Recycling Plastic Waste for 3D Printing Filament by Extrusion Processing

António Saldanha Santos Barreiros Cardoso

antonio.saldanha.cardoso@tecnico.ulisboa.pt

Instituto Superior Técnico, Lisboa, Portugal

September 2021

Abstract

The excess of plastic waste and its mismanagement due to an ever-increasing production volume worldwide have led to a serious environmental crisis. Concurrently, additive manufacturing has gained considerable adoption from hobbyists up to industrial scale. The most widespread 3D printing (3DP) technology for plastics is Fused Deposition Modelling. The only raw material required is plastic filament. This presents a great potential for mitigating the waste management crisis: repurposing plastic waste into 3DP filament, bolstering circular economy. Polypropylene (PP) is one of the most produced plastics albeit little used in 3DP. In this context, this research aims to: (1) study filament extrusion processing, printability and characterisation of PP sourced from a waste management facility (rPP) and (2) compare the characteristics of rPP to those of commercial PP filament (vPP) to understand how to optimize filament processing. Initially, the material was separated by density and dried with varying parameters. This was followed by rheological, thermal and chemical characterisation of rPP and vPP. Filament extrusion was then tested to obtain optimal parameters followed by the same characterisation techniques. Tensile tests were performed with rPP and vPP for comparison. It was shown that rPP had higher content of inorganic additives (3.7% vs 0.2%) and melt flow rate (11.1 vs 4.5 g/10min at 200ºC) compared to vPP. Mechanically, rPP showed higher rigidity but the noteworthy difference was the strain at failure and strain ratio ($\epsilon_f/\ \epsilon_y$): 4.1% and 8.4 for rPP, 848% and 675 for vPP. Finally, rPP filament suitable for 3DP was not achieved.

Key-words: Extrusion, Recycled Plastics, rPP, Polypropylene, 3D Printing, Additive Manufacturing

1. Introduction

This dissertation is motivated by the necessity of finding alternative ways of improving the plastic waste management problem.

Throughout the last decades the production, use and waste generation of plastic has increased sharply. It is expected that from 1950s up to 2050 the cumulative production of plastics will reach an appalling value of 26 000 million metric tonnes[1]. As a consequence of the continuous rise in production of plastics and the excessive use of these materials several environmental issues have risen. The negative impacts arising from the excessive use and waste mismanagement have been seen in all environmental aspects: land, soils, fresh water, food chain, oceans, animals, human health and greenhouse gases to atmosphere. The problem is even worse in developing countries where landfills are usually done in poor conditions, in open landfills causing a much higher impact on the surrounding

environment [2]. From the waste mismanagement impacts some are of high relevance. Some of these include polychlorinated biphenyls, bisphenol A, phthalates and polybrominated diphenyls (flame retardant present in plastics), which cause changes in metabolism, enzyme activity, developmental defects, hepatic stress, cancer, and others; some of the plastic materials involved are Polyvinyl chloride (PVC), low-density polyethylene (LDPE) and polyethylene (PE) [3] [2]. The impact of microplastics on humans which are at the top of the food chain has research ongoing but little evidence exists. The plastic waste that is most concerning is the micro and nano (between 0.1 μm and 1 mm and lower than 0.1 μm, respectively) particles that could be ingested, inhaled or absorbed through skin.

The available amount of plastic waste has the potential to be reintroduced into the supply chains as recycled feedstock for 3D printers. Bearing this in mind, the problem to be addressed is how to turn plastic waste of a specific material into recycled filament to be used with 3D printers. This strategy has the potential to increase the value of plastic waste, reintroducing it in the economy and mitigating the disposal issue. Moreover, this can also contribute to reducing the costs of 3D printing raw materials that still pose an obstacle on the adoption of this technology. Research is still being done on improving the production of recycled filament using extrusion but further investigation is necessary. The most used commercial filaments in 3DP are made of polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol-modified (PETG). In the domain of reprocessing plastic waste for 3DP filaments with extrusion, the most studied materials in the literature are, again, PLA, ABS and PETG. However, two other materials make for a very considerable percentage of all plastic waste and production worldwide: polyethylene (for this specific context high-density polyethylene, HDPE) and polypropylene (PP). Moreover, not only are these polymers seldom-used in 3DP but also the available studies on their repurposing by extrusion for 3DP filaments are scarce. This constitutes a literature gap and as such, this dissertation focuses on addressing the case of polypropylene. This work may provide information and data that can lead to an increased rate of adoption of filament recycling with enhanced quality and applicability. This sets the motivation to address the problem at stake.

In the literature 2 articles were found that address PP. Iunolainen[4] performed a research in order to assess the suitability of rPP to produce filament for 3DP. The main objectives were to experimentally test the production of filament from rPP, study the mechanical and flow properties of the material and finally to measure melt flow rate (MFR) values of commercial ABS and PLA filaments to compare with rPP. Several cooling systems were tested, namely, cold-air gun and cooling water bath with a heating element and thermostat. A pulling device was also employed. For the optimization of the extrusion 3 experiment setting were carried out. In the first experiment the cooling method used was the cold air gun (pressurized) and the temperatures were the same as for the virgin PP. In the second experiment the cooling method was changed to heated water bath using a heating element and thermostat. The temperatures were raised as an attempt to obtain a smoother filament surface since there were swelled areas caused by parts that did not melt completely. In the third experiment the temperature of the cooling bath was increased to try to obtain better filament roundness and the material used to clean the extruder prior to the experimentation was changed from Asaclean purging compound to virgin PP (brand Sabic, violet). To control the dimensions of the filament produced the diameter was measured twice at one point in intervals of 1 m with a digital calliper. The melt flow index was measured for virgin PP (Sabic), rPP (provided by a recycling company), rPP filament sample, COTS ABS and PLA. Tensile specimens were obtained from injection moulding with rPP and virgin PP pellets. The properties measured were tensile strength, elongation at yield and Young's Modulus according to ASTM Standard D638. Regarding the results, the most successful experiment was the third, which showed the best results in terms of filament quality. However, the resulting filament was still unsuitable for use in a 3D printer due to surface flaws and diameter variations. The

temperatures used were 210-215-215-225-225 ºC (zones 5 to 1 respectively), the extrusion speed was 25 rpm and the water bath was heated to 50 ºC. The filament surface was less rough but there were considerable diameter variations and the shape was more elliptical than round shaped. The MFR obtained was, in increasing value, virgin PP, rPP and rPP filament (7.2, 14.4 and 16.4 g/10min respectively). The stress at yield, Young's modulus and strain at yield were higher for the virgin PP. A summary of the obtained results is provided in table 1

In another research on rPP, Domingues et al.[5] have established a solution for the management of used waste recovered from tires and used PP plastics. Using a blend of 60% tire waste granulate and 40% rPP the authors were able to generate components with added value such as urban furniture through 3DP. For such a prototype of a 3D printer was adapted in-house, composed of a robotic arm, modified extruder and heated print bed. The blend used was made of polymeric matrices from rPP and tire waste in micronized state. A twin-screw extruder was used for the polymer processing. The resulting processed material was characterized with tensile tests and thermal analysis after printing six specimens of PP/Tires blend. The printing was done with a heated base at 120 ºC and extrusion nozzle at 198 ºC. Tensile tests were performed as well as thermal analysis with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The properties assessed were heat of fusion, melting temperature and crystallization temperature. The results from the tensile testing showed that the ultimate tensile strength was 6 MPa with a corresponding deformation of 0.03 (3%). From the thermal analysis it was concluded that when comparing PP with the blend PP/Tire the former had a lower crystallization temperature (T_C 107 ºC vs 116 ºC) thus showing that the presence of tire waste lead to an increase of T_C. According to the authors knowing the melting point is important in order to optimize the printing parameters. The PP/Tire blend showed a marginally higher melting point compared to PP (161 ºC vs 157 ºC). For PP/Tire the thermal analysis showed two different peaks. The first is associated with the beginning of melting of one of the blend constituents and the second leads to the polymer fusion at higher temperature value. The authors demonstrated that it is possible to do 3DP of large parts using a blend of tires and PP plastic waste. The blend ratio still needs to be optimized and further investigated. They intend to study in future work the use of curable resins as binder material for the blend so that when applying UV lights stronger bonds can be achieved during printing.

Prior to the experimental procedure, a complete review on process parameters, mechanical and rheological properties of the rPP and PP (used for baseline comparison) obtained has been carried out and summarised in table 1:

Table 1: Summary of results from Iunolainen's research comparing rPP and virgin PP (baseline material)[4].

	PP (baseline)	*rPP)*
MFI [g/10min]	N.A	16.4
Pre Processing	None	None
D_d [mm]	N.A	N.A
T_{ext} [ºC]*	N.A	210 (Z1),215 (Z2),215 (Z3), 225 (Z4), 225 (Z5)
v_{ext} [rpm]*	N.A	25
*Cooling Method**	N.A	Water bath (50ºC)
Pooling [V]*	N.A	N.A
d [mm]	N.A	N.A
d target [mm]	1.75	1.75
TS [MPa]	31.65	25.18
E [MPa]	677.1	594.32
Strain at Yield [%]	10.81	9.83
Key Factors Quality	N.A	Clean extruder with virgin PP material Warm water bath

The main objective of this work is to understand whether polypropylene sourced from waste treatment facilities can be repurposed for use in 3D printing. For such, optimisation of processes and characterisation of the material is performed to achieve adequate filament for printing. The research questions to be addressed in the experimentation were the following:

(1) What are the main characteristics (composition, chemical, thermal, rheological, mechanical) of PP flakes sourced from waste treatment facilities and of the subsequently produced filament by extrusion? What are the similarities and differences with those of 3DP PP filament?

(2) How can the processes by which rPP filament is obtained from heterogeneous bulk rPP flakes be improved in order to attain effective 3DP printability?

An overview of the research is show in figure 1 below:

Figure 1: overview of research work.

2. Methods

The research boundary starts with the entrance of the PP material under study in the laboratory of CERENA Research Centre. The PP was obtained from a recycling facility that receives plastic waste and subsequently separates by type of polymer and grinds the materials into flakes. After the material was received it was then processed and characterised prior to the extrusion process. The second stage was the optimization of the extrusion of rPP with selected variables. The third stage comprised the characterisation (thermal, chemical, mechanical) of the filament obtained and its comparison with virgin PP filament for 3DP, vPP(3DP), available in 3DP related stores.

The main material used is the recycled PP that was provided by the recycling company, namely, Lipor. The material provided is henceforth labelled as rPP(bulk). This is due to the fact that there is no certainty of the exact composition of the flakes provided in bulk. The 3DP virgin filament used, vPP(3DP), sometimes called commercial off the shelf (COTS) filament, was purchased from the Portuguese online store of RepRap [6] a company devoted to 3D printing and related equipment. It is referenced in the online shop as *PP (Polipropileno) RepRap PT – 1.75mm 500gr Natural.* The supplier did not have a technical data sheet but was able to provide the following properties: melt flow rate 8g/10min (230ºC, 2.16Kg), flexural modulus of 400 MPa and density of 0.92 g/cm^3. Another widely used material was the silicone H plastic mould release agent (produced by Henriquímica, Produtos Químicos Lda). Equipment and software used is shown in table 2.

Table 2: List of equipment, devices and software used for the research work.

Category	Equipment
Process	Twin screw extruder Brabender DSK 42/7 Co-Rotating, Plasti-Corder PL2000, Eurotherm Temperature Controller
	Conveyor belt with cylinder and motor
	Pelletizer
	Oven
	Hot Press Carver M-2089 25 ton-force, heated plate 30ºC-500ºC
	Mini extruder 3devo Composer
Characterise	Plastometer CEAST 6540/010/011
	Thermal scale
	FTIR-ATR PerkinElmer Spotlight 200i
	TGA Hitachi STA7200 Thermal Analysis System
	Microscope with digital head
	Instron 5966K9184 with Max Load 10 kN Test Frame
Measure	Scale Shimadzu AUY220
	Scale Metler Toledo PB3002
	Camera Fujifilm XT-2, iphone 7
	Digital calipers Mitutoyo, Mahr Tyepe 16 ER
	Digital Micrometre an Insize Digital Spherical Anvil Tube
	Microsoft Office 2016 (MacOS version)
Software	QtiPlot ver. 1.0.0-rc14 (64-bit)
	Python3 (3.8.5), Anaconda (1.10.0), Spyder (4.1.5)

The experimentation procedure is organized 6 steps: Pre-extrusion Separation and Drying, Pre-Extrusion Characterisation, Extrusion Processing, Post-Extrusion Characterisation, Second Extrusion in Mini Extruder and Mechanical Testing. During the separation and drying phase, the rPP(bulk) material was placed in water for separation by density. Floating flakes were removed and labeled rPP(mix). Given that the specific density of PP is similar to that of water, only the floating flakes were considered for rPP from this point onward. Drying in oven was performed at 60ºC and several time intervals were tested: 18.50h, 21h, 24h, 43.37h and 63.50h. Each drying consisted on a material batch. After drying, moisture content was determined for each batch sample using Karl-Fischer method on a thermal balance. The parameters used were: maximum temperature 80ºC, auto-stop at 0.1%/10s, pre-heating off, units %M (mass). For each batch 3 trials were performed and the target average was to be lower than 0.20% moisture content. In step 2 pre-extrusion characterisation was performed: separation of flakes by every colour, melt flow rate determination (MFR), fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) of flakes with same colour but very different densities and

optical microscopy. For MFR determination ASTM D1238-13 was followed but the parameters used were 200ºC, 2.16 Kg and 30s-time intervals. For FTIR, resolution of 4 cm^{-1} and 8 scans were used and device supplier's database provided a match list of spectra. For the latter, temperatures used were in the range 30-600ºC with temperature increase rate of 10ºC/min with constant flow of 200ml/min nitrogen stream. For the third step, extrusion processing, 2 sets of experimentations were performed. The parameters for the first set are shown in table 3 and the second set is shown in table 4. Pictures of samples were taken for later comparison of results.

Table 3: Extrusion parameters for first extrusion plan.

Screw (RPM)	Die (ºC)	Z3 (ºC)	Z2 (ºC)	Z1 (ºC)
15	200	200	190	170
15	210	210	200	170
15	210	210	200	170
15	210	220	210	170
15	220	220	210	170
20	220	220	210	170

Table 4: Extrusion parameters of the main extrusion plan.

Screw (RPM)				Die (ºC)	Z3 (ºC)	Z2 (ºC)	Z1 (ºC)
25	20	15	10	200	200	190	170
25	20	15	10	210	210	200	180
25	20	15	10	220	220	210	190
25	20	15	10	230	230	220	200
25	20	15	10	240	240	230	210

The fourth step corresponds to the second extrusion which was done in the mini extruder using the rPP(cmp) pellets due to low availability of material to use the twin-screw extruder. Simple test runs were performed after initial adaptions of parameters in the 3devo extruder. Extrusion parameters were: screw speed (S) =3.5 RPM, T= {200, 200, 200, 200} and cooling fan at 40%. Pictures of samples were taken for comparison. In the fifth step, post-extrusion characterisation, the following analyses were performed to rPP(cmp) and vPP(3dp) after pelletizing the filaments: MFR, FTIR, TGA and diameter control. For the latter, the following diameter analysis was performed to the best filaments: diameter control chars with length vs diameter with measurements taken every 10 cm using a digital calliper. Lastly, in the sixth step, test specimens of rPP and vPP were produced in a hot press and tensile testing was performed for comparison. Specimens produced were type IV in accordance with ASTM D638 – 14 [7]. The mechanical tests were carried out using the same standard. The grip displacement speed used was 5 mm/min and digital image correlation (DIC) was used for extensometry. The analysis of results was performed in Excel and QtiPlot to determine stress, strain, Young's Modulus and Moduli of resilience and toughness (using numerical integration). A diagam block of that summarises the experimentation steps is provided in Figure 2:

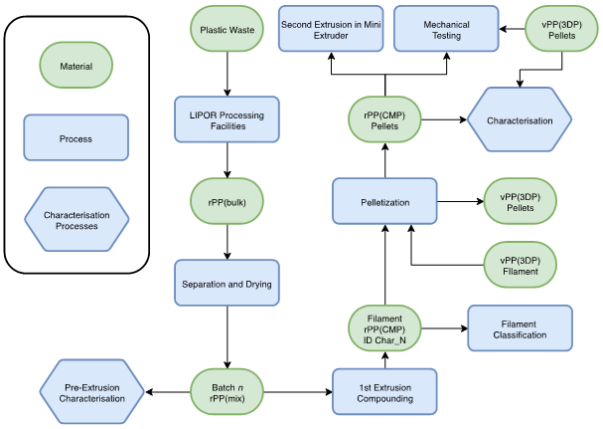


Figure 2: Diagram block of the experimentation phase of the work.

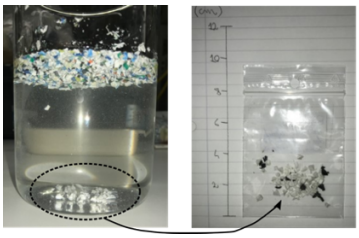
3. Results and Discussion

The material received from the waste management facility was supposedly PP but no certainty regarding the exact composition existed. It is observable in figure 3 that the material is extremely heterogenous. As such it can be composed by different polymers. The composition of rPP(bulk) is thus assumed unknown. The density of PP is approximately 0.90 $g.cm^{-3}$. The density of water at 25ºC and 1 atm is 0.997 $g.cm^{-3}$. The difference is density was used as a simple method of separation. Upon placing the flakes on water, the separation was relatively fast.

For all separations there were white and black flakes deposited in the bottom, thus, with higher density. The majority were white flakes indistinguishable from the white flakes with lower density that floated. The hypothesis regarding the mixture composition was the following:

- Lower density flakes: PE (LDPE, HDPE), PP or copolymers;

- Higher density flakes: PP (copolymers or with high additive/filler content), ABS, PET;



Polymer	Density ($g.cm^{-3}$)
PP	0.90
LDPE	0.92
HDPE	0.95
Water (25ºC, 1 atm)	0.997
ABS	1.18
PVC	1.4

Figure 3: Separation of rPP(bulk) in a beaker and density data of the main polymers that could be present in the material.

The total weight variation (∆m Total) refers to the difference between weight before drying and immediately after drying in oven. The cooling weight variation (∆m Cooling) refers to the difference between weight immediately after taking flakes from oven and weight after cooling to room temperature (approximately 45-50 minutes after). The target moisture content of at most 0.20% was achieved by using at least 21h drying time at 60ºC. The difference in moisture content from the later established 24h drying interval to the maximum value used (43.37h) is negligible for the quantities used (0.12%-0.17% vs 0.16%). For the weight variations upon cooling a positive value implies a decrease in weight while a negative value implies an increase in weight. The highlighted batch S2 had a much higher variation but it could due to the fact that a glass beaker was used which has a much smaller bottom surface area in comparison to the large tray. As such, the drying might not have occurred homogeneously through all layers of polymer flakes. The batches S3-S7 had either zero change or at most a 0.02% decrease in weight when cooling from 60ºC to room temperature (RT) which is negligible. This confirms the material is not prone to absorb moisture. In fact, this is a characteristic of PP. However, given that the exact composition of rPP(mix) is unknown, the negligible moisture absorption hypothesis was tested and confirmed. Moreover, according to literature PP does not required drying prior to extrusion since it does not absorb moisture[8]. The low water absorption can be explained by the nonpolar nature of polymer PP[9].

The MFR determination was done with a temperature lower than that specified in the ASTM standard because it was extremely difficult to obtain consistent results at 230ºC due to the high fluidity of rPP. An average value of 11.71 g/10min was obtained with a standard deviation of 1.31 g/10min (11.2% relative to average value). Specific optimal values of MFR for extrusion and injection moulding were not found (particularly, two polymers with the same MFR value can have very different extrusion behaviour). However, it is common assumption that for extrusion low MFR values are more appropriate whereas for injection moulding higher values are preferable. On the website of Exxon Mobile Chemical, one of the biggest producers of polymers[10], an extensive list of PP polymer products is available with data sheets. Of all listed products, only the polymers with MFR in the interval 1.8 to 5.5 g/10min are categorized for extrusion processing. From that value onwards, all products' data sheets attribute injection moulding for processing method. The melt flow rate is characteristic of injection mould PP grades. As such, the rPP tested could be originated from a mixture of items mostly produced by injection moulding. In this case reprocessing in extrusion might not provide the best results without appropriate conditions (fillers and water cooling). In the graph from Figure 4 it can be seen that the process of MFR determination is not under control given that 24 test run values fall outside of the control interval. This could be explained by the fact that the process is entirely manual and the polymer has a relatively high fluidity. However, if much longer time intervals were used this issue might have been mitigated.

Separation of all flakes by colour in a large sample was carried out to understand how heterogeneous the material is. Upon conclusion, 19 distinct colour flakes were identified and labelled according to overall colour and colour pitch. The identified flakes are presented in table 6.

Table 5: Identified flakes after individual separation of colours and their assigned codes.

#	Code	Colour	Colour Pitch	#	Code	Colour	Colour Pitch
1	BL1	BLUE 1	LIGHT	11	GR1	GREY 1	LIGHT
2	BL2	BLUE 2	MID	12	GR2	GREY 2	MID
3	BL3	BLUE 3	DARK	13	GR3	GREY 3	DARK
4	G0	GREEN 0	BRIGHT	14	B1	BLACK 1	-
5	G1	GREEN 1	LIGHT	15	Y1	YELLOW 1	LIGHT
6	G2	GREEN 2	MID	16	R	RED	-
7	G3	GREEN 3	DARK	17	MG	MAGENTA	-
8	W1	WHITE 1	LIGHT	18	UNKW1	WHITE 1	LIGHT
9	W2	WHITE 2	BEIGE	19	UNKB	BLACK 1	-
10	W3	WHITE 3	DARK				

FTIR spectra were obtained for the 10 flakes that appeared with higher frequency in the sample. The spectral data was uploaded to the equipment's software database the obtain for the best matching material results. The matching provided the following information: 5 flakes (50%) isotatic PP, 2 flakes (20%) PE, 3 flakes (30%) were mixtures (PE with calcium carbonate, ethylene propylene diene monomer (EPDM) and Poly(1-Butene). EPDM and Poly(1-Butene) are frequently added to PE and PP to enhance the material characteristics according to desired properties. For the higher density flakes identified as being PP they could have high inorganic additive/filler content of materials, e.g., talc, titanium dioxide, carbon black, cobalt blue. To understand the difference between the higher and lower density flakes, both identified as PP, TGA was performed for White1 (W1) and UnknownWhite (UnkW) flakes. The degradation temperature and maximum rate of degradation were found to be 457.4ºC and 25.68%/min for W1 and 432.3ºC and 19.49%/min for UnkW. The final residual weight was the most notable difference: 3.45% for W1 and 10.08% for UnkW (3 times higher). The density difference between both flakes might be due to the presence of much higher content of inorganic additives (and other compositional differences not identified). Flake W1 shows 2 local maxima points in the derivative weight curve pointing to 2 extremely close steps of degradation. For UnkW only 1 step of degradation was identified based on the weight curve and derivative weight curve. MFR graph (A), FTIR spectra (C), TGA graph (D) and microscopy image examples (B) are provided in figure 4.

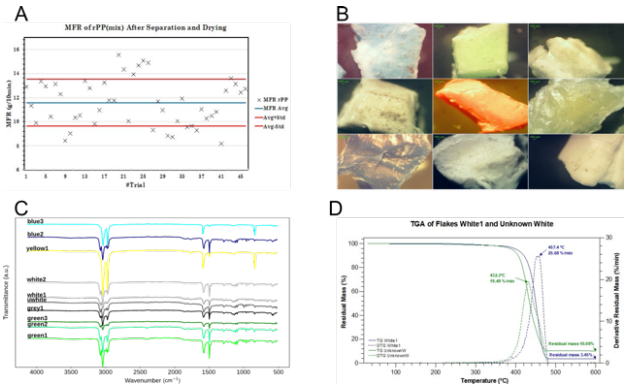


Figure 4: (A) MFR data for rPP(mix), (B) microscopy examples, (C) FTIR spectra and (D) TGA graph analysis for W1 and UnkW flakes.

Regarding the extrusion processing all parameters with screw speed of 25 RPM were not possible to perform given how bad the results were on first attempts. Only a few parameters with screw speed of 20 RPM were possible to test for the same reasons. A first set of experiments was carried out to gain sensitivity to the material and equipment. A second main extrusion plan was followed. With the remaining rPP(mix) material the parameters that provided the best results were used for a third set of extrusions in an attempt to obtain filament suitable for 3DP. Using the same best parameters (labelled D1) previously found the results were worse this time. Curiously, by mere chance, better results were obtained when the extruder was left unattended and the die temperature decreased significantly and stabilized around 170-180ºC. The temperature could be considered considerably low for die exit and more appropriate for feeding zone. An error might have occurred with the temperature controller or otherwise it showed that low exit temperatures in a twin-screw extruder with non-linear residential times is appropriate. The compilation of the best results (from all extrusion plans previously described) is provided in table shown in figure 5 with filament samples of some of the parameters.
So far, the best results were obtained with the following set of parameters (using RT cooling):
S=15 RPM, T = {200,200,190,170}
S=15 RPM, T = {170-180,200,190,170}.
After the first cycle extrusion study on the twin-screw extruder was completed, a selection of filament samples was pelletised for post-extrusion

characterisation and production of test specimens for tensile tests. The remaining pellets were not enough for a second cycle of extrusion in the twin-screw extruder and as such a small experimentation was performed in a mini extruder 3devo composer. Since this device has an internal control feedback loop with diameter measurer, the filaments obtained (P1, P2 and P3) had a much better consistency of diameter overall. Even though some melting inconsistencies were found (more so than in the twin-screw extruder) all filament samples obtained showed better results.

The post-extrusion characterization pertains mostly the good result materials obtained from the twin-screw extruder rPP(cmp) and vPP(3dp). Filaments were pelletised and the following analyses were performed: MFR determination, FTIR, TGA and diameter control processing (for most of the good results from twin-screw extruder and mini extruder). MFR of rPP(cmp)(A) and vPP(3dp)(B), FTIR(C) and TGA(D) graphs are shown in figure 6.

Screw Speed (RPM)	Die (ºC)	Zone 3 (ºC)	Zone 2 (ºC)	Zone 1 (ºC)	Belt Speed (a.u.)
15	210	210	200	170	—
15	210	210	200	170	—
20	220	220	210	170	—
10	240	240	230	210	25-35
15	200	200	190	170	30
15	210	210	200	180	40-50
15	170-180	200	190	170	35

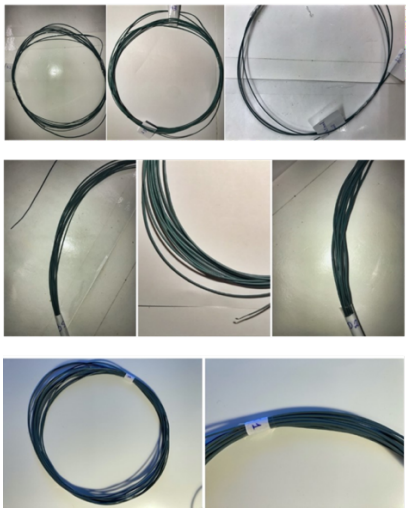


Figure 5: Table with the extrusion parameters of best filaments (top) and samples of the filaments (bottom).

With MFR trials (200ºC, 2.16 Kg) the obtained average values for rPP(cmp) and vPP(3dp) were 11.06 g/10min (standard deviation 0.81 g/10min, relative value 7.4%) and 4.53 g/10min (standard deviation 0.36 g/10min, relative value 8.0%), respectively. Moreover, extruded rPP(cmp) pellets showed a decrease of 0.65 g/10min in MFR compared to rPP(mix) prior to extrusion (5.55% decrease). The difference in MFR between rPP(cmp) and vPP(3dp) is noteworthy. This confirms previous remarks that the rPP material under study seems more suitable for other manufacturing processes other than extrusion due to the relatively high value. Filament vPP(3dp) is optimally produced for the specific purpose of being extruded in 3D printers. It is common to use low MFR polymers for extrusion processing. After all, it was verified that MFR of vPP(3dp) is approximately 2.4 times lower than that of rPP(cmp). At standard ASTM conditions (i.e., 230ºC, the gap might have been be higher).

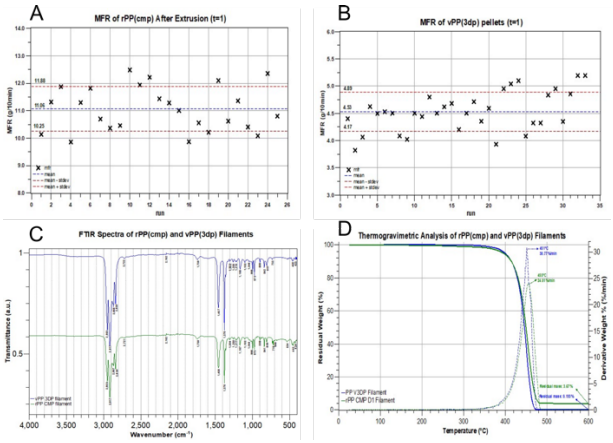


Figure 6: (A) MFR data (A, B), (C) FTIR spectra and (D) TGA graph of rPP(cmp) and vPP(3dp).

After obtaining the FTIR spectra of rPP(cmp) and vPP(3dp) some results are worth noting. The total number of identified peaks was 25 and 23 for rPP and vPP, respectively. From these, 22 peaks are common to both materials. Regarding unique peaks, 3 were found in rPP(cmp) and 1 in vPP(3dP). The FTIR spectra of both samples match the typical spectrum of PP[11] whose characteristic IR peaks are located at 2952 cm^{-1}, 2917 cm^{-1}, 2838 cm^{-1}, 1455 cm^{-1}, 1375 cm^{-1}, 1165 cm^{-1}, 997 cm^{-1}, 972 cm^{-1}, 840 cm^{-1}. All of these peaks were clearly identified in both materials. With TGA analysis a considerable difference in final residual weight was verified: 3.67% for rPP(cmp) vs 0.193% for vPP(3dp). Thus, the former value is 18 times higher than the latter. This may indicate that rPP has a much higher content of inorganic fillers and additives in

comparison to vPP. The polymer temperature of degradation was found to be similar for both filaments but with considerable differences in rate of degradation: 451ºC and 30.77 %/min for rPP(cmp); 455ºC and 24.01 %/min for vPP(3dp). Based on the residual weight curve and first derivative curve shapes both materials presented only 1 step of degradation and thus, only 1 major constituent is likely present in each material. For the volatiles content the temperature interval considered was [T_i, 350ºC]. The volatiles content was found to be 1.609% for the former and 0.72% for the latter material. A such, the volatiles content of rPP(cmp) sample is approximately twice of vPP(3dp) sample. With the diameter control process, it was possible to obtain graphical profiles of the best filaments and statistical data. From the first cycle of extrusions (performed in the twin-screw extruder) the best results were D1 and X1 and for the extrusion in mini extruder the best result was P1. Overall, all filaments from 2nd extrusion in mini extruder were better than those from the twin-screw extruder. These are shown in table 7.

Table 6: Diameter control process statistics for filament samples D1, X1 and P1.

Filament D1				
#Points	Length (m)	Avg Diam (mm)	Stdev (mm)	Stdev/Avg (%)
46	4.50	1.75	0.23	13.35
Filament X1				
#Points	Length (m)	Avg Diam (mm)	Stdev (mm)	Stdev/Avg (%)
103	10.20	1.90	0.22	11.39
Filament P1				
#Points	Length (m)	Avg Diam (mm)	Stdev (mm)	Stdev/Avg (%)
40	3.90	1.72	0.12	6.86

Filament P1 presented an average diameter close the target value (1.75 mm) while having a low standard deviation (0.12 mm or 6.86%) and thus, a more consistent filament in terms of shape. However, it was rather short at 3.90 m length. For the tensile tests 5 specimens of rPP(cmp) and 3 specimens of vPP(3dp) were used. The stacked stress-strain curves for rPP(cmp) and vPP(3dp) are presented figure 7 along with bar charts for main properties of each specimen for comparison and an image from the trial with one of vPP specimens. The main results obtained are shown in table 8 below with the average values:

Table 7: Main results from tensile tests.

Filament	Young's Modulus *E*		
	Avg (GPa)	StDev (GPa)	R^2 Min (%)
rPP CMP	1.024	$2x10^{-3}$	99.96
vPP 3DP	0.371	0.001	99.94

Filament	σ_y		ϵ_y		UTS		ϵ_f		ϵ_f/ϵ_y
	Avg (MPa)	StDev (MPa)	Avg (%)	StDev (%)	Avg (MPa)	StDev (MPa)	Avg (%)	StDev (%)	Avg (a.u.)
rPP CMP	2.96	0.39	0.489	0.042	17.48	2.43	4.08	0.46	8.4
vPP 3DP	4.102	1.02	1.264	0.082	26.02	1.81	847.8	327.3	675.2

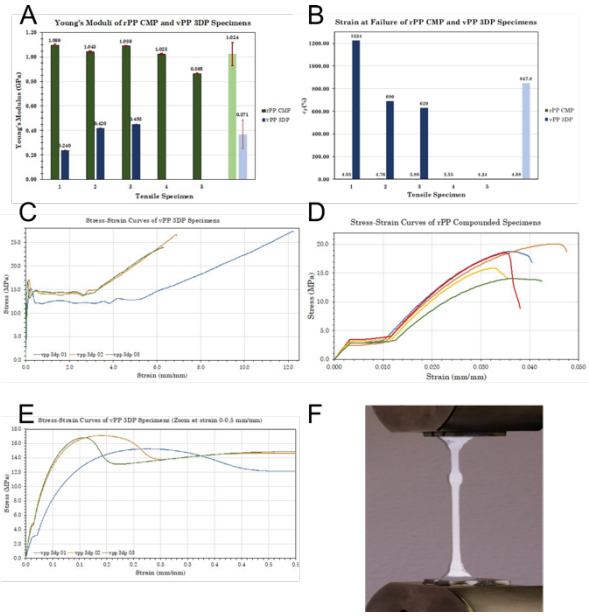


Figure 7: Bar charts with Young's Moduli (A) and strain at failure (B) for rPP(cmp) and vPP(3dp) specimens. Overview (C) and zoom-in (E) of stress-Strain plots of vPP(3dp) and rPP(cmp) (D); Example of vPP(3dp) specimen under tensile load (F).

According to Young's Modulus, rPP(cmp) specimens are 3 times stiffer than vPP(3dp). vPP(3dp) reached yielding later in the tests with tensile strength around 2 times higher and tensile strain approximately 3 times higher than rPP(cmp). The most notable (and abysmal) difference is regarding failure point, namely, the strain at failure. UTS was higher for vPP(3dp) at 26 MPa compared to 17.5 MPa for rPP(cmp). The nominal strain of failure of vPP is 2 orders of magnitude higher which indicates it has a much better capacity at accommodating plastic deformation after yielding until it reaches failure compared to rPP(cmp). This shows that vPP(3dp) has much higher ductility (ratios of 8.4 for rPP(cmp) vs 675.2 for vPP(3dp)). When the test specimens were inspected to assess quality prior

to testing it was possible to note that upon handling them they seemed somewhat rubbery, elastic, very flexible and malleable. A hypothesis for such is that vPP(3dp) material contains elastomeric additives that provide such characteristics.

4. Conclusions

With this work several conclusions can be highlighted. It was verified that the rPP(bulk) sourced directly from the waste treatment facility is mostly composed by PP, PE and high-density PP (high content of inorganic additives according to TGA data). Some additives identified by FTIR were EPDM, calcium carbonate and poly(1-butene). The best extrusion results on the twin-screw extruder, first cycle of extrusions, were obtained with the following parameters:
S=15 RPM, T = {200,200,190,170}
S=15 RPM, T = {170-180,200,190,170}.
According to diameter control process the best filaments were all obtained from the mini extruder. This is possibly due to the control feedback loop with integrated diameter measurer. P1 was identified as the best filament overall: 1.72 mm average diameter, standard deviation of 0.12 mm (6.86%) and 3.90 m length. It was not possible to obtain adequate filament for printing. During characterisation, major differences were identified with TGA analysis regarding inorganic content. MFR values for rPP(cmp) and vPP(3dp) were 11.1 4.5 g/10min, respectively. The most notable difference in the mechanical tests was the strain at failure and UTS: 4.08% and 17.5 MPa for rPP(cmp), 857.8% and 26.0 MP for vPP(3dp). This work contributes to some identified gaps in the literature: complete data of characterisation of PP material sourced directly from a waste treatment facility and commercial PP filament for 3DP used for benchmarking. One gap was not possible to address: no printable rPP filament was obtained. Suggestions for future work include the following: experimenting with mixtures of rPP(mix) and vPP(3dp) for extrusion, compatibilizers (e.g. maleic anhydride) and additives (elastomers for higher flexibility and elasticity, e.g. EPDM to approximate vPP(3dp) behaviour). Promotion of open-source commercial polymers and open-source recycling hardware for better recyclability and efficiency could also be interesting approaches given that some existent solutions already provide very good results[12–14].

5. References

1. Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. Sci Adv. 2017 Jul 1;3(7):e1700782.
2. Ritchie H, Roser M. Plastic Pollution. Our World in Data [Internet]. 2018 Sep 1 [cited 2019 Oct 28]; Available from: https://ourworldindata.org/plastic-pollution
3. Rochman CM, Hoh E, Kurobe T, Teh SJ. Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. Sci Rep. 2013 Dec;3(1):3263.
4. Iunolainen E. Suitability of recycled PP for 3D printing filament. 2017;48.
5. Domingues J, Marques T, Mateus A, Carreira P, Malça C. An Additive Manufacturing Solution to Produce Big Green Parts from Tires and Recycled Plastics. Procedia Manufacturing. 2017 Jan 1;12:242–8.
6. RepRap PT. RepRap 3D Printer Shop | Filamento, Peças e Impressoras 3D - Filamento, Peças e Impressoras 3D [Internet]. 2021 [cited 2021 May 1]. Available from: https://reprap.pt/
7. ASTM D638. Test Method for Tensile Properties of Plastics [Internet]. ASTM International; 2015 [cited 2021 Jun 2]. Available from: http://www.astm.org/cgi-bin/resolver.cgi?D638-14
8. Giles HF, Wagner JR, Mount EM. Extrusion: the definitive processing guide and handbook. Amsterdam: William Andrew, an imprint of Elsevier; 2014. 620 p. (PDL handbook series).
9. Harper CA, editor. Handbook of plastics, elastomers, and composites. 4th ed. New York: McGraw-Hill; 2002. 884 p. (McGraw-Hill handbooks).
10. Exxon Mobile Chemical. Polypropylene Product Data Sheets | ExxonMobil Chemical [Internet]. 2021 [cited 2021 Jun 16]. Available from: https://www.exxonmobilchemical.com/en/resources/product-data-sheets/polypropylene
11. Gopanna A, Mandapati RN, Thomas SP, Rajan K, Chavali M. Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and wide-angle X-ray scattering (WAXS) of polypropylene (PP)/cyclic olefin copolymer (COC) blends for qualitative and quantitative analysis. Polym Bull. 2019 Aug 1;76(8):4259–74.
12. Woern AL, McCaslin JR, Pringle AM, Pearce JM. RepRapable Recyclebot: Open source 3-D printable extruder for converting plastic to 3-D printing filament. HardwareX. 2018 Oct;4:e00026.
13. Capotexl. Filament Factory – A 3D Printer Filament Extruder [Internet]. Capotexl. 2014 [cited 2021 Jul 25]. Available from: https://capotexl.de/diy-filament-extruder/
14. Lyman, Mulier. Lyman / Mulier Filament Extruder V5 by hlyman [Internet]. Thingiverse.com. 2014 [cited 2021 Jul 10]. Available from: https://www.thingiverse.com/thing:380987