

A comparative study of recycled PET, PETG, and virgin opaque PET for material extrusion

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Abstract: Additive manufacturing using material extrusion (MEX) is a widely used technology that facilitates the creation of durable, lightweight, and stable components for various applications. Polyethylene terephthalate (PET), the most used plastic for bottles, cannot be printed due to inadequate rheological properties. This study aims to characterize recycled PET (PETr) to identify the optimal parameters and conditions necessary for this polymer to compete effectively with conventional thermoplastic filaments used in 3D printing. A comparative study is conducted between PETr, virgin opaque PET (PETo) to assess PETr's performance against virgin opaque PET, and PETG (polyethylene terephthalate glycol), one of the most used materials in MEX. This work is part of a larger project whose ultimate goal is to modify PETr to achieve rheological properties similar to PETG. Materials undergo different transformations through extrusion, drying, and thermocompression, followed by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and rheological testing to assess thermal and mechanical properties. Initial DSC results indicate that PETr and PETo are semi-crystalline, melting at approximately 238°C-257°C, while PETG is amorphous. TGA results show a degradation temperature of 443°C – 451°C. Rheological tests reveal a Newtonian plateau whatever the temperature for PETG in the frequency range, whereas the viscosity of recycled PET and opaque PET exhibit a significant change in viscosity curves with temperature. Findings suggest that recycled PET is currently not a viable option, the polymer must be formulated to adjust its thermal and rheological properties to be considered as a competitive option for 3D printing applications, aligning environmental benefits with the mechanical standards of commercial filaments.

Introduction

Polyethylene terephthalate (PET) is a widely produced thermoplastic polymer, with approximately 26 million tons manufactured in 2020 [1], accounting for a significant portion of the 460 million tons of plastics produced globally in 2019 [2]. PET, a non-biodegradable material derived from petroleum, is primarily utilized for bottle manufacturing 69 %, films 14 %, packaging 10 %, and other applications 7 %. Its exceptional barrier properties against water, moisture, and oxygen, along with high tensile strength and impact resistance, make it indispensable in industries like food, pharmaceuticals, and cosmetics [3].

However, PET's predominant use in single-use applications results in large amounts of plastic waste, contributing to environmental pollution and microplastic dispersion. In 2019, among the 353 million tons of plastic waste generated worldwide, only 9 % were recycled [2]. And for PET, just 7 % undergoes closed-loop recycling [3]. Mechanical recycling is the most adopted PET recycling method to reprocess PET with an adapted formulation for a targeted application [4]. However, thermomechanical and hydrolytic degradation occurs during recycling via molecular



chain scission, leading to a reduction in molecular weight and intrinsic viscosity [5]. As a result, the properties and performance of the recycled material are impacted, limiting its use for specific applications. But this problem can be mitigated by adding virgin polymers or chain extenders to maintain material properties [6, 7, 8].

3D printing through Material Extrusion (MEX) enables the production of robust, durable parts for diverse applications [9, 10]. Progress over the years have led to the development of a diverse range of thermoplastics suitable for 3D printing including polylactic acid (PLA) [11], acrylonitrile butadiene styrene (ABS) [9], polyethylene terephthalate glycol (PETG) [10], thermoplastic polyurethane (TPU) [12]. Each thermoplastic material has its own properties, and printing conditions must be adapted to the materials considering their intrinsic characteristics. Key parameters include printing speed, printing temperature and bed temperature, all of which influence the quality of printed parts [13]. Additionally, the mechanical behavior of printed parts, such as stiffness, elasticity, tensile strength, compressive strength, and torsional resistance, depends on the initial material properties and layer adhesion. Viscosity being a crucial factor in successful 3D printing [11]. Most 3D printing materials, including PETG, ABS, and PLA, possess a shear thinning behavior, which promotes good adhesion to the print bed and between layers. PET fails to meet these rheological requirements due to its rheological properties in the melted state and its semi-crystalline nature, which leads to a sudden viscosity drop at printing temperatures. Moreover, recycled PET (PETr) undergoes molecular chain scissions caused by mechanical recycling, resulting in lower viscosity and modification of the rheological behavior.

This study focuses on characterizing recycled PET (PETr) to determine the optimal parameters and conditions for enabling this polymer to compete with standard thermoplastic filaments used in 3D printing. A comparative study is conducted between PETr, virgin opaque PET (PETo) to assess PETr's performance against virgin opaque PET and PETG, one of the most used materials in MEX.

Experimental

Material. The PETG, smartfil® PETG, was supplied by smart materials 3D (Spain). The filament is 1.75 mm in diameter with a glass transition temperature (T_g) of 78 °C, a density of 1.27 g/cm³ and a recommended printing temperature range of 230 – 245 °C [14].

The virgin opaque PET pellets (PETo) Arnite A04 900 in white, were purchased from the Dutch company Plast. The information provided by the supplier are an intrinsic viscosity (IV) between 0.5 dl/g and 0.6 dl/g, a density of 1.17 g/cm³ and a melting temperature (T_m) between 243 °C to 250 °C [15]. Water bottles made from PET were collected from domestic waste. These bottles were shredded with a pellet mill.

PET is a homopolymer synthesized through the esterification of terephthalic acid (TPA) and ethylene glycol (EG) [16] as presented in the chemical scheme shown in Fig. 1. PETG is chosen because of its similarity in a part of its chemical structure with PET as seen in Fig.1. PETG is a random copolymer obtained through polycondensation of bis(hydroxyethyl)terephthalate (BHET) and bis(hydroxymethylcyclohexane)terephthalate (BHCT), themselves obtained by the esterification reaction of terephthalic acid (TPA) with ethylene glycol (EG) for BHET, with 1,4-cyclohexanedimethanol (CHDM) for BHCT [13]. The PETG random copolymers consist of ethylene glycol terephthalate (ET) and 1,4-cyclohexanedimethanol terephthalate (CT) units.

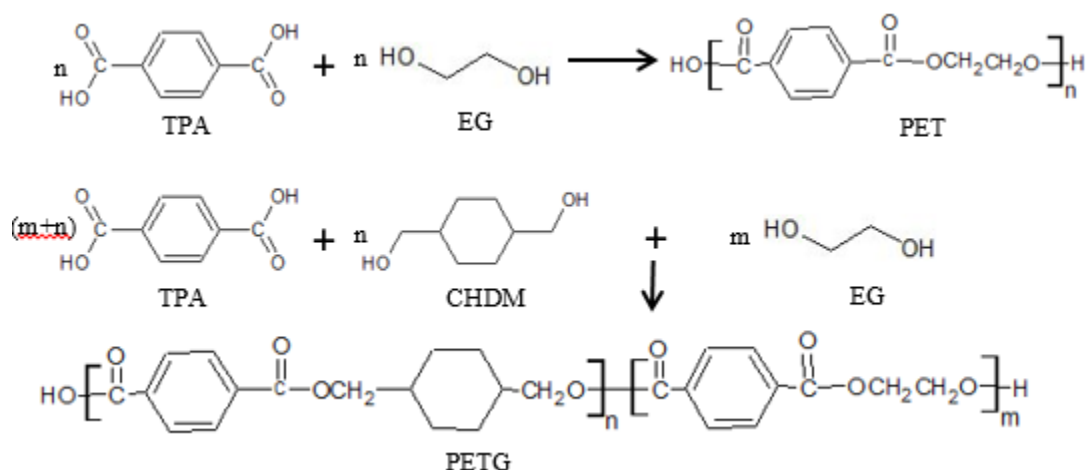


Figure 1 – PET and PETG synthesis reactions

Extrusion process and production of testing plates. PETo pellets and PETr flakes are turned into filaments by extrusion. The both were dried for 12 hours at 100 °C before being processed in a Thermo Fisher Process 11 counter-rotating twin-screw extruder, cylinder length 40, barrel diameter 11 mm with different temperature zones, as shown in Fig. 2. The temperature profiles for each zone of the extruder, determined after multiple attempts to successfully extrude the filament and wind it, are presented in Table 1 for PETo and PETr. The screw speed was set at 100 rpm. PETG was initially supplied in filament form. PETG, PETo and PETr filaments were pelletized into 1-2 mm length pieces and moved to the subsequent steps.

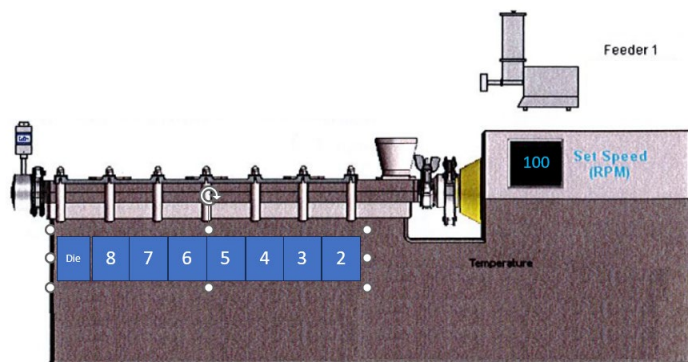


Figure 2 – Twin-screw extruder with different temperature zones [17]

All pellets were dried at 70 °C for 8 hours before undergoing thermocompression. The upper and lower plates of the thermocompression press were heated to 250 °C for PETG and 270 °C for PETo and PETr, with a heating rate of 10 °C/min. Each material was subjected to a force of 50 kN, applied at a rate of 10 kN/s, and held for a duration of 600 seconds into a mold. The so-obtained plates were cooled to 80 °C for PETG and 95 °C for PETo and PETr at a rate of 10 °C/min before being demolded. The 102 mm long, 50.2 mm wide and 1.0 mm thick plates, were dried again at 70 °C for 3 hours and stored at room temperature in sealed bags inside a desiccator. Specimens for thermal and rheological tests were cut into these plates.

Small pieces weighing a few milligrams were cut from the plates for Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Circular and rectangular samples were cut for rheological tests on PETG, PETo and PETr. All circular samples with a diameter of 25 mm were prepared using a disc cutter with a hydraulic press and were used for parallel plates experimentations. Rectangular samples, measuring 45 mm in length and 10 mm in width, were cut using an electric circular saw and used for dynamic mechanical analysis (DMA) in rectangular torsion mode.

Table 1 – Temperature zones of the extruder for PETr and PETo

	Temperature zones [°C]							
	1 (Die)	8	7	6	5	4	3	2
PETr	220	220	255	265	265	260	240	220
PETo	258	250	260	265	270	270	265	260

Characterization of polymers

Thermogravimetric Analysis (TGA). The TGA analysis of PETG, PETo, and PETr samples were carried out using a Mettler Toledo TGA thermogravimetric analyzer. This test measures the mass loss of materials with temperature. Samples used for the test weighed 8 to 10 mg. Each sample was heated from 25 °C to 600 °C at a rate of 10 °C/min in a nitrogen atmosphere with a flow rate of 50 ml/min to assess the thermal stability of the materials. The tests were repeated twice for each material.

Differential Scanning Calorimetry (DSC). Differential Scanning Calorimetry (DSC) scans were carried out on a DSC Mettler Toledo. Samples of around 10 mg were heated with a temperature ramp of 10 °C/min from 25 °C to 300 °C, then cooled from 300 °C to 25 °C and finally heated from 25 °C to 300 °C, under a nitrogen flow of 50 ml/min. Between each step, the temperature was maintained for 1 min. Experiments were repeated 3 times. The first heating is done to cancel the thermomechanical history of the material. The aim is to compare the structure of PETG, PETo, and PETr without considering their processing conditions. Finally, a second heating was undertaken to measure the thermal transitions. Glass transition temperature (T_g), melting temperature (T_m), were obtained on heating and crystallization temperature from the melted state (T_c) on cooling. The results were analyzed with TA Universal Analysis 2000 software (TA Instruments). The degree of crystallinity is calculated by divided the measured melting enthalpy by the theoretical melting enthalpy of the PET if 100% crystallized, which is 140 J/g for PET [18].

Rheological characterization. Rheological behavior of the studied polymers was investigated using an ARES LN2 rheometer from Rheometric Scientific. The samples were dried for 12 hours at 80 °C prior to testing to eliminate any moisture that might interfere with the results. Two types of tests were conducted: dynamic mechanical analysis in rectangular torsion mode, which included strain sweep and temperature sweep measurements (DMA), and parallel plate tests, which included strain sweep and frequency sweep measurements. All tests were performed under an air flow. The DMA tests were conducted with a ramp of 3 °C/min, a fixed frequency of 1 rad/s, and a strain of 1 %. The temperature ranged from 25 °C to 300 °C. The parallel plate tests were performed using with 25 mm diameter specimens and a fixed gap of 1.5 to 2 mm. During the frequency sweeps, the strain was fixed at 10 %, and the frequency varied from 100 to 0.01 rad/s at different isothermal conditions. Previously, the strain sweeps were performed under isothermal conditions at different frequencies to determine the linear visco-elastic (LVE) domain. The strain and frequency were chosen within the LVE domain for both types of tests. The storage (G') and loss moduli (G'') were measured and used to calculate the dynamic complex viscosity η^* by using (Eq. 1) with the angular frequency ω (Eq. 2) where T is the period:

$$|\eta^*| = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad (1)$$

$$\omega = \frac{2\pi}{T} \quad (2)$$

Results and discussion

Thermogravimetric analysis was carried out on PETr, PETo and PETG to assess the thermal stability and degradation stages. Fig. 3 shows mass loss (TGA) and derivative mass loss curves

(DTG) with temperature. In all cases, no weight loss is observed on a wide temperature range which is followed by a single step of mass loss. This mass loss is attributed to PET polymer degradation process due to random scission of ester bonds in the main chain leading to smaller chains (i.e. oligomers). It is clear from all the TGA curves that all the samples present a thermal stability on a temperature range of 25 – 380 °C and that the overall degradation occurs in one-step. Under this inert atmosphere, degradation reaction ceased at a residual waste of around 20 % for PETr and PETo and under 10 % for PETG. This difference between PETr, PETo and PETG is due to the different chemical structures as seen in Fig.1. Further degradation appears to continue at a negligible rate. The T_{onset} , T_{max} et T_{end} of the degradation obtained from DTG analysis are presented in Table 2. The degradation temperature difference observed between PETr et PETo, i.e. the lower T_{max} for the recycled PET, is due to chain scissions occurring during the recycling process. In view of 3D printing, these tests provide information on the temperatures not to be reached at the risk of damaging the material. Whereas manufacturers' specifications set printing temperatures in the range 230 – 245 °C for PETG [19], TGA tests also enable us to estimate the changes within the material when it has a longer residence time in the nozzle, the nozzle being the part of the printing head where the filament is melted. Since the residence time in the nozzle can influence the output material properties, isothermal TGA tests with time can help to determine the printing speed, to prevent the filament from degrading as much as possible. These isothermal tests will be carried out soon. However, such results demonstrate that the thermal stability of PET and recycled PET is closed to PETG's one, making them suitable to continue further this study.

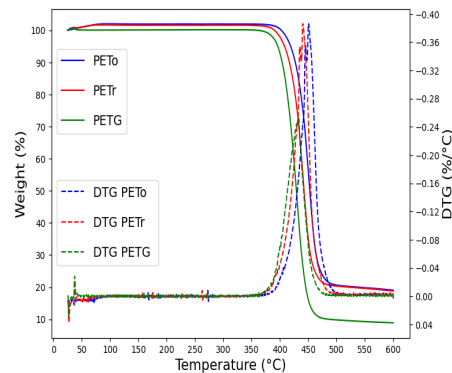


Figure 3 – TGA and DTG thermograms of PETo, PETr and PETG at 10 °C/min under nitrogen

The DSC curves presented in Fig. 4 show the heat flow with temperature during heating and cooling cycles. The thermal transitions that undergo the samples are summarized in Table 3: glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c). For PETo and PETr, the glass transition temperature was measured at 87 ± 2 °C during the first heating cycle. Then an endothermic peak attributed to the melting of the crystalline phase is observed at 257 ± 2 °C for PETo whereas a double-melting peak at 238 ± 2 °C and 247 ± 2 °C is visible for the PETr that can be due to crystal sizes or phases that melt differently [20]. While a single melting peak at 254 ± 2 °C for PETo and 249 ± 2 °C for PETr is observed during the second heating. A more uniform crystalline structure after controlled cooling in the DSC experiment can explain the single melting peak during the second heating.

Table 2 – Data of DTG curves

	T_{onset} [°C]	T_{max} [°C]	T_{end} [°C]
PETo	369	451	498
PETr	366	440	494
PETG	364	443	479

These results show that the thermomechanical history has an influence on the melting temperature. This melting phenomenon indicates that PETr and PETo undergo a structural rearrangement at these temperatures. In 3D printing, these temperatures correspond to the extrusion temperature, where the material starts to flow and can pass through the nozzle. During the cooling stage, an exothermic peak is observed for both PET, at 225 ± 2 °C for PETo and at 206 ± 2 °C for PETr, due to recrystallization from the molten polymer. From this point, the material enters a solidification phase. During printing, this cooling must be controlled to ensure proper adhesion of layers. A similar study on PLA showed that the exothermic peak indicating the crystallization kinetics, is observed at 3 °C/min, this rate represents the cooling rate that must be applied during 3D printing to guarantee complete crystallization and improve the rigidity of the printed parts [11]. Similar degree of crystallinity, $\chi_c = 22 \pm 1\%$, is observed for PETr and PETo. Apart from the molecular weight and the cooling rate, other factors influence the degree of crystallinity like the polymer formulation with the presence of plasticizers and additives such as TiO₂ nanoparticles in PETo and dye in PETr. A more uniform crystalline structure after controlled cooling in the DSC experiment can explain the single melting peak during the second heating.

For PETG, the glass transition temperature was measured at 82 ± 2 °C during the first heating cycle and at 75 ± 2 °C during the second heating. The PETG curve during the first heating show above the glass transition temperature perturbations due to weak exothermic and endothermic phenomena which may be related to crystallization [21]. But DSC analysis alone is insufficient to confirm the presence of a crystalline phase in PETG. Also, these perturbations are absent during the second heating, confirming that PETG is an amorphous polymer and that the first heating effectively removes the material's thermomechanical history. This amorphous structure gives PETG greater dimensional stability during 3D printing. Since no crystallization happens, no molecular re-organization takes place under the effect of heating, PETG does not require strict control of cooling temperatures; the material layers would adhere more easily to each other, and the PETG printed parts would be less prone to distortion than PET.

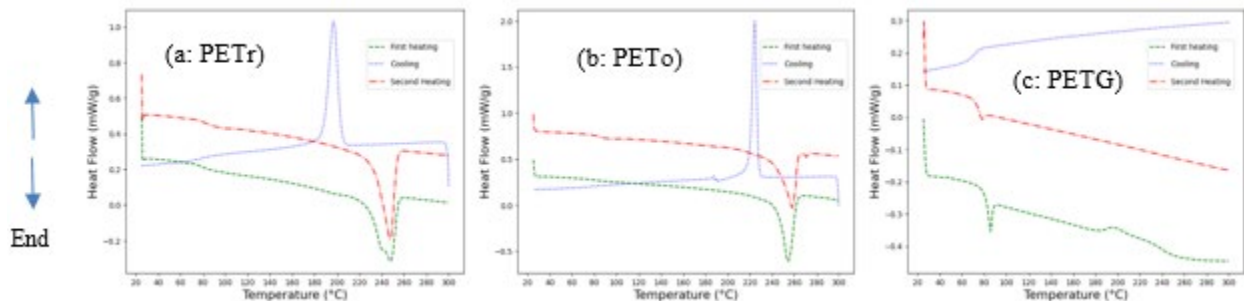


Figure 4 – DSC curves determined at 10°C/min for (a) PETr, (b) PETo and (c) PETG

Table 3 – Summary of DSC results for PETr, PETo and PETG

Material	First Heating			Cooling	Second Heating		
	Tg [°C]	Tm [°C]	ΔH_m [J/g]		Tg [°C]	Tm [°C]	ΔH_m [J/g]
PETr	86 ± 3	238 ± 2 and 247 ± 2	29 ± 1	206 ± 3	86 ± 3	249 ± 3	32 ± 1
PETo	85 ± 2	257 ± 2	28 ± 1	224 ± 2	88 ± 2	254 ± 2	32 ± 1
PETG	83 ± 2	-	-	-	75 ± 2	-	-

Fig. 5 shows the storage modulus (a) and loss modulus (b) of PETo, PETr, and PETG, heated from 25 °C to 300 °C. The decrease in the storage modulus G' (which indicates the material's elasticity) observed in Fig. 5a is characteristic of the glass transition. The glass transition temperature (Tg) of PETG occurs between 80 °C and 90 °C, while that of PETr and PETo is

between 85 °C and 90 °C. These results agree with the T_g measured by DSC. The storage modulus of PETo and PETr is slightly higher than that of PETG, indicating that these two materials are more rigid. The difference in G' between PETo and PETr may result from the recycling process, which reduces the rigidity properties of PETr because of shorter macromolecules. Additionally, the melting of PETr and PETo is observed between 240 °C and 250 °C. For PETG, G' drops sharply after the T_g , explained by its amorphous nature, transitioning from a glassy into a rubbery state. The viscous modulus or loss modulus G'' rises sharply with increasing temperature, showing the glass transition peaks. For PETG, G'' then decreases abruptly, while PETr and PETo maintain a higher G'' over a broader temperature range. The viscous modulus indicates the ability of the material to dissipate macromolecules' energy into heat. The sharp peak as passes the glass transition is attributed to a narrower molecular mass distribution in PETG compared to PET.

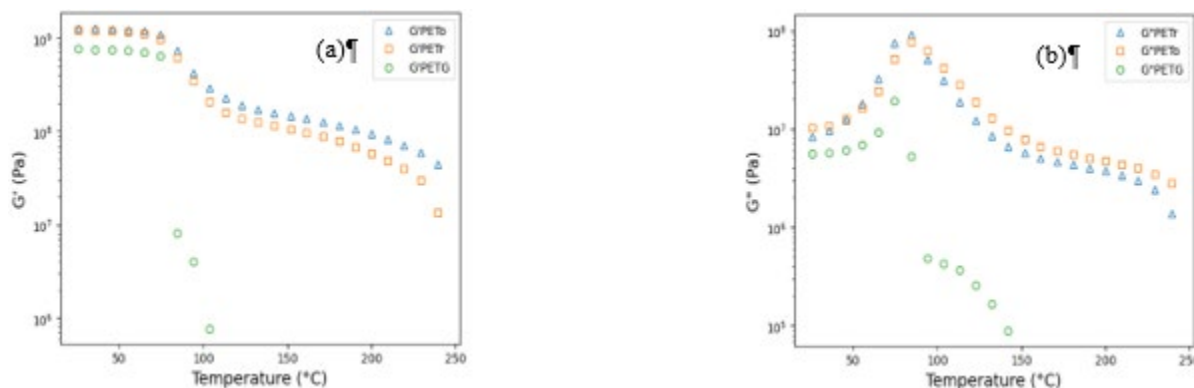


Figure 5 – DMA diagrams recorded during heating at 3°C/min of PETo, PETr, and PETG: (a) variation in storage modulus; (b) variation in loss modulus

Fig. 6 illustrates the storage modulus G' and the loss modulus G'' as a function of angular frequency for PETo, PETr, and PETG at a temperature of 240 °C. It is worth noticing that the measurements are performed on a narrow frequency range starting from the highest frequency to prevent degradation of the material. This experiment was reproduced at different temperatures for each polymer, only 240 °C is shown for the sake of brevity. All the curves demonstrate a similar behavior. A plateau of G' and G'' is observed for PETr and PETo, indicating a gel-like behavior in the range 100 to 0.1 rad/s. On the contrary, PETG demonstrates a quasi-typical behavior of molten polymer in the terminal zone. According to the Rouse model, the moduli follow the rule of $G' = G\omega^2\tau^2$ and $G'' = G\omega\tau$ with G the modulus, ω the angular frequency and τ the relaxation time. So, the slope of $\log G'$ and $\log G''$ are supposed to be of, respectively, 2 and 1 in the terminal region at low shear rate. In our case, the slopes of PETG's curves are 1.44 for G' and 1.01 for G'' . Regarding the values of G' and G'' , the highest values are reached for PETo, followed by PETr which agrees with the expectation due to shorter chains in recycled polymer. In the terminal zone, PETG demonstrates lower G' and G'' compared to PET. As mentioned previously, the rheological behavior of PETG is different than those of PET, explaining that regular PET cannot be printed due to higher viscosity at the same frequency.

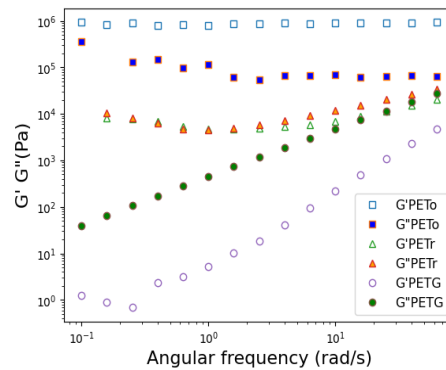


Figure 6 – Evolution of the moduli, G' and G'' of PETo, PETr and PETG with frequency at 240°C

Fig. 7 shows the curves of the dynamic complex viscosity of (a) PETr, (b) PETo and (c) PETG versus the angular frequency at different temperatures. The temperatures were selected according to the DSC results to ensure that the polymers were melted. It is worth noticing that PET is characterized in the range 240 to 270 °C whereas PETG has a broader range: 160 to 240 °C. From the selected temperatures, we point out another issue limiting the ability to print PET.

For PETG, the curves exhibit a Newtonian plateau and a shear-thinning region above around 10 rad/s, following the well-known flow curve for melted polymers.

Both PET show a strong shear-thinning behavior at 240°C in the frequency range without Newtonian plateau at low shear rate. On the contrary, the complex viscosity increases at low frequency, indicating structural changes with time. Time sweeps will be needed to confirm this hypothesis. When rising the temperature, the viscosity of both PETr and PETo decreases, it can be noticed that the gap in viscosity between 240 and 250 °C is much higher than in the range 250 to 270 °C. Both PET are very rigid at 240 °C: the complex viscosity is about $7 \cdot 10^3$ Pa.s for PETr and $8 \cdot 10^5$ Pa.s for PETo at 1 rad/s, making them very difficult to flow in these conditions. For instance, at 250°C and 1 rad/s, η^* is about 10^2 Pa.s for PETr and 10^3 Pa.s for PETo. PETr shows a lower viscosity than PETo, due to chain breaks within the material.

From these results, it can be concluded that PETG can be printed at temperatures up to 240 °C, whereas this temperature is not suitable for PETr and PETo due to too high viscosity. Indeed, the viscosity of polymer for printing is generally about 10 to 10^3 Pa.s [11], PETo can be printed at 250 and 270 °C whereas for PETr, 240 and 250 °C could be suitable temperatures.

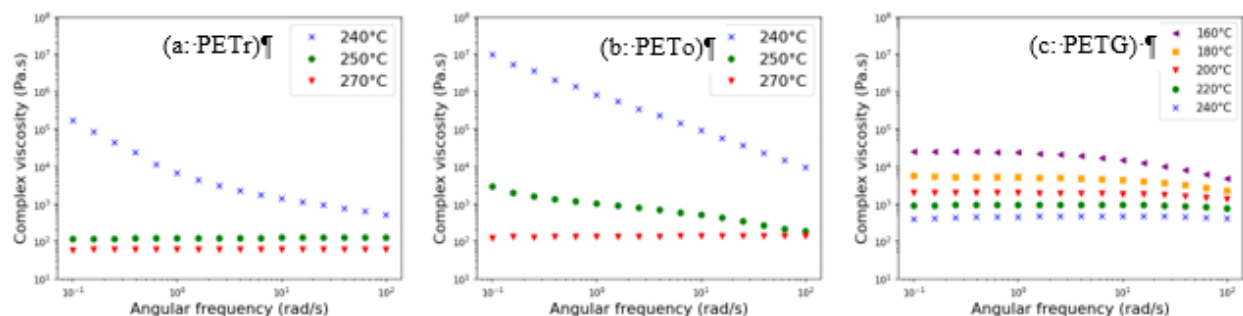


Figure 7 – Complex viscosity of (a) PETr, (b) PETo and (c) PETG at different temperatures

Conclusion

This study highlights the potential and limitations of recycled PET (PETr) for 3D printing applications through a comparative analysis with virgin opaque PET (PETo) and PETG. Using thermal and rheological characterizations, we determined their ability for extrusion. For PETr, its melting temperature is between 247 °C and 250 °C. This temperature is slightly lower than that of

PETo, which ranges from 254 °C to 257 °C measured by DSC and DMA. PET are more sensitive to thermal degradation than PETG as seen by TGA.

The glass transition of PETG is between 75 °C and 85 °C. However, it is recommended to print it between 240 °C and 250 °C, as rheological studies in plate/plate configuration show a behavior of a typical melted polymer with a Newtonian plateau in the terminal regime and a shear-thinning behavior at high frequency, with a stable complex viscosity within this range. In contrast, PETr and PETo change from rigid to low viscosity after melting, which is a disadvantage for the stability of flow needed when printing.

The viscosity drop in PETr is attributed to the mechanical recycling process, which causes issues such as molecular weight reduction due to chain scissions within the material. This underscores the importance of restoring PETr's molecular weight, either by blending it with virgin polymer or by using chain extenders.

References

- [1] Information on <https://www.enviroscope.com/les-plastiques-pet-un-marche-mondial-de-21-millions-de-tonnes/>
- [2] OECD, Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options. OECD, 2022. <https://doi.org/10.1787/de747aef-en>
- [3] Information on <https://cefic.org/a-solution-provider-for-sustainability/chemistrycan/driving-the-circular-economy/recycling-more-plastics/>
- [4] Information on <https://ramenetessciences.wordpress.com/2017/05/10/le-polyterephthalate-dethylene-pet/>
- [5] I. Cusano, L. Campagnolo, M. Aurilia, S. Costanzo, et N. Grizzuti. Rheology of Recycled PET. *Materials*, 16 (9), 2023. <https://doi.org/10.3390/ma16093358>
- [6] F. Awaja et D. Pavel. Recycling of PET. *Eur. Polym. J.*, 41(7), 2005, pp.1453-1477. <https://doi.org/10.1016/j.eurpolymj.2005.02.005>
- [7] M. Kruse et M. H. Wagner. Rheological and molecular characterization of long-chain branched poly(ethylene terephthalate). *Rheol. Acta*, 56(11), 2017, pp.887-904. <https://doi.org/10.1007/s00397-017-1043-y>
- [8] F. n. Cavalcanti, E. t. Teófilo, M. s. Rabello, et S. m. l. Silva. Chain extension and degradation during reactive processing of PET in the presence of triphenyl phosphite. *Polym. Eng. Sci*, 47(12), 2007, pp. 2155-2163. <https://doi.org/10.1002/pen.20912>
- [9] M. Samykano, S. K. Selvamani, K. Kadirgama, W. K. Ngui, G. Kanagaraj, et K. Sudhakar,. Mechanical property of FDM printed ABS : influence of printing parameters. *Int. J. Adv. Manuf. Technol*, 102(9), 2019, pp. 2779-2796. <https://doi.org/10.1007/s00170-019-03313-0>
- [10] Information on <https://www.mdpi.com/2073-4360/14/13/2564>
- [11] S. Bakrani Balani, F. Chabert, V. Nassiet, et A. Cantarel, (2019). Influence of printing parameters on the stability of deposited beads in fused filament fabrication of poly(lactic) acid. *Addit. Manuf*, 25, 2019, pp.112-121. <https://doi.org/10.1016/j.addma.2018.10.012>
- [12] V. M. Bruère, A. Lion, J. Holtmannspötter, et M. Johlitz. The influence of printing parameters on the mechanical properties of 3D printed TPU-based elastomers. *Prog. Addit. Manuf*, 8(4), 2023, pp. 693-701. <https://doi.org/10.1007/s40964-023-00418-7>
- [13] T. Chen, G. Jiang, G. Li, Z. Wu, et J. Zhang. Poly(ethylene glycol-co-1,4-cyclohexanedimethanol terephthalate) random copolymers: effect of copolymer composition and

microstructure on thermal properties and crystallization behavior. RSC advance, (2015).
<https://doi.org/10.1039/C5RA09252C>

[14] Information on <https://www.smartmaterials3d.com/fr/petg-filament>

[15] Information on
<https://www.campusplastics.com/campus/fr/datasheet/Arnite%C2%AE+A04+900/DSM/50/73406abe/US>

[16] E. Barnard, J. J. R. Arias, et W. Thielemans. Chemolytic depolymerisation of PET: a review. Green Chem, 23(11), 2021, pp.3765-3789. <https://doi.org/10.1039/D1GC00887K>

[17] Information on <https://assets.thermofisher.com/TFS-Assets/MSD/Specification-Sheets/PS53132-process-11-parallel-twin-screw-extruder.pdf>

[18] Information on <https://www.tainstruments.com/pdf/literature/TN048.pdf>

[19] Information on <https://www.smartmaterials3d.com/fr/petg-filament>

[20] C. A. Gracia-Fernández, S. Gómez-Barreiro, J. López-Beceiro, S. Naya, et R. Artiaga. New approach to the double melting peak of poly(l-lactic acid) observed by DSC. J. Mater. Res, 27(10), 2012, pp. 1379-1382. <https://doi.org/10.1557/jmr.2012.57>

[21] M. Kattan, E. Dargent, J. Ledru, et J. Grenet. Strain-induced crystallization in uniaxially drawn PETG plates. J. Appl. Polym. Sci, 81(14), 2001, pp. 3405-3412.
<https://doi.org/10.1002/app.1797>