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PYROLYSIS OF PLASTIC WASTE FROM 3D PRINTING

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Abstract: The amount of plastic waste generated by 3D printing is growing dramatically; thus, recycling is becoming increasingly vital. This research aims to investigate the potential of pyrolysis technology for the recycling of 3D printing plastic waste by employing thermogravimetric analysis. The pyrolysis of Polyethylene Terephthalate Glycol (PETG), Polylactic Acid (PLA), and Acrylonitrile Butadiene Styrene (ABS) was studied using three different heating rates of 5, 10, and 20 °C/min. As a result, all three materials showed one step of degradation based on thermogravimetric analyses. In addition, different mixtures were also investigated to see the influence of polymer combinations. The thermogravimetric analysis of the three heating rates described above demonstrated two stages of mixture decomposition in the presence of PLA. The findings suggest that the thermal behavior of a mixture, including mass loss and solid residue, can be estimated by calculating a weighted average of the solid residues of individual plastic waste components. This method provides a useful tool for predicting the thermal behavior of mixtures and can aid in the development of more efficient waste management strategies.

Keywords: Pyrolysis, plastic waste, 3D printing, thermogravimetry, heating rate

INTRODUCTION

Because of the expanding global energy need for sustained economic advancement, the energy supply problem has grown to be one of the most critical matters of the twenty-first century [1]. Clean energy management prioritizes the utilization of renewable energy and the energy transition [2]. Natural gas, oil, and coal have been the dominant energy sources for many years, but their expected future scarcity increases the need for alternative substitutes at the moment.

In 2016, the global value of 3D printing activity hit $5.8 billion. This dramatic growth trend is expected to continue, and the global 3D printing market is predicted to be worth $13.84 billion in 2021 and $16.75 billion in 2022 [3]. Furthermore, its worldwide value is expected to reach $55.8 billion by 2027 at a compound annual growth rate of 23.0% [4].

In comparison to other thermochemical processes, pyrolysis generates more energy with greater fuel-to-feed ratios [5], as well as higher net calorific values (10–20 MJ/m^3) than gasification and combustion (4–15 MJ/m^3) [6]. In light of these features, pyrolysis has piqued the interest of many researchers as an efficient and viable process for converting plastic waste to energy. Pyrolysis transforms biomass into oil, charcoal, and syngas, all of which have promising commercial potential. Fuel derived from biomass pyrolysis has been proven to be

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a clean and ecologically friendly fuel with lower greenhouse gas emissions during burning than traditional fossil fuels [7]. Furthermore, pyrolysis is claimed to be an energy source accounting for around 14% of world energy consumption [8], and is expected to contribute between 15% and 50% of energy by 2050 [9].

The PLA, ABS, and PETG 3D Printing Global Markets are estimated to increase with a CAGR of 19.8%, 30.62%, and 1.1% from 2020 to 2027, respectively, and reach $818, $989, and $812 million by 2027 [10], [11], [12]. The pyrolysis process of three 3D print materials, including PETG, ABS, and PLA, is investigated in this paper by thermogravimetric measurements.

1. MATERIALS AND METHODS

1.1. Materials

Polyethylene Terephthalate Glycol (PETG), Polylactic Acid (PLA), and Acrylonitrile Butadiene Styrene (ABS) were the waste plastics used in this study. *Table 1* contains pictures of the materials used.

Table 1
The used materials

		
PETG	ABS	PLA

1.2. Thermogravimetric measurements of neat plastics and their mixtures

To initiate thermogravimetric measurements, the plastics were chopped into 1 mm pieces and weighted with a Mettler Toledo XP26 scale capable of measuring weight with 0.001 mg resolution. In this research, thermogravimetric analysis (TG, DTG) was utilized as the primary approach to investigate the thermal stability of plastic waste materials and their mixes. To simulate real-world conditions, all materials were measured in a thermogravimetric equipment (MOM Derivatograph C/PC) in an inert environment (nitrogen). The sample was heated at three different rates: 5, 10, and 20 °C/min from room temperature to 1000 °C in alumina ceramic crucibles with a sample mass of 30 mg, while sample mass and temperature were continually monitored. As an inert gas, an 8 ml/min flow of high purity nitrogen flow (5.0 N_2) was utilized. *Table 2* shows how the plastic wastes were blended with a varying fraction of each ingredient.

Table 2
The concentration summary of the investigated materials

Materials	Concentration, w_i%						
	PETG	PLA	ABS	Mixture			
				1	2	3	4
PETG	100			50	50		33.33
PLA		100		50		50	33.33
ABS			100		50	50	33.33

The thermogravimetric influences of various polymers on each other may be noticed by comparing experimental data with results predicted from the mixing ratio from the single components, which can be computed as:

$$Y = \sum_{i=1}^{n} x_i * w_i \tag{1}$$

where Y is the overall mass loss of the mixture, x_i is the experimental value of mass loss achieved during single material degradation, and w_i is the proportion of the designated material in the mixture provided in *Table 2.*

The interpolation method is used to estimate the properties of a mixture from individual materials' thermogravimetric analysis data. This is necessary because the data obtained for each material may not have the same temperature steps. The method involves calculating the weighted average of each component's properties at the same temperature steps to determine the mixture's properties. This helps optimize the values nearest to the experimental mixtures and determine the average of each mixture's distinct components at the same temperature.

2. RESULTS AND DISCUSSION

2.1. Investigation of individual plastics

All of the plastic waste materials were pyrolyzed in a thermogravimetric analyzer, with the amount of mass loss measured as a function of temperature. *Figure 1* demonstrates the influence of different heating rates (5, 10, 20 °C/min) on the decomposition process of PETG, PLA, and ABS.

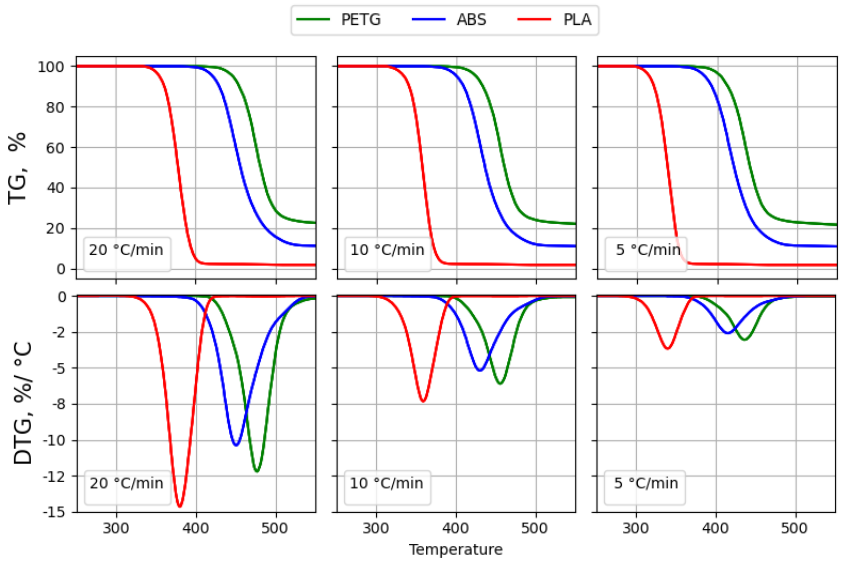

Figure 1
TG/DTG results of single materials

The thermogravimetric analyses were usually similar and verified a single complete degradation process for each polymer type, which was related to the minimal residue quantity seen in *Table 4*.

Lower heating rates, as predicted, shifted the degradation process to begin and finish at lower temperatures, as seen in *Table 3*.

When the heating rate was raised, the thermogravimetry analysisindicated that these materials had greater thermal stability.

A low heating rate can result in a longer residence time at a certain temperature range, which may accelerate deterioration and decrease thermal stability compared to a rapid heating rate. Therefore, the heating rate can have a significant impact on the thermal stability of plastics. Although the observed temperature varied from ambient to 1000 °C, the temperature range in the graphs is limited to 250–550 °C for clarity, as seen in *Figure 1*.

The TG curves in *Figure 1*, as well as the data are presented in *Table 3* show the percentage of the residue of distinct materials made of PETG, PLA, and ABS with varied heating rates (20 °C/min, 10 °C/min, and 5 °C/min). The results demonstrate that PETG and PLA had a larger percentage of residue than ABS. These measurements showed that the percentage of residue was less than 6% for ABS and much more for others.

Table 3

Temperatures of DTG peaks

Temperature peaks of single materials, °C			
Materials	**Heating rates, °C/min**		
	5	**10**	**20**
PETG	435	457	476
ABS	412	432	450
PLA	341	360	380

Table 4

The amount of residue of plastic materials at 900 °C

Heating rate, °C/min	Amount of residue of single materials at 900 °C, %		
	PETG	**ABS**	**PLA**
20	17.52	7.69	1.71
10	17.36	7.50	1.67
5	17.22	7.37	1.63

2.2. Investigation of plastic blends

In the absence of PLA, the investigation of Mixture 1 indicated one step of degradation, as demonstrated by the existence of just one peak in the DTG curves of the mixture. On the other hand, the results revealed two phases of deterioration Mixtures 2, 3, and 4, as demonstrated by the existence of two peaks in the DTG curves and two inclinations seen in the TG curves during the degradation process.

All the mixes showed that as the heating rate increased, so did the degradation temperature, which can be explained by improved thermal stability.

PETG, ABS, and PLA were the three components of Mixture 4, with all components having weight fractions of 33.33 wt%. Both the TG and DTG curves showed two stages of degradation.

With a heating rate of 5 °C/min, the first step of degradation was the degradation temperature of PLA, which was at roughly 340 °C. The temperature range for the second stage degradation of PETG and ABS was 370–500 °C. As seen in *Figure 3* and *4*, both two-stage

degradations progressed to higher temperatures as the heating rate increased. Furthermore, the DTG curve exhibited a quite high intensity peak during the initial stage of degradation. This effect might be explained by the fact that the combination of PETG and ABS had a high degradation rate, but the PLA component had a stable and low degradation rate even at high heating rates.

As with all other mixtures and single materials, the residual percentage at 900 °C increased with the increasing heating rate, as shown in *Table 5*, with 9.24, 9.16, and 9.09% for heating rates of 20, 10, and 5 °C/min, respectively. Additionally, as demonstrated in *Table 5*, the predicted mixtures had a significant correlation with the experimental mixtures, exhibiting only a 3% deviation. *Figure 2* shows that the four mixtures had a correlation coefficient equal to 1, indicating a perfect positive linear connection between the experimental and calculated findings.

Table 5

Residue of different mixtures at 900 °C

Residue of different mixtures at 900 °C, %					
Heating rate, °C/min	Mixture	**1**	**2**	**3**	**4**
20	Experimental	12.47	9.04	6.46	9.24
	Calculated	12.61	9.57	4.67	8.97
10	Experimental	12.30	9.02	6.41	9.16
	Calculated	12.43	9.51	4.58	8.84
5	Experimental	12.05	9.01	6.36	9.09
	Calculated	12.30	9.40	4.48	8.74

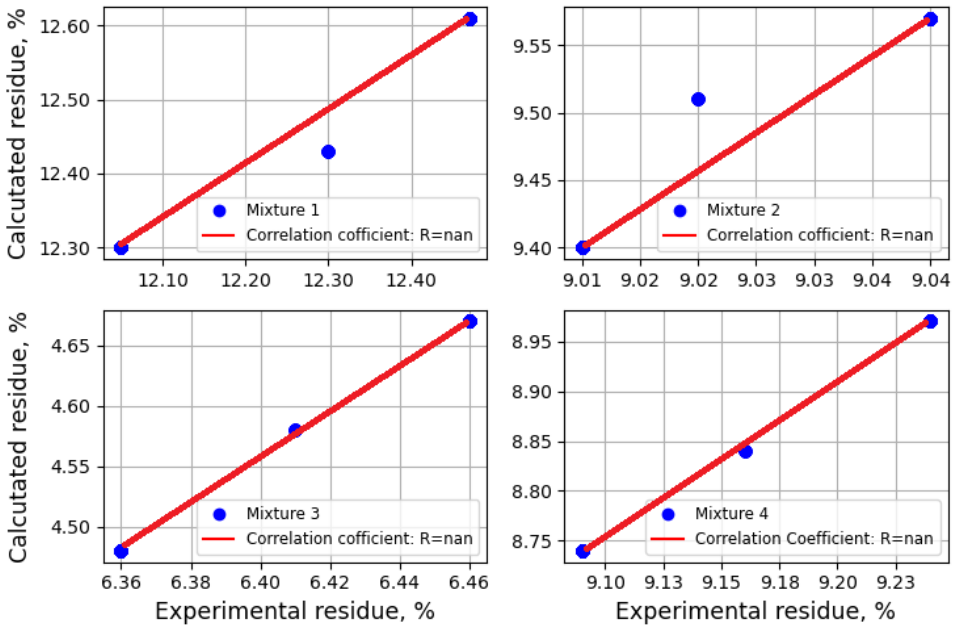

Figure 2

Deviation of the amount of residue between the experimental and the calculated mixtures at different heating rates

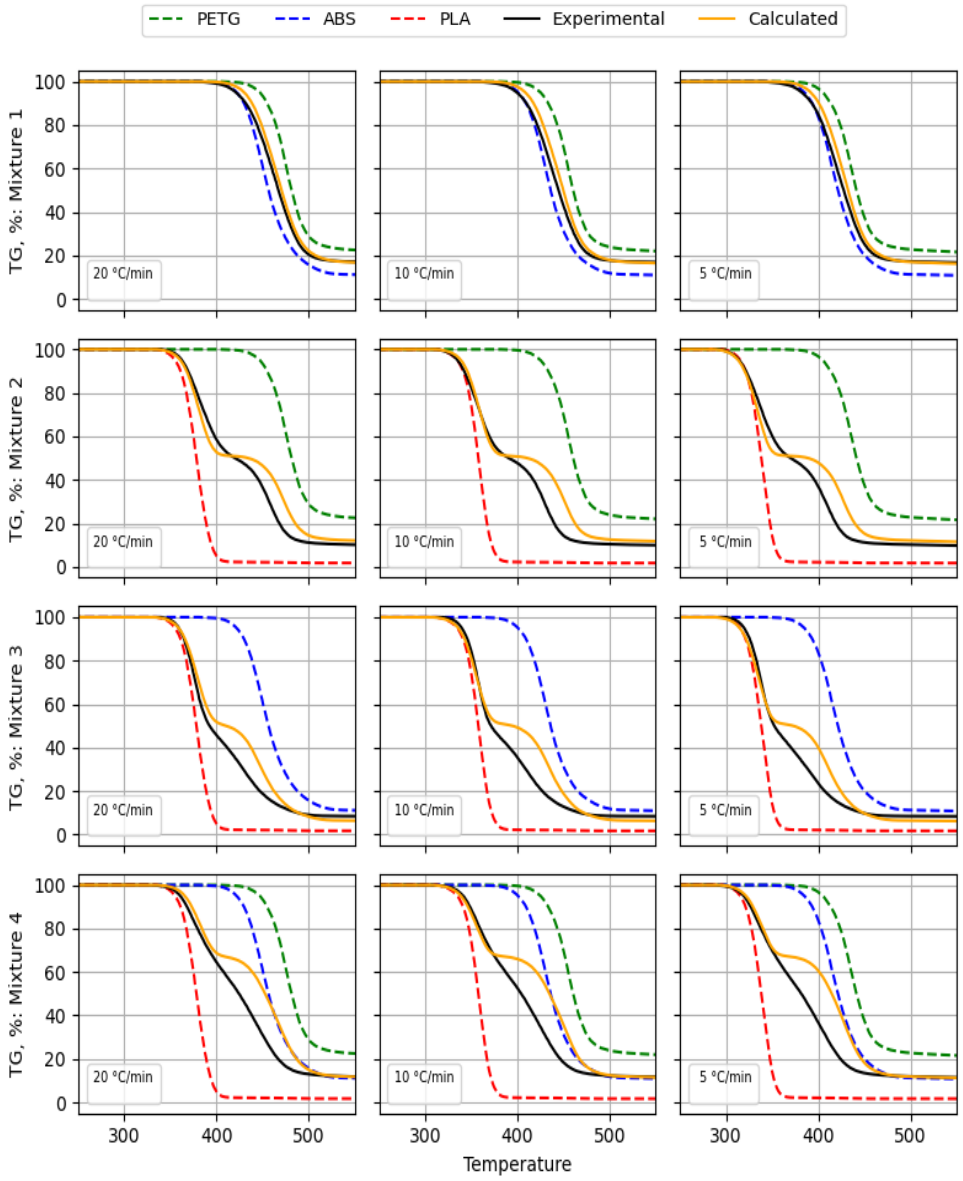

Figure 3
TG curves of different mixtures at different heating rates

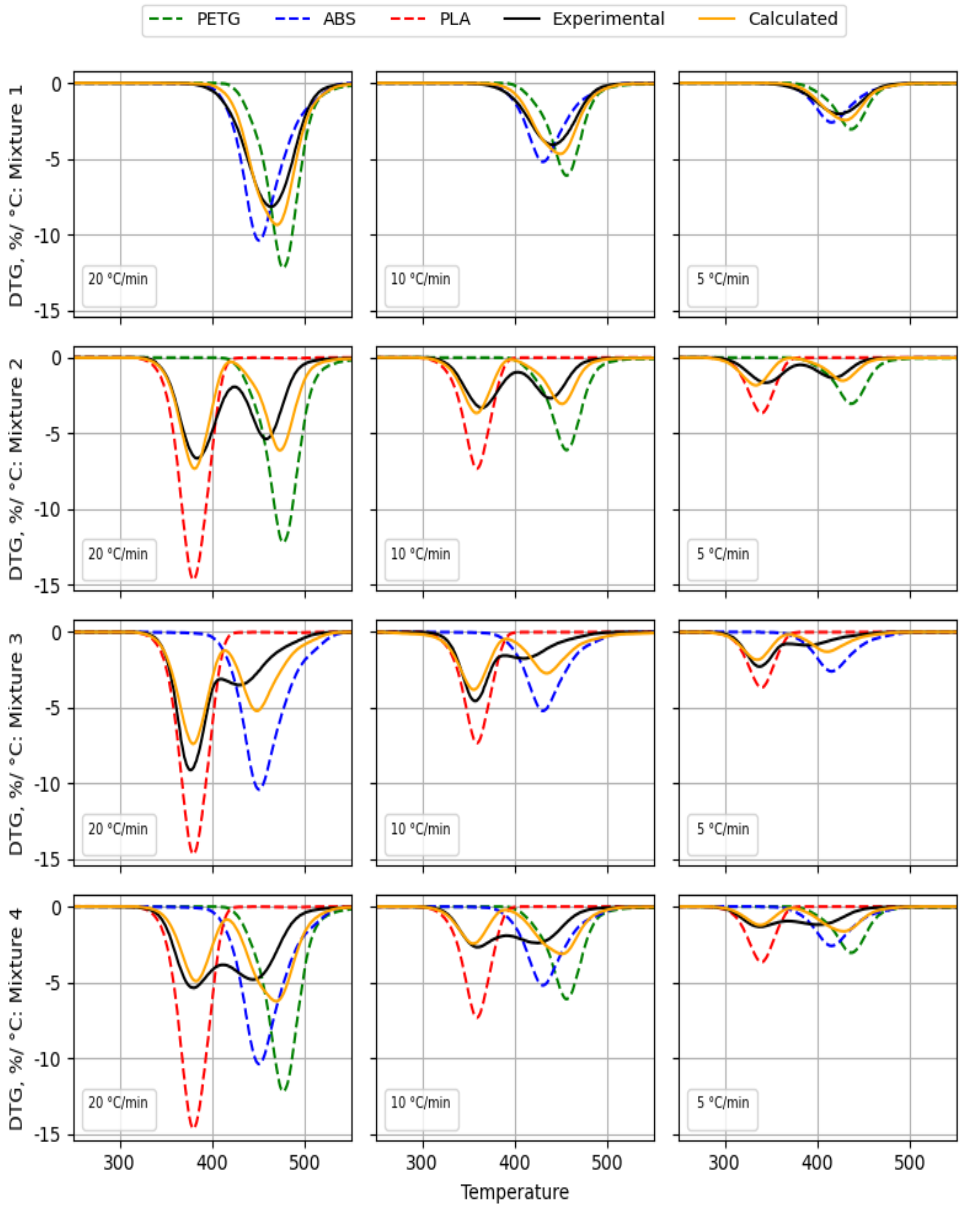

Figure 4

DTG curves of different mixtures at different heating rates

CONCLUSION

Under varied heating rate settings, thermogravimetric analysis was utilized to evaluate the pyrolysis behavior of three distinct polymers (PETG, ABS, and PLA). Based on the DTG curves of specific materials, it was possible to conclude that these graphs had just one peak, indicating a single (or one) step pyrolysis process. However, the DTG behavior of various

blends varied because the superposition of separate curves frequently did not adequately cover the measurement.

Conversely, when the heating rate was doubled, the start degradation temperature, end degradation temperature, and maximum weight loss temperature were all delayed, indicating a significant shift to a higher temperature. Based on the DTG peaks, the required temperature for the pyrolysis process may be classified from low to high as follows: PLA < ABS < PETG.

Plastic waste mixes were also investigated in addition to individual plastic. Except for Mixture 1, all mixes had two deterioration phases.

The outcomes indicated that the main degradation of the materials proceeded at temperatures ranging from 275 to 500 °C, 300 to 525 °C, and 325 to 530 °C, corresponding to heating rates of 5, 10, and 20 °C/min, respectively.

The solid residues may be calculated using the TG curves and the TG characteristics of the different polymers. By knowing simply these curves and the initial blend composition, we may evaluate the predicted blend behavior under real-world settings.

The results showed that the DTG curves were not exactly a superposition of the separate components, and this behavior should be studied further. Even if a plastic waste is made up of a variety of polymers, the interaction of the various plastics during the pyrolysis process is still worth researching. The interaction of two or more component blends, as well as their pyrolysis characteristics and kinetics, will be the focus of ongoing study.

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