



Article Additive Manufacture of Recycled Poly(Ethylene Terephthalate) Using Pyromellitic Dianhydride Targeted for FDM 3D-Printing Applications

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Abstract: The suitability of recycled poly(ethylene terephthalate) (R-PET) for 3D-printing applications was evaluated by studying the melt flow characteristics of the polymer. R-PET is known to experience significant deterioration in its mechanical properties when recycled due to molecular weight loss that results from reprocessing. Lower molecular weight hinders R-PET from being 3D-printable due to low viscosity and melt strength. The hypothesis was that R-PET can be modified with reasonable effort and resources to a 3D-printable thermoplastic if the low viscosity problem is tackled. Higher viscosity will enhance both the melt strength and the melt flow characteristic of the polymer, making it more suitable for processing and 3D printing. Reactive extrusion was selected as the method for modifying the polymer to achieve the objective via a coupling reaction with chain extender PMDA (pyromellitic dianhydride). A decrease in the melt flow index (MFI) from 90 to 1.2 (g/10 min) was recorded when PMDA was added at 0.75 wt% which lowered the MFI of modified R-PET to a comparable value to commercial 3D-printing filaments. Furthermore, FT-IR analysis was performed to investigate the chemical composition of the product. Finally, a 3D-printing filament was made from the modified R-PET by mimicking the main processing stations that exist in the filament-making process, which are the extrusion stage, water bath cooling stage and spooling stage. With 0.75 wt% PMDA, the melt strength was satisfactory for pulling the filament and, therefore, a filament with on-spec dimension was produced. Finally, a small object was successfully 3D-printed using the filament product at a minimum recommended temperature of 275 °C.

Keywords: 3D printing; poly(ethylene terephthalate); reactive extrusion; recycled thermoplastic

1. Introduction

The additive manufacturing, or 3D-printing, market has been growing fast in recent years as many companies and entrepreneurs see great potential in the market. In 2019, world plastic manufacturing was around 368 million tons as per Plastics Atlas [1], of which a majority of the thermo plastics can potentially be processed for additive manufacturing [2]. Today, 3-D-printing technologies have a wide range of applications from the construction industry [3–5], automobile applications [6–8], the food industry [9], the aerospace industry [10] and in jewelry collections [11], to more sophisticated medical applications and the manufacturing of artificial human organs [12–14]. Among several technologies, fused deposition modeling (FDM) is recognized as the most popular due to its simplicity and low capital cost [15–17]. In the last 15 years, 3D printing has become increasingly popular as



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). people realize the diversity of applications that 3D printing can contribute to. Therefore, more researchers and entrepreneurs dedicated time and effort to developing new technologies as well as enhancing existing ones. As a result, the additive manufacturing industry thrived unprecedentedly with the invention of various robust and commercially viable machineries. The classification of technologies of additive manufacturing processes can be achieved in many different ways based on the specific aspect the consumer is looking for. For example, it is common to classify 3D printers based on the technology baseline of the device, whether it uses a laser source to construct the object or an extrusion-based technology, as is the case in Fused Deposition Modelling (FDM) processes. However, this classification does not consider the type of the raw material (i.e., liquid photo-polymer, powder, solid polymer, etc.), which is an essential piece of information to end-users. Therefore, a more inclusive classification was developed that specifies two important dimensions in any additive manufacturing process: the method of constructing layers and the type of raw material. Firstly, the method of constructing layers was divided into two main subcategories: a one-dimensional source of construction, such as a nozzle, and a two-dimensional source which is essentially an array of one-dimensional sources of construction methods, such as those used in PolyJet technologies. The second dimension recognizes four types of raw material used in additive manufacturing: liquid polymers, discrete particles, molten materials and solid sheets. Among the different technologies, Fusion Deposition Modeling (FDM) technology is by far the most popular 3D-printing technology due to its relatively low cost and simplicity. It was first developed by the American company Stratasys, but competition from many other entities led to lowering the cost of this technology, making it feasible for home uses. In this type of 3D printing, raw materials are supplied as rounded filaments of a thermoplastic, or sometimes, a metal wire. In this technology, the 3D-printing device is equipped with a small nozzle, or in some cases two nozzles, that is connected to a heating element which allows the setup of the temperature of the nozzle at the melting point of the thermoplastic, or metal, raw material. The inlet I.D. of the nozzle comes in two different standard sizes: 3.0 mm and 1.75 mm, whereas the printer's nozzle size is often 0.4 mm (although it can be modified). The principle of this technology is that the raw material is fed to the heated extrusion nozzle where it melts, while maintaining specific melt flow characteristics. Then, it is ejected through the nozzle outlet on the printer's bed. This bed is movable by a motor and is often connected to a heating element to allow the melt to adhere to the heated bed. With the bed being movable in the *y*-axis and the nozzle movable on the *x*-axis, the printer uses the object's digital code and the 3D model to construct the first layer on the bed by continuously dispositioning the melt on specific x and y coordinates. Once the first layer is constructed, the nozzle moves in the z-axis to start constructing the second layer on top of the first one (which has already solidified). This move in the z-axis is as small as the thickness of the first layer (often 0.1 mm), and the smaller the thickness of each layer, the higher the object's resolution will be. The nozzle moves to the third layer after completing the second, and continues, until the whole object is constructed.

FDM technology mainly serves home users and enthusiasts as well as serving educational purposes, and it mainly utilizes thermoplastics, most commonly ABS (acrylonitrile butadiene styrene), PLA (poly(lactic acid)), and nylon, as the building materials for printed objects. With FDM 3D-printing technology being the most affordable and widespread, thermoplastics are the most suitable material for this extrusion-based technology. In FDM technology, raw materials should experience a phase change, from solid to viscous and paste-like, when heated in the extrusion chamber and should retain the mechanical properties when cooled down. Furthermore, melting and solidification must be well studied with respect to temperature and time to evaluate the suitability of a thermoplastic for additive manufacturing. It is suggested that amorphous thermoplastics are generally more suitable for FDM 3D printing than crystalline polymers. This is because amorphous polymers do not have a specific melting point; therefore, keeping them in the semisolid (paste-like) phase can be easily achieved by finding the right temperature. Having said that, some semi-crystalline thermoplastics, such as PLA, have been proven very suitable and are popular polymers for FDM printing.

ABS is one of the two most popular thermoplastics used in FDM machines (along with PLA). It is known for being a uniquely tough and ductile amorphous polymer that can withstand heavy uses. Moreover, ABS has excellent temperature resistance as it starts softening at relatively high temperatures (around 230 °C). ABS is also cheaper than other thermoplastics used for 3D printing. On the other hand, ABS has some disadvantages from an environmental and health point of view. Since it is a petroleum-based polymer, it is a non-biodegradable plastic. Furthermore, while 3D printing with ABS, it is anticipated that mild fumes will be released that can be easily smelled. Therefore, it is often recommended to have some ventilation in the room where ABS is being 3D-printed. ABS requires a heated bed in the printing machine to avoid warping. Polylactic acid (PLA) is a biodegradable polymer and is relatively easy to use. PLA has become one of the most favorable materials for 3D printing. Compared to ABS, PLA is considered a healthier and safer material to work with since it is not toxic and produces much safer fumes than ABS when 3D-printed. From the mechanical performance point of view, however, it is not as tough as ABS and is more brittle. Moreover, PLA starts to soften at relatively low temperatures (around 50 $^{\circ}$ C), which makes it less heat-resistant than ABS. The process of 3D-printing with PLA is carried out at roughly 210 °C, and it does not require a heated bed (although having a heated bed at around 60 °C can enhance the product's quality, depending on the object's size and shape). Since it is derived from renewable resources, such as corn starch, PLA can be used in printing parts with biomedical uses. High-Impact Polystyrene (HIPS) is known to have similar properties to ABS, but it is slightly more expensive. Because HIPS is soluble in Limonene, it is often used as a structural support for 3D printing other objects. Then, it is quickly dissolved and removed, resulting in cleaner finishing of the supported object. This saves users the effort of sanding their built object, which is a comparatively much more tedious job. HIPS is usually printed at 250 °C on a heated bed and is likely to experience less warpage than ABS. Nylon, which is also known as polyamide, is an increasingly used material in FDM printing. It has several desirable properties, such as strength, flexibility and durability. On the other hand, it is one of the most hygroscopic polymers among all kinds of thermoplastics. It absorbs moisture significantly and, as a result, users might need to dry it in an oven before using it to obtain good printing quality. Nylon is printed at around 250 °C and requires a heated bed at around 65 °C.

Poly(ethylene terephthalate), or PET, is the most recycled thermoplastic in Canada and arguably worldwide [18]. Additionally, it has unique desirable properties over other thermoplastics, including thermal and chemical stability and stiffness [19,20]. Therefore, utilizing PET waste in producing a 3D-printing filament can bring both economic opportunity and environmental benefits. On the other hand, like other thermoplastics, R-PET suffers drastic change in its mechanical properties when it is recycled, mainly due to degradation that causes loss in molecular weight [21–23]. Hence, it was expected that making filaments from R-PET and 3D printing with them would be challenging due to the deterioration in the polymer's melt flow characteristics mainly because of loss in molecular weight. However, it is believed that the polymer can be 3D-printable when modified by reactive extrusion.

Reactive extrusion is a popular method for modifying polymers since it offers several advantages over conventional polymerization processes, such as being a continuous process, massively reducing processing times and providing precise thermal control throughout the process. Several reaction types have been conducted by reactive extrusion (REX) including coupling reactions [24–27]. In coupling reactions, a functional coupling agent, or chain extender, is used to link separated polymer chains by reacting with end-groups in polymer chains. This linkage produces longer polymer chains with higher molecular weights (MWs) and, therefore, increases the polymer's viscosity. Qin et al. [28] used triphenyl phosphite as a chain extender in the reactive extrusion of PET. Yang et al. [29] used reactive extrusion with a multi-functional epoxide to produce PET with high melt elasticity. Among the several additives, pyromellitic dianhydride (PMDA) is an important additive

that has the promising attribute of increasing the intrinsic viscosity due to an increase in the molecular weight. It has been used to make foamable PET with supercritical carbon dioxide as a blowing agent and had an effect on intrinsic viscosity [30]. In this work, the chain extender PMDA was used as an additive for the reactive extrusion of PET due to its effectiveness and economic feasibility [31]. In addition, we show that actual printing is feasible and successfully carried out using recycled PET.

2. Materials and Methods

2.1. Sample Mixing and Drying

It was important to ensure proper mixing of R-PET flakes and PMDA powder since they were in different forms. Because the volumetric concentration of the additive was negligible in the mixture, a high-intensity mixer was selected for mixing the two components since this was the most suitable type in this case [32]. A single-screw-type extruder was used for the four samples of different wt% of PMDA (0%, 0.25%, 0.50% and 0.75%). Moreover, drying was achieved by allowing the sample mixture to dry in a vacuum oven overnight at 100 °C. For this, each sample was placed in a beaker covered with perforated aluminum foil.

2.2. Extrusion

The extrusion of compounded samples was achieved using two types of extruders: single-screw and twin-screw, for the purpose of comparison. The single-screw miniextruder was manufactured by Filabot and designed for private home-use where 3Dprinting enthusiasts can use the extruder to recycle their 3D-printed objects and produce a filament. This extruder has a fixed screw rotational speed of 35 rpm, whereas the temperature can be varied up to 400 °C. One unique feature of this extruder is the ability to replace the extruder's die with various die sizes that can be purchased from Filabot. Samples are fed into this extruder by simply pouring the sample into the extruder hopper, and the screw draws the material into the barrel until the hopper is empty. Design sheets for the extruder's barrel and screw were obtained for reference. The other extruder is a co-current self-wiping twin-screw mini-extruder manufactured by Thermo Fisher Scientific Company (Mississauga, Ontario, Canada). This extruder is a more advanced piece of equipment than the first and, therefore, provides many additional features such as the ability to manipulate the rotation speed and display the value of the die pressure and the torque and the pressure difference across the barrel. These features are useful as they can indicate the melt behavior inside the barrel. For example, a higher torque reading can be attributed to higher melt viscosity which can also be observed by an increase in the die pressure. The Filabot single-screw extruder was used for the filament manufacturing for two reasons: firstly, being a desk-top extruder, it has the advantage of being moveable and conveniently aligned with the other equipment; secondly, the sample from the hopper to the barrel can be drawn without any interference as opposed to when the twin-screw extruder is used. This latter feature is considered important because when interference is required by pushing the material to the extruder's barrel, it is expected that this might result in inconsistent discharge of the melt which results in inconsistency in the product's dimensions. In other words, if excessive pushing was applied at some point throughout the experiment, then the melt would have been discharged at a faster rate which would create variation in product specifications. Samples were compounded in the extruder, and the product was tested for the melt flow index (MFI) and then re-extruded for filament shaping.

2.3. Lab-Scale Filament Production Process

The filament production process included three main pieces of equipment: an extruder, cooling water bath and a spooler (or puller), which is the equivalent of the tractor system in conventional manufacturing processes. Filabot's spooler and a single-screw extruder were used. Further, a 3D-printed cooling water bath was used for the quenching stage.

The first step in the experiment was to establish a steady flow of warm water into and out of the cooling water bath. The temperature of the cooling water in the bath was in the range of $40 \sim 47$ °C throughout the experiment.

Once the flow to the cooling water bath was stabilized, extrusion was started at around 280 °C and 35 rpm. As a standard, we waited for about a minute to let the extruder's operation stabilize in order to have a consistent residence time for the polymer inside the extruder. Then, the melt was pulled manually, then immersed in the water bath and fed to the spooler. The spooling speed was adjusted to have the filament at the desirable diameter and also to maintain tension on the melt being pulled from the extruder's die. The filament diameter was measured manually every 30 s using a digital dial caliper tool, and the spooler's rotational speed was adjusted accordingly. The measuring point was chosen to be downstream of the spooler's rollers in order to avoid disturbance of the pulling process. Figures 1 and 2 show the laboratory filament extrusion setup that was used.



Figure 1. Laboratory filament-making setup.



Figure 2. Modified R-PET filament being pulled from the extruder.

We were able to produce few short-segments of modified R-PET that have on-spec filament dimensions when PMDA concentrations was approximately 0.75 wt%. Measurements of the filament diameters were taken at 4 different angles.

FDM filaments are produced commercially with a filament diameter of 1.75 mm and 3.00 mm with a tolerance of \pm 0.05 mm. Therefore, the commercial standard (1.75 mm \pm 0.05 mm) was considered as the baseline for determining an on-spec product.

3. Results and Discussion

3.1. Benchmarking MFI Values of Commercial Filaments and Unmodified R-PET

The MFI values of several commercial filaments were measured and compared against reprocessed R-PET. The temperature at which the MFI test was conducted for each filament was the printing temperature of that filament as recommended by the manufacturer since this allowed us to investigate the melt flow characteristics that occurred while printing with the filament. Further, the load that was used in the MFI test was kept constant for all materials (2.15 kg). The results are shown in Table 1. MFI values of all commercial filaments fell within a relatively narrow range (from 5 to 30 g/10 min), whereas R-PET (reprocessed in a single-screw extruder) had a significantly higher value.

Sample	Material (Manufacturer)	MFI T (°C)	Test 1 (g/10 min)	Test 2 (g/10 min)	Mean	Standard Deviation
1	PLA (Dremel)	215.0	24.64	21.11	22.87	2.50
2	PLA (Wanhao)	215.0	25.49	31.71	28.60	4.40
3	R-PET (reprocessed)	260.0	100.51	80.6	90.56	15.04
4	ABS (HATCHBOX)	245.0	5.18	5.60	5.39	0.29
5	Nylon (Taulman)	240.0	4.19	4.68	4.44	0.34
6	TPE elastomer (Filaments.ca)	240.0	17.31	19.10	18.21	1.26
7	PETG (MG Chemicals)	260.0	5.37	5.26	5.32	0.08

Table 1. Summary of MFI results of various filaments.

3.2. Effect of Chain Extender Concentration on Decreasing MFI of R-PET

The effect of PMDA concentration on the MFI value was studied at three different concentrations. Furthermore, MFI values were measured for all samples at three different temperatures, 260, 275, and 290 °C, in order to obtain a broader understanding of the melt behavior at various temperatures. These temperatures were carefully selected since they are within the suitable region for 3D printing with R-PET. Table 2 summarizes the MFI test results for modified R-PET.

Table 2. MFI results of unmodified R-PET (sample 1) and modified R-PET with 0.25%, 0.5%, 0.75% PMDA (samples 2, 3 and 4, respectively).

Sample	MFI at 260 $^\circ$ C (g/10 min)			MFI at 275 $^{\circ}$ C (g/10 min)			MFI at 290 °C (g/10 min)					
	Test 1	Test 2	μ_{260}	SD ₂₆₀	Test 1	Test 2	μ_{275}	SD ₂₇₅	Test 1	Test 2	μ ₂₉₀	σ ₂₉₀
1	100.51	80.6	90.56	14.08	>200	>200			>200	>200		
2	4.33	4.12	4.22	0.15	5.46	5.10	5.28	0.26	15.55	16.27	15.91	0.51
3	1.43	1.51	1.47	0.06	3.13	3.38	3.25	0.18	9.79	9.14	9.47	0.46
4	1.26	1.17	1.21	0.06	2.80	2.83	2.81	0.02	6.33	6.49	6.41	0.11

The results confirmed that the viscosity of the polymer was successfully increased via reactive extrusion with the PMDA chain extender. The figure shows a significant decrease in the MFI value that correlated with PMDA presence. Figure 2 demonstrates the MFI values as a function of temperature at various PMDA concentrations. Finally, the modified product had an MFI value that is comparable to those of commercial 3D-printing filaments.

3.3. Fourier Transform Infrared (FT-IR) Spectroscopy

In this analysis, all polymer samples were tested in a thin-film form that was made using a hot-press machine. The air signal was used as the background signal when testing polymeric materials. For powdered PMDA, the tested sample contained a mixture of PMDA and KBr that was made into a flake form using a cold-press, and pure KBr was the background signal. Figure 3 shows FT-IR spectra of modified R-PET at different PMDA concentrations as well as the IR spectrum of the PMDA additive. In this figure, a mild difference can be seen in transmittance between the samples in the region around 3250 cm⁻¹ to 3280 cm^{-1} . This region is important for characterizing PET in general since it is the carboxyl end-group absorption region [33,34]. Figures 3 and 4 show that when PMDA concentration was at the highest level (0.75 wt%), lower signal intensity was captured at around 3270 cm⁻¹, which indicates lower -COOH end-group presence. The difference between the other two samples (0.25% and 0.50%), however, was not clear. In the PMDA spectrum, the strong signals around 1770 cm⁻¹ and 1859 cm⁻¹ were assigned to the C=O stretching in the O=C-O-C=O that exists in the PMDA molecule [35].





Figure 3. FTIR results of modified R-PET (single-screw) and PMDA.



Figure 4. Carboxyl end-group region for modified R-PET.

3.4. Manufacturing a Lab-Made 3D-Printing Filament

Samples were ground and dried prior to extrusion for filament making. The first step in the experiment was to establish a steady flow of warm water into/out of the cooling water bath. The temperature of the cooling water in the bath was in the range of 40~47 °C throughout the experiment. Then, extrusion was started at 280 °C and 35 rpm. The melt was pulled manually, then immersed in the water bath and fed to the spooler. The spooling speed was adjusted to have the filament at the desirable diameter and also to maintain tension on the melt being pulled from the extruder's die. The filament diameter was measured by a digital dial caliper tool, and the spooler's rotational speed was adjusted accordingly.

In this study, a few short segments of modified R-PET that have on-spec filament dimensions could be produced when PMDA concentration was around 0.75 wt%. Figure 5 shows a magnified image of the filament's cross-sectional area that validates the good ovality that was achieved. Additionally, two other attempts were made to pull a filament of R-PET modified with PMDA concentrations of 0.5 wt% and 0.25%, but these were not successful due to melt breakage.



Figure 5. Magnified image of cross-sectional area of lab-made filament from modified R-PET showing good ovality (magnification: X12.6).

3.5. D-Printing with Lab-Made R-PET Filament

Finally, using the lab-made filament, with an extrusion temperature of 275 $^{\circ}$ C and a bed temperature of 120 $^{\circ}$ C, a first layer of a small object was successfully 3D-printed, as shown in Figure 6. As shown in Figure 6, the green object was made with ABS material, while the black object was made by using the modified R-PET obtained in our study. This clearly shows that modified R-PET can be successfully used for 3D printing by adjusting its melt flow characteristics with the proposed PMDA additive.



Figure 6. Small dog shape 3D-printed with modified R-PET (right).

4. Conclusions

Modification of R-PET was performed by reactive extrusion with the chain extender PMDA in order to enhance its melt flow, which is desirable for FDM 3D-printing applications. The MFI results showed that PMDA successfully increased the viscosity of the used polymer when used as chain extender. A decrease in MFI from 90 to 1.2 (g/10 min) was recorded when PMDA was added at 0.75 wt%. Furthermore, FT-IR results showed a mild indication of lower carboxyl end-group content for the sample that had PMDA at 0.75 wt% concentration. Furthermore, a 3D-printing filament was made from the modified R-PET via by a mimicked filament-making process which included an extrusion stage, a water bath cooling stage and a spooling stage. R-PET was processed with 0.75% PMDA, and segments of on-spec filaments were obtained. Finally, an attempt was made to print with the produced filament, and the printing temperature was set at 275 °C. This attempt yielded the successful printing of a small object.

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