Feasibility Study of the PET Fines Incorporation into Recycling Processes

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Abstract. Circular economy principles focus on the need to preserve natural resources and foster the use of environmentally sustainable practices. Concerning the use of plastics in a circular economy, increasingly demanding solutions have to be developed towards the zero-waste goal sought after by researchers and society alike. Particular attention has been put into the recycling of PET, mainly due to its wide spectrum of use and, consequently, to large volumes of related waste. The PET mechanical recycling process requires these waste materials to be shredded into PET flakes. Following such a procedure, these flakes are pelletized to be used again as feedstock. Considering the main stages of the mechanical recycling processes, which include plastic screening, shredding and washing, significant amounts of end waste materials are generated. This end-waste integrates small scale particles that are designated by plastic fines. Concerning the PET recycling process, the PET fines resulting from its mechanical recycling are not currently valued due to several technical issues, such as their high contamination level and the complexity of sorting them from other small-size particles. Current research focuses on the feasibility of incorporating these PET fines into the film/injection extruders, avoiding this way the need for an intermediate pelletization stage. To allow for such direct incorporation of PET fines into recycling processes, different decontamination and sorting solutions were implemented and tested. The current study is based on analyzing the mechanical properties of PET fines, using laboratory tests such as FTIR, DSC, MFI, moisture content, tensile tests and bending tests. Preliminary results allow foreseeing the successful direct incorporation of PET fines into PET recycling.

Keywords: Plastic · Recycling · Circular economy · PET fines

P. S. Duque de Brito et al. (Eds.): ICoWEFS 2022, *Proceedings of the 2nd International Conference on Water Energy Food and Sustainability (ICoWEFS 2022)*, pp. 228–239, 2023.
https://doi.org/10.1007/978-3-031-26849-6_24

1 Introduction

Since the 1970s, when the concept of sustainable development was first introduced by United Nations Conference on the Human Environment [1], there has been a significant effort to find alternatives to existing products and processes to promote not only sustainability but also the circular economy, as both of these notions are key to foster sustainable development in our current and future society.

Among the various alternatives to the linear economy principles of take-make-dispose, the circular economy concepts of recycling and reuse are by far more sustainable. Thus, the ability to use waste materials to be transformed into new raw materials for the process brings positive impacts to all three main perspectives of sustainability, namely the economic, social, and environmental dimensions [2].

Particularly, when trying to apply the concepts of sustainability and circular economy to the plastics sector different challenges arise. Nonetheless, such efforts are critical since the plastics industry is one of the fastest-growing in recent years, with all the benefits and drawbacks of conventional and advanced manufacturing processes [3]. Again, one of the most promising solutions to be adopted to promote the sustainability of plastics is recycling [4].

When looking at the plastics industry, it's unavoidable to look for improvements in processes and alternatives that use fewer resources and/or allow these resources to be reintegrated into the production chain due to the production circumstances, which include the use of petroleum shunt raw material and its scarcity.

Even in the recycling chain, there is waste produced and some sub-materials that are not used during the process, thus generating by-products that don't get valued or reused. PET fines, which are the consequence of the breakage and washing of PET during its recycling process, are among those whose economic and energetic potential has not been considered in current value chains and that also can have harmful impacts on the environment [5]. The amount of PET fines generated from the mechanical recycling of PET bottles can reach 2 to 5% and from the mechanical recycling of PET trays can reach up to 20 to 30%. Because of their small size, these microplastic fines are not currently recycled with PET flakes, which result from the recycling of PET bottles.

As a result of the challenge of finding alternatives that allow integrating the highest amount of waste to be reused in the material recycling of PET while also optimizing the recycling process to minimize unwanted by-products, the current research focuses on characterizing the PET fines to study their properties and to discuss the feasibility of reintroducing this waste material into the production cycle.

2 PET Fines from Plastics Recycling

Plastics have become increasingly valuable since their discovery, serving as a cost-effective solution in a variety of industries, including construction, automotive, electrical and electronics, agricultural, domestic use, and packaging, among many others. So much so that, despite the 2020 crisis, Europe's plastics manufacturing dropped by barely 5%. And, while this figure appears significant, given that 58 million tons of plastics were manufactured in 2019 and 55 million tons in 2020, these figures can still be regarded

as very high. It's also worth noting that these figures just pertain to Europe; they don't necessarily imply that the scale has shrunk globally, given China's increase from 31% to 32% of global plastic manufacturing, as well as North America [6].

However, due to its future productivity shortfall, as well as the harm caused by high persistence under abrasive conditions, which transforms plastic into microplastics (plastic pieces smaller than 5 mm), it was decided that the Member States of the European Union (EU) should reduce disposable plastic consumption [7] and improve plastic waste management [8, 9].

According to Plastics Europe [10], to promote better waste management, more than 29 million tons of post-consumer plastic waste was collected in the EU27+3 in 2020. Nevertheless, only a third were delivered to recycling facilities within and outside the EU27+3, about 23% were sent to landfills and more than 40% were sent to energy recovery operations.

Given that the packaging industry produces around 40% of the total plastic waste, additional attention must be paid to encouraging recycling in this sector [10].

However, there are still many difficulties to be overcome in the recycling process. One of them would be, according to Elamri *et al.* [11], the fact that the post-consumer PET suffers during the recycling process: thermal exposure and shear degradation with the simultaneous presence of retained moisture and physical contaminants which lead to a significant average macromolecular weight loss during reprocessing at high temperatures, resulting in reduced mechanical properties. Besides, the intensive cleaning and drying of PET flakes before extrusion, the sorting of impurities and the use of chain extenders or modifiers are options to improve those properties.

Another relevant point is that PET fines are generated during the recycling operations, which are smaller fractions than flakes and are a by-product resulting from the shredding of the materials. Therefore, it can be inferred that there will be even greater structural and mechanical differences between PET fines and PET flakes. It has also to be noticed that PET fines cannot be included in the recycling process, as they melt before the larger dimension flakes, making material flow difficultly when producing pellets of rPET [12]. In other words, as these differences become greater and more evident, it requires increased effort on the search for solutions that make it possible to incorporate PET fines into recycling processes.

In a nutshell, it is key to look for ways to reuse this type of by-product materials from the PET recycling process to limit the amount of non-recycled PET and therefore contribute to the circular economy principles.

3 Experimental

3.1 Material

In this study, the sample of PET fines was collected after washing, in the drying process, resulting from several stages of the mechanical recycling of PET post-consumer waste. The mechanical recycling system is composed of NIR and manual sorting, shredding, washing and drying. These samples are known to contain contaminants such as different types of polymers, metals, and small pieces of wood. The maximum dimension of the PET fines is 4 mm.

It was important to conduct multiple tests to characterize the samples to gain a better understanding of their composition and, as a result, find acceptable methods to promote recycling. Initially, contaminants in the samples were examined. A sample of roughly 10 g of material was separated, measured on a precision balance from Precisa, model 262SMA-FR, and evaluated by manually removing metals, wood, colored and yellowish components, using tweezers, to get a sample just with white and blue PET material.

3.2 Density

Several tests were carried out to determine the density using the pycnometer method. The solvent was water at 23 ºC with a density of 0.99751 g/cm^3. The mass of sample and water in the picnometer of solids were measured on a precision balance from Precisa, model 262SMA-FR and the density was calculated by Eq. (1).

$$Density = \frac{m_{pic+sam} - m_{pic}}{\frac{m_{pic+w} - m_{pic}}{d_w} - \frac{m_{pic+sam+w} - m_{pic+sam}}{d_w}} \quad (1)$$

where m_{pic} is the mass of dried pycnometer of solids, $m_{pic+sam+w}$ is the mass of pycnometer with sample and water, $m_{pic+sam}$ is the mass of pycnometer with sample, m_{pic+w} is the mass of pycnometer full of water and d_w is the density of water at 23 ºC.

3.3 Moisture Content

The subsequent set of tests followed the procedures outlined in ISO 15013:2007 [13] to determine the moisture content in the samples. The method is based on the gravimetric method by the measurement of the variation of mass between the mass of the sample as received and the mass of the sample after drying at 105 ºC for 24 h. The mass was measured at ambient temperature with a precision balance from Precisa, model 262SMA-FR.

3.4 Melt Flow Index

The Melt Flow Index (MFI) was carried out at 265 ºC, using ATS Faar equipment, according to the procedure prescribed in ISO 1133-1:2011 [14] with the 2.16 kg of weight to force the sample to flow through the flow chamber. To adapt the standard to the given experimental flow, the method was modified for 10 g of sample to be inserted into the equipment and a cutting time of 25 s.

3.5 DSC Analysis

The equipment DSC131 from Setaram Instrumentation was used to perform the Differential Scanning Calorimeter (DSC) analysis, test for determining thermal characteristics, glass transition temperature, Tg, crystallization temperature, Tc, melting temperature, Tm, and crystallinity, X_c %. The results were obtained after the second scan with a temperature range from 30 ºC to 300 ºC, without purge gas, with a scanning speed of 10 ºC/min and sample weight ranging between 30 mg and 35 mg. The crystallinity was calculated based on the heat of fusion of 100% crystalline PET of 120 J/g.

3.6 FTIR

The presence of additives and contaminants, including polymers and monomers, was analyzed using the FTIR technique (Fourier-transform infrared spectroscopy). This technique allows identifying the composition of a material with high levels of precision. The FTIR spectrometer used was the Spectrum Two from PerkinElmer and the resulting spectrum was studied using the software Spectrum IR, in a multisearch analysis.

3.7 Bending and Tensile Tests

Bending and tension tests were also undertaken to characterize the mechanical properties of the samples, which were preceded by a step of specimen preparation in which 3.30 kg of dried PET fines were injected at two different pressures, 60 bar and 80 bar, at a temperature of 140 ºC. The mold used to inject is in accordance with standards for 3-point bending and tensile tests, the ASTM D638 standard [15]. The 3-point bending tests were carried out using a Zwick/Roell Z100 universal test machine in accordance with the ISO 178:2003 standard [16], with a test speed of 5 mm/min, a load cell of 100 kN, and a distance between supports of 68 mm.

4 Results Discussion

According to the procedures presented in the previous section a set of tests was carried out to characterize contaminants in the samples, densities, moisture content, melt flow index, DSC, FTIR and tensile and bending tests.

Table 1 presents the analysis of visible contaminants on the samples, which were sorted by the manual removal method.

Table 1. Analysis of visible contaminants on the samples.

Test	Material	Mass (g)	Relative weight (%)
1	Metals and Wood	0.047	0.5%
	Miscellaneous materials	0.278	2.7%
	Blue and White	9.708	95.4%
	Yellowish	0.162	1.8%
2	Metals and Wood	0.242	2.1%
	Miscellaneous materials	0.271	2.9%
	Blue and White	9.420	93.5%
	Yellowish	0.140	1.5%

As a result of the foregoing analysis, it was possible to observe that most of the samples were composed of white and blue plastic. Nevertheless, a significant percentage of metal contaminants and pieces of wood were identified as specimen contaminants in various amounts. Other contaminants identified in the analyzed specimens relate to different percentages of various polymers that may be recognized and distinguished by their colors, as well as yellowish materials that indicate the presence of polyolefins.

Table 2 presents the density and moisture content of PET fines, measured in triplicate, according to the methods described in Sects. 3.2 and 3.3.

Table 2. Density and moisture content of PET fines.

Test	Density (g/cm^3)	Moisture content (%)
1	1.062	0.65
2	1.295	0.62
3	1.277	0.65

It can be observed from the results presented in Table 2 that the density of the samples is consistent, but they differ from the density values for virgin PET, which has values between 1.29–1.43 g/cm^3 [17]. This can be explained by the presence of polymers like polystyrene and polyolefins and/or additives that can decrease the density of the sample.

It can be observed from Table 2 that the two tests had approximately the same moisture content. However, given the variability of the sample, a margin of 5% error level can be considered acceptable.

Table 3 presents MFI results, which were conducted using the procedure prescribed in ISO 1133-1:2011 and it was carried out at 265 ºC, as described in Sect. 3.4.

Table 3. MFI results of PET fines.

Test	MFI (g/10 min)
1	355.72
2	191.02
3	67.250
4	50.866
5	82.094
6	88.238

The MFI results allowed identifying that the material under research had particles beyond the visible spectrum, given that the findings differed significantly from what had been expected based on the literature [18], which indicates that ground bottles have a Melt Flow Index of 15.98 g/10 min.

It should be noted that tests 1 and 2 of Table 3 were conducted without any contaminant removal treatment, with results that were about 12 to 22 times higher than expected. This may be due to the presence of metals and wood particles, which could disrupt the flow of the material due to the obstruction of the nozzle at the end of the flow chamber of the MFI equipment. Metal and wood contaminants were removed from Tests 3 and 4 as the initial step and the results were 3 to 4 times higher than expected. In tests 5 and 6, all visible contaminants were removed and the sample was the same as the one used for the contamination analysis where the fraction of white and blue plastics was used. The results of tests 5 and 6 are more consistent but still around 5 times higher than expected. Nevertheless, there should still be a significant presence of impurities, additives, or multilayer material, which would explain the wide range of readings. In addition, the irregular shape of the input material with lower dimensions in comparison to those of the pellets, that are usually used to measure MFI, may affect the final output.

Table 4 presents DSC results for 3 tests, in which Tg refers to the glass transition temperature, Tc refers to crystallization temperature, Tm refers to melting temperature and X_c % the crystallinity of PET fines.

Table 4. DSC results of PET fines.

Test	Tg (ºC)	Tc (ºC)	Tm (ºC)	X_c%
1	97.97	161.76	267.10	12
2	102.62	156.92	269.60	5.1
3	99.52	157.25	265.71	10

The reported results in the literature [19] refer that the virgin PET has a glass transition temperature of 72.8 °C, a crystallization temperature of 135.7 °C and a melting temperature of 251.9 °C. However, the tests have divergences from the reported values, according to the DSC test analysis. It is possible to infer from the readings obtained in Test 2 as being the result of a non-fused particle, *i.e.*, a plastic substance that could not reach the melting point at 300 ºC. On what concerns Test 3, since there are more colored materials, *i.e.*, materials that are not PET, thus having different values than expected.

Figure 1 shows the graph of heat flow versus temperature resulting from the DSC analysis of the PET fines.

In accordance with the presented in Fig. 1, the values were consonant with each other, however, it can be observed that there are differences in the graph which, as mentioned above, can be explained by the presence of other materials besides PET.

According to the FTIR analysis, most of the samples contain more than one layer of polymer and/or present additives or contaminants (80% of the samples), as well as materials that do not contain PET at all (16%) and only 4% of the samples analyzed were made entirely of PET, as shown in the chart of Fig. 2.

The FTIR tests also showed that Vinyl Acetate, Adhesive of Vinyl Chloride, Poly(trimethylene terephthalate (PTT), Poly(Phenylene Disulfide) and Quaternized Polyimidazoline are some of the components found in the analysis, here referred to as PET +, in reference to the presence of additives.

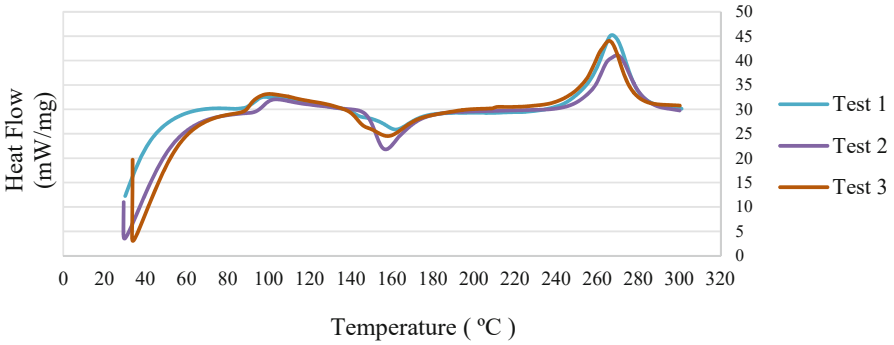

Fig. 1. DSC analysis of the PET fines.

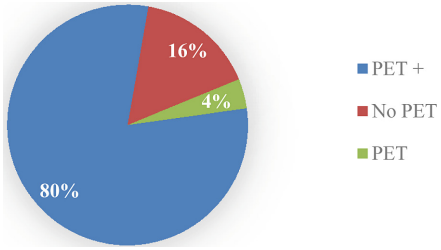

Fig. 2. Percentage of PET, PET samples with multilayers and/or contaminants and additives and non-PET materials.

On what concerns the mechanical characterization of the sample materials, 3-point bending tests were performed with the specimens injected at 60 and 80 bar and the results are presented comparatively in Fig. 3.

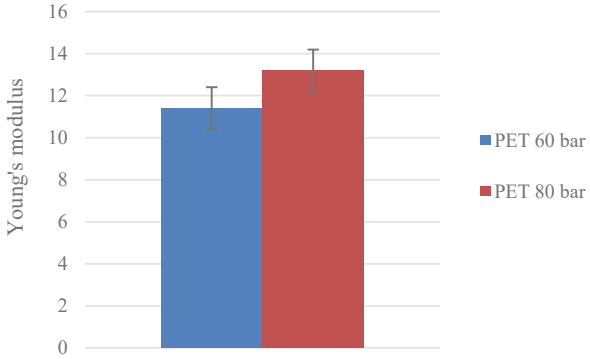

Fig. 3. Comparative graph of bending tests with specimens injected at 60 bar and 80 bar.

In Fig. 3 it can be seen that Young's Modulus has similar values for injection at 60 bar and 80 bar, indicating that there are no significant differences regarding the

injection pressure used. On what refers to the virgin material, the values found are above expectations, considering that, according to the literature, the values should oscillate between 2.76 and 4.14 Gpa [20].

Figure 4 shows the stress and strain curves until the limit of the fracture of samples of PET fines injected at 60 bar and Fig. 5 shows the stress and strain curves until the limit of the fracture of samples of PET fines injected at 80 bar.

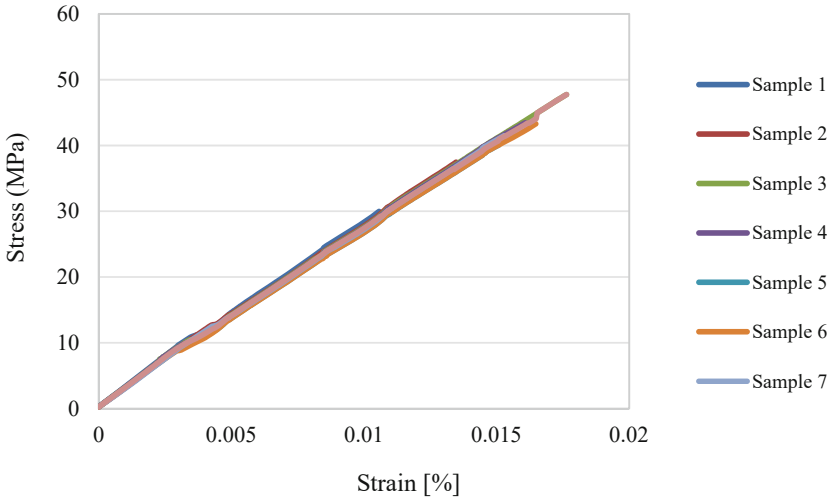

Fig. 4. Stress-strain curve of PET fines injected at 60 bar.

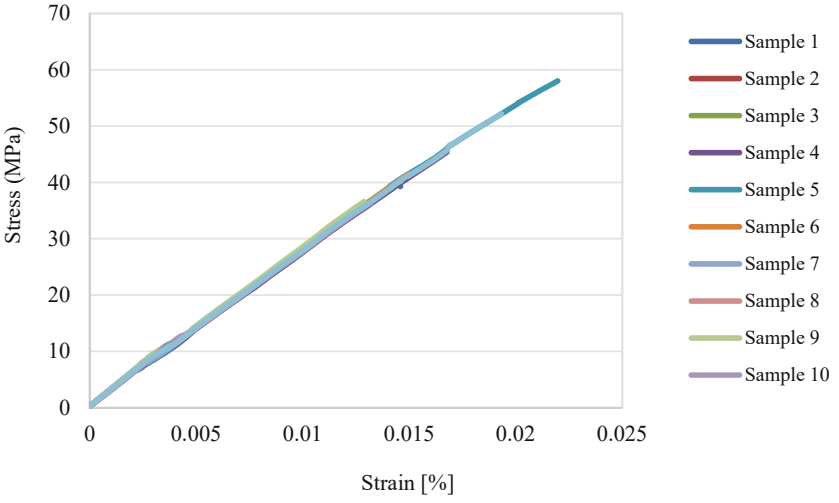

Fig. 5. Stress-strain curve of PET fines injected at 80 bar.

The specimen has a very low deformation with no significant differences regarding injection pressure.

The values found for both the 60 bar and the 80 bar samples are quite different from the values reported in the literature [18] for virgin PET, given that they support a maximum strain between 50 and 60 MPa, with a strain of more than 30%. It is also worth noting that the curves don't match those predicted from a PET-only material, and the material doesn't yield, making it impossible to determine its yield strength. This indicates the sample's brittleness by the fact that it breaks before yielding.

5 Summary and Discussion

The tests conducted with the PET fines collected after washing and drying PET residues resulting from several stages of the industrial recycling of PET post-consumer waste allowed finding that despite the number of visible contaminants found being relatively small (5%–7.5%), the presence of additives found from FTIR in the fraction of PET and other polymers that resemble PET is significant and may be the explanation for a large part of the differences in values found, as density, which has lower values because the polymers present have lower densities than PET, such as polystyrene and polyolefins.

The MFI values were substantially higher than expected according to the literature [18], in which the values should be close to 30 g/10 min. However, this result can be explained both by the material not being entirely composed of PET and by its smaller dimension than the standards, which facilitates its fusion.

On what concerns the DSC tests, the results showed to be higher than expected according to the literature [19], but the generated curves are similar to the pattern found in virgin PET. The crystallinity is significant, and it can contribute to increasing the stiffness found in the bending and tensile tests. The specimens for the bending and tensile tests were not subjected to DSC analysis but were injected into the mold at ambient temperature. In order to decrease the stiffness and avoid the crystallinity, the mold could be refrigerated to about 8 ºC. On the other hand, refrigeration would increase the need for energy in the production of the specimen.

Finally, on what refers to the mechanical properties, the bending and tensile tests showed no significant differences regarding the injection pressure of the molds, but as there are large differences when comparing the results expected for virgin PET, being much more rigid, residual deformation and do not show yield.

6 Conclusion

One of the methods to increase the material's circularity is by improving its recyclability, thus extending its life. Nonetheless, the mechanical recycling of plastics must be improved to avoid significant amounts of rejected material. In the PET recycling process, after automatic and manual sorting, washing and drying, the sieving gets about 2 to 5% of PET fines, which are particles smaller than 4 mm. These PET fines are contaminated with metal, wood, sand, additives, organic contaminants, and other polymers in addition to PET.

In this study, several characteristics of the PET fines were assessed using different methods, such as FTIR, DSC, MFI, moisture content, tensile tests and bending tests.

The contaminants (metal, wood, yellowish and miscellaneous materials) were evaluated and although they are about 5%, they strongly affect the mechanical and thermal characteristics. Besides the contaminants, polymeric multilayers on the PET fines were detected by FTIR. This allows assuming that they can contribute to the deviation of the mechanical and thermal characteristics of PET fines when compared to virgin PET.

Given that the material analyzed is obtained from post-consumer packaging bottles, which still have labels attached to them, it's also possible to infer that the contaminants found in the samples are from such labels, which may not have been removed completely. Therefore, considering these results it is not possible to directly insert PET fines into recycling processes, given the significant differences in physical and mechanical properties when compared to virgin PET. Based on these results, the increase of the intrinsic viscosity may not be enough to successfully recover the PET fines properties.

It is recommended that to provide improvements to the material properties, the PET fines are subjected to a separation process to remove metal, wood and miscellaneous material, in order to obtain samples with a high degree of PET and multilayer material.

More research is needed to develop efficient methods to separate contaminants that, as known, are below 4 mm and magnetic, NIR sorters and others have limitations. Another recommendation would be the assessment of an additional step of mechanical drying before shredding to minimize fines production, although further research is required to quantify this aspect.

Acknowledgments. Financial support for this work was provided by the Project Better Plastics - Plastics in a Circular Economy. COMPETE 2020 (Lisboa, PT) GRANT_NUMBER: POCI-01-0247-FEDER-046091.

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