stability. The only deviation is evident for PET_1 with shorter degradation time (PET_1_25). This can be explained by the decreasing effect of stabilizers, which effect can be reduced after a longer period of time [43, 44]. Conversely, PET_6 and PET_10 were shifted significantly. The flakes have a larger surface area than the pellets, so they have been subjected to more intensive surface thermal degradation. For PET_10, this implies that the process for non-food use shows a higher rate of degradation (or less chain repair) than for food contact.

In summary, these changes suggest that shift does not depend entirely on the processing method but also on the structural changes in the polymer itself. That implies that samples exposed to higher temperatures for a longer time do not necessarily only degrade, but they may also remediate in some way (location in A quadrant). However, the structural changes are undeniable (Figure S5), and it is only a question of interpreting whether these changes are the result of degradation or only structural changes in the polymer.

Our results also indicate that there is a significant difference between samples that are degraded under controlled conditions or "naturally", i.e. via ageing. PET degraded under controlled conditions can be found mostly in the middle between quadrate A and B. In contrast, recycled products and rPET bottles are located around the line between

Fig. 8 Shift of controlled degradation samples (indicated by arrows)
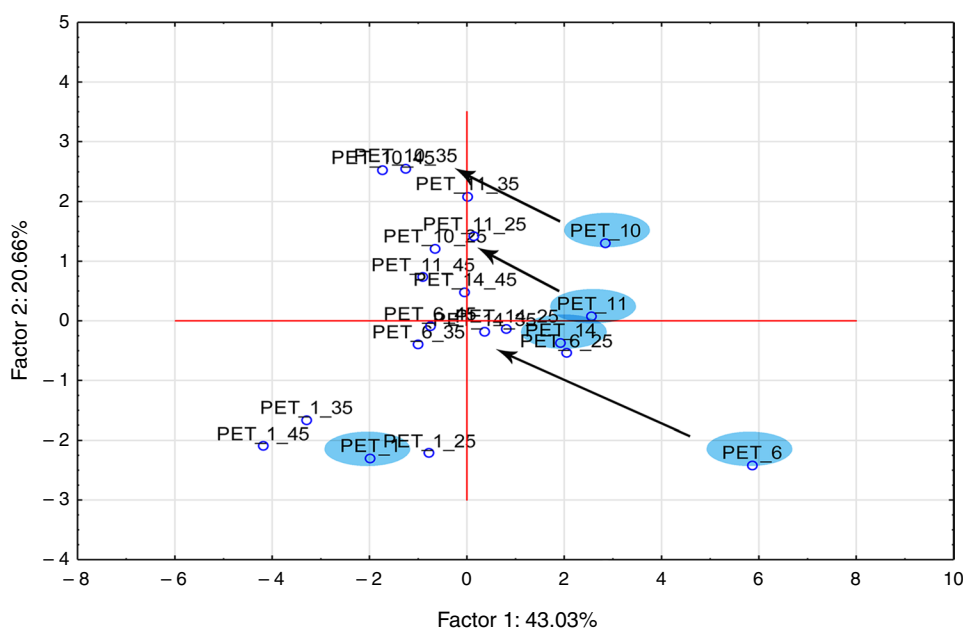
quadrant B and C. This is also confirmed by results of HCA, where controlled degraded samples are in section A1 and A2, while naturally degraded samples are mostly in section A3. We attribute these differences to the different treatment of the samples. During natural degradation, PET is exposed to all recycling steps. In particular, the purity of the material plays a key role in the process, and there is no sorting system that guarantees 100% purity of PET. Thus, new contaminants are added in each cycle. In the regranulation phase, additives can be added to improve the properties (either colour or structure) [45]. In addition, the concentration of antimony (used as catalyser during PET production) and other substances in PET increases during recycling. The volume of PET decreases due to the remelting process, while the amount of antimony and other substances remains, and their content may increase in each recycling cycle [46–48].

As mentioned before, most PET degradation studies use repeated extrusion to model degradation in which they still use the same sample. This eliminates the contamination from other PET waste and the processes associated with production and recycling. Thus, the phenomena described in natural degradation process do not occur during repeated extrusion.

Our results, therefore, indicate differences between controlled and natural degradation of samples. Controlled degradation gives only partial answers to the process of PET degradation, especially in the field of the environment and the issue of microplastics caused by defragmentation and partial degradation of PET. In order to identify the processes contributing to the degradation of PET, it is necessary to focus on the natural degradation, which occurs not only during extrusion, but also in the entire recycling process from

PET production to its reuse. It is, thus, not possible to fully mimic the natural degradation of the material under laboratory conditions. This difference is potentially a key to a better understanding of degradation processes and how to influence them in a desired way.

Also, according to EN 15343:2007: "At present, there are no reliable technologies for the analytical determination of the content of recycled material in the material or product. Therefore, traceability information will be needed to calculate the content of recycled material both recycled and primary material".[49] In practice, this means that the use of various types of PET (rPET/bioPET) is stated by the manufacturer of packaging material, but there is no method to confirm or disprove the statement.

As our results indicate, there is a large grey area in the use of rPET in PET bottles because although the use of rPET has been declared, its content in some of the bottle samples is disputable. EU legislation does not yet provide a suitable tool to verify their use outside of declarations of use. Therefore, we would like to point out the need to develop a robust method for identifying the different chemical composition of bottles. We conclude that DSC has a great potential.

Moreover, there is currently no reliable method for recognizing and sorting such bottles from the recycling process. Therefore, it is necessary to find a way to identify them and exclude them from the recycling stream. We believe that the method presented here may help to prove that these bottles can be identified from others suitable for recycling. However, DSC is still a relatively time-consuming method and unusable in industry if it is necessary to analyse every waste PET bottle. Further research and development of a faster method is therefore needed. Needless to say that similar

approaches based on the combination of thermoanalytical methods with chemometrics have already been published and proved to be important tool for identification of various substrates, i.e. [50, 50].

Discriminant function

The discriminant analysis is a suitable tool for deriving optimal combinations of variables to differentiate main groups of XY. The discriminant analysis was used to find such values of the coefficients that the distance between the mean values of DF is maximum for the two groups and these coefficients were used to derive the discriminant function equation (DF).

The obtained discriminant function equations from DSC results are follows. The following abbreviations were used to shorten the notation: $T_{\text{peak melting}} = T_{\text{pm}}$, $T_{\text{peak crystallization}} = T_{\text{pc}}$, $T_{\text{onset crystallization}} = T_{\text{oc}}$, $T_{\text{onset melting}} = T_{\text{om}}$.

$$DF1 = -56.003 - 0.0819\left(T_{\text{pm}}\right) + 0.0085\left(T_{\text{pm}}\right) + 0.0398\left(T_{\text{pc}}\right) - 0.0615\left(T_{\text{oc}}\right) + 0.0454\left(2T_{\text{pm}}\right) + 0.2942\left(2T_{\text{om}}\right) \tag{1}$$

$$DF2 = -0.9725 + 0.0698\left(T_{\text{pm}}\right) + 0.00477\left(T_{\text{pm}}\right) - 0.08401\left(T_{\text{pc}}\right) - 0.01578\left(T_{\text{oc}}\right) - 0.1799\left(2T_{\text{pm}}\right) + 0.1970\left(2T_{\text{om}}\right) \tag{2}$$

$$DF3 = -20.1766 - 0.0433\left(T_{\text{pm}}\right) - 0.0082\left(T_{\text{om}}\right) + 0.0448\left(T_{\text{pc}}\right) - 0.0522\left(T_{\text{oc}}\right) - 0.0589\left(2T_{\text{pm}}\right) + 0.1833\left(2T_{\text{om}}\right) \tag{3}$$

$$DF4 = 0.5404 - 0.0033\left(T_{\text{pm}}\right) - 0.0055\left(T_{\text{pm}}\right) - 0.0384\left(T_{\text{pc}}\right) + 0.0698\left(T_{\text{oc}}\right) - 0.1262\left(2T_{\text{pm}}\right) + 0.1379\left(2\,T_{\text{om}}\right) \tag{4}$$

The calculated equations show [Eqs. (1)–(4)] (that the most important parameters for discrimination of PET samples are onset and peak of melting temperatures ($T_{\text{onset melting}}$ and $T_{\text{peak melting}}$), onset and peak temperatures of crystallization ($T_{\text{onset crystallization}}$ and $T_{\text{peak crystallization}}$) and onset and peak of melting temperatures in second run. Those six parameters are fundamental properties of semi-crystalline polymers, and it is therefore a question, if they can be used to distinguish also other polymers for recycling. The other parameters (e.g. Cp) appeared to be too close to each other for many samples and were not useful to distinguish the PET samples from each other using PCA.

Conclusions

In our proof-of-concept study, we focused on the potential of DSC to identify PET samples types. We used parameters obtained from a DSC runs such as temperatures and enthalpies of melting, crystallization and glass transitions of the first, second heating and cooling cycles. The parameters were used as primary parameters for simple and advanced statistical analyses. We applied two statistical methods such as PCA and HCA.

By using PCA, we are able to divide the samples into the appropriate quadrants distinguishing virgin PET, degraded PET or with addition of other substances, modified composition PET and materials suitable for further recycling.

As a result, we were able to determine the groups of PET type, according to their history, properties, rate of degradation and places in the recycling cycle. Subsequently, determine the PET's suitability for further recycling. We demonstrated that DSC can be used to distinguish PET materials of different origins and recycling degree based on the interrelationship between thermophysical properties. This identification concept could thus serve as a basis for a robust method of verifying the use of different types of PET. We conclude that DSC has a great potential to become this method for identifying different chemical compositions of PET.

This study further revealed inconsistencies in the properties of bottles labelled as rPET/bioPET and the questions of recyclability of products labelled as PETG. Also, our results indicate that controlled and natural degradation samples show different properties. With the quickly expanding amount of recycled material, the opportunities arise to study natural degradation and also different types of bottles in larger scale. Therefore, our further research will be focused specifically on these areas.

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