ADDITIVE MANUFACTURING OF SELF-EXTINGUISHING FLAME-RETARDANT NYLON 6/66: PROCESSING AND CHARACTERIZATION

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ABSTRACT

Additive manufacturing, also known as 3D printing, is a transformative method for rapid prototyping or small-scale industrial production of parts in complex shapes or geometries. Fused Filament Fabrication (FFF) is the most widely used 3D printing technology due to its simple operation and low-cost. FFF is usually printed with thermoplastic filaments. Nylon, known for its toughness and flexibility, is popular for load-bearing 3D printed parts. However, flammability and melt dripping are major issues for nylons and many industries, especially automotive and aviation, require flame-retardant materials. This paper introduces a formulation of a 3D printable flame-retardant nylon 6/66 material. The formulating process is illustrated in detail. The resulting material is extruded into 1.75mm diameter filaments through a twin-screw extruder and printed into rectangular bars using a commercially available FFF printer. The printed bars are tested to the UL94 procedures and passed V0 rating. Material samples are taken during the formulating processes. Microscale combustion calorimetry (MCC) and thermogravimetric analysis (TGA) are used to characterize flammability and thermal properties of the samples.

Keywords: Additive Manufacturing, 3D print, Flame-retardant, Nylon, PA6/66, UL94
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1. INTRODUCTION

Additive manufacturing refers to a variety of processes that construct three-dimensional objects by adding layer-upon-layer of material [1-3]. According to the specific method that the material is added, deposited, joined, or solidified, the processes are sorted into different technologies. For example, Fused Filament Fabrication (FFF) is a process in which thermoplastic filaments are melted and deposited through a heated head and extruding nozzle. Nylon 6/66 is a thermoplastic copolymer of polyamide 6 and polyamide 66. Like most nylons, nylon 6/66 offers superior toughness, high elongation, elevated melting point, and low cost. These favorable properties made it a preferred candidate for 3D printed load-bearing parts. However, the drawback of pure nylon on flammability and melt dripping issues limited its application in automotive and aviation industries, where flame resistance is a significant requirement on their products [4]. Current existing 3D printable flame-retardant materials either tend to be expensive or barely achieve the

UL94 V0 rating. For example, flame-retardant ULTEM 9805, a polyetherimide (PEI) filament, costs 3-4 times in comparison to nylon 6/66 filament.

In this study, a 3D printable flame-retardant nylon 6/66 material will be formulated. The material is extruded into 1.75mm diameter FFF filament through a twin-screw extruder and printed into rectangular UL94 testing bars using a commercially available FFF printer. The printed bars are tested to the UL94 procedures. Material samples taken during and after formulative processes are characterized using microscale combustion calorimetry (MCC) and thermogravimetric analysis (TGA).

2. EXPERIMENTATION

2.1 Material

Nylon 6/66 was provided by Zig Sheng Industrial Co. Ltd. from Taiwan. Figure 1 shows the behavior of the material under dynamic scanning by a differential scanning calorimeter (DSC). The material melts around 205°C and degrades significantly after 400°C. The melting temperature of the material is tested to be 204.2°C (averaged from measurements of three samples).

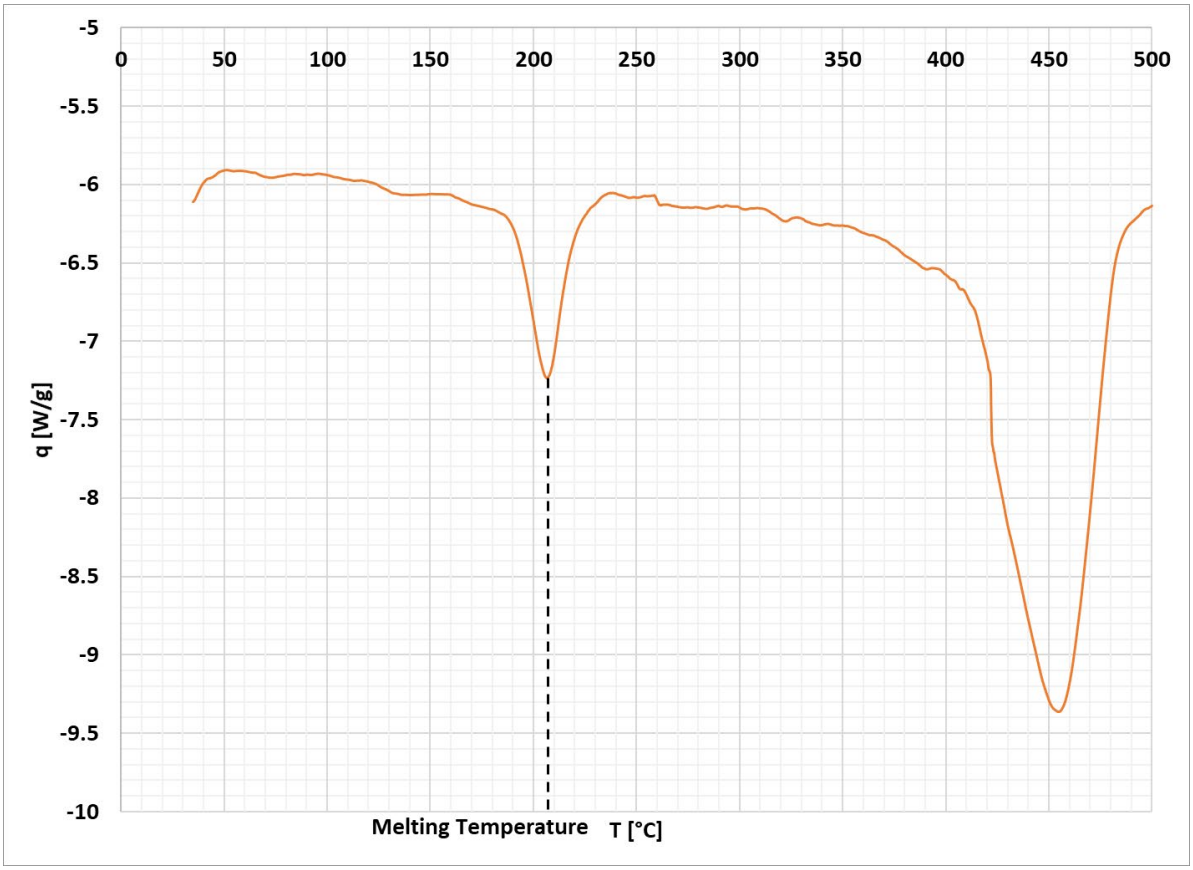

Figure 1. DSC test on nylon 6/66 by Zig Sheng Industrial Co. Ltd. (Test method: 35°C to 500°C at 10°C/min in N_2).

The main additive used in this study is a non-halogenated flame retardant (FR) provided by Clariant. The product achieves its flame-retardant effect through intumescence. Nylon 6/66 with the flame-retardant foams and crosslinks on exposure to flame and forms a stable char at the surface of the material. The char creates a thermal insulation layer, reduces oxygen access, and prevents dripping of molten nylon. In this study, the FR is jetted into micro-sized powder for easier processing and better distribution. 95% of the FR particles are below 8.78 μm. The micro-jetting is expected to preserve the mechanical properties of the formulated composites.

A thermoplastic elastomer (TPE) is also added to the material to tailor its mechanical properties. The elastomer is purchased from Kraton Polymers Inc. Kraton® elastomers are used as synthetic replacements for rubber, offering many properties of natural rubber, such as flexibility, high traction, but with increased resistance to heat and chemicals. The thermoplastic elastomer is a triblock copolymer consisting of polystyrene blocks, polybutadiene blocks, and polyisoprene hydrogenated equivalents. The glass transition temperature (T_g) of polybutadiene blocks is typically -90°C and the T_g of the polystyrene blocks is 100°C, between which, the thermoplastic elastomer acts as physically crosslinked elastomer. Above 100°C, the material transitions from rigid glassy regions to flowable melt regions. Kraton G elastomer is commonly processed at 200-230°C.

2.2 Material Processing

Pure nylon 6/66 pellets are pre-dried at 70°C for 48 hours followed by 80°C for 48 hours. A total of 90g of materials are weighed, consisting of 85 wt.% nylon 6/66 and 15 wt.% TPE. The mixture is mixed by a Thinky® Planetary Mixer at 1,500 RPM for 1 minute and then extruded into filaments via a Thermo Scientific Parallel Twin Screw Extruder. The extruded filaments are air cooled and spooled by a Filabot Airpath and a Filabot Filament Winder, as shown in Figure 2. Temperatures used on the twin-screw extruder are listed in Table 1. The filaments are cut into pellets using the Filabot filament winder and a Filabot pelletizer, as shown in Figure 3. The pelletized pellets are measured to be 57 grams, due to loss during the processing (*e.g.,* filaments that are not properly pelletized).

Figure 2. Filament extrusion process equipment (from right to left is Thermo Scientific Parallel Twin Screw Extruder and Filabot Airpath and Filabot Filament Winder).

Table 1: Temperatures used on Thermo Scientific Parallel Twin Screw Extruder

Twin-Screw Extruder Temperature [°C]							
Die	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7
270	280	280	280	280	280	260	210

Figure 3. Filament pelletizing process equipment (from right to left is Filabot Filament Winder and Filabot Pelletizer).

After samples are retrieved, extra nylon 6/66, TPE, and FR are added into the pellets of 85 wt.% nylon 6/66 and 15 wt.% TPE to make a mixture of 80 wt.% nylon 6/66, 15 wt.% TPE, and 5 wt.% FR. The process is repeated until all the samples listed in Table 2 are formulated.

Table 2. Flame-retardant nylon 6/66 formulation matrix (in weight percentage)

Sample ID	**Nylon 6/66**	**TPE**	**FR**
1	100	-	-
2	85	15	-
3	80	15	5
4	75	15	10
5	70	15	15
6	63	15	22

It is noticed that adding more than 22 wt.% of FR results in a rough filament surface. Thus, 22 wt.% FR is the maximum FR loading used in this study.

Filaments of 63 wt.% nylon 6/66, 15 wt.% TPE, and 22 wt.% FR are printed into five UL94 testing bars (125mm × 13mm × 3mm) using a commercially available FFF printer, CraftBot Plus Pro. Main parameters used in the printing are listed in Table 3. The printed bars are shown in Figure 4.

Table 3. Main Parameters used for 3D printing of the UL94 testing samples

Infill Type	Parallel Lines, 30%
Infill Density/Width	30%/120%
Bed Temperature	80°C
Head Temperature	240°C
Draw Speed	30mm/s
Total Printing Time for Each Bar	35 minutes
Nozzle Diameter	0.4mm
Filament Diameter	1.65±0.10mm

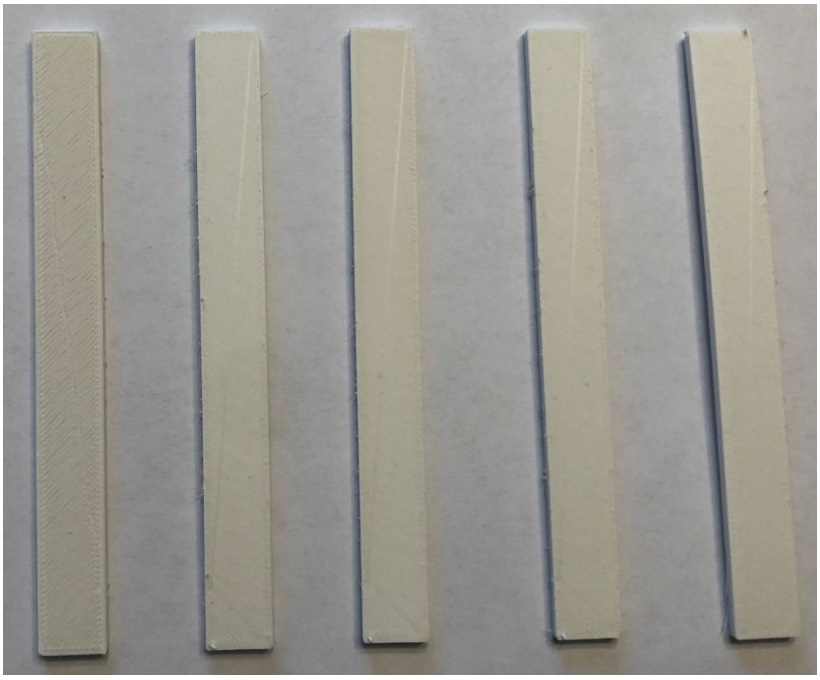

Figure 4. FFF printed UL94 testing samples (material contains 63 wt.% nylon 6/66, 15 wt.% TPE, and 22 wt.% FR).

2.3 Material Characterization

2.3.1 UL94 flammability test

UL94 flammability test evaluates the performance of a material on exposure to flame. In the test, a rectangular specimen is hanging vertically by a holding clamp, as shown in Figure 5.

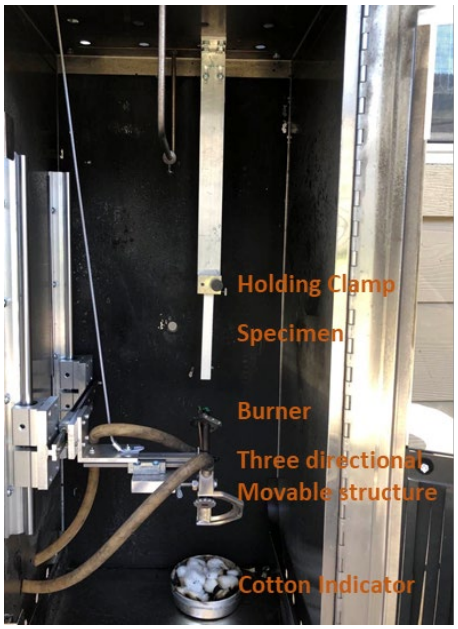

Figure 5. UL94 test setup.

A flame approaches to the center of the lower end of the specimen. The flame is about 20 mm in height. The burner is about 10 mm to the lower end of the specimen. Natural gas is used as the source of the flame. The specimen exposes to the flame, twice, for 10 seconds each time. Afterflame period is defined as the time that the specimen takes to self-extinguish after each 10-second burning. The classification criteria for the UL94 vertical tests are listed in Table 4.

Table 4. Classification criteria for the UL94 vertical flammability test

Criteria	**V-0**	**V-1**	**V-2**
Afterflame for each individual specimen (t_1 and t_2)	≤ 10s	≤ 30s	≤ 30s
Total afterflame for any condition set (t_1+t_2 for the 5 specimens)	≤ 50s	≤ 250s	≤ 250s
Afterflame plus afterglow time for each individual specimen after the second flame application	≤ 30s	≤ 60s	≤ 60s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignition	No	No	Yes

2.3.2 MCC

MCC is used to measure the heat release of a material at elevated temperatures to predict its combustion properties. In this study, a MCC (MCC-2) by Govmark Organization Inc is used, as shown in Figure 6. ASTM D7309-2007 is followed. Materials (2-3mg) are heated up from 100°C to 700°C at 1°C/s in the environment of 80 mL/min N_2 and 20 mL/min O_2. Heat release flux are recorded as temperatures. From MCC tests, the heat release (HR) capacity, peak heat release rate

(HRR), total HR, and peak temperature of the material can be obtained. Triplicate samples of each formulation are tested.

Figure 6. Micro-Combustion Calorimeter (MCC-2) by Govmark Organization Inc.

2.3.3 TGA

Samples of different formulations are also analyzed by a TGA (TGA/DSC 1 STAR® System) by Mettler Toledo, as shown in Figure 7.

Figure 7. Thermogravimetric Analyzer (TGA/DSC 1 S STAR® System) by Mettler Toledo.

TGA measures the decomposition of materials as the temperature increases in terms of weight loss. In TGA tests, materials (8-10mg) are heated from 100°C to 1,000°C at 20°C/min in both air and N_2. Weight losses of samples are recorded as temperatures.

3. RESULTS

3.1 Nylon 6/66 Moisture Study

Neat nylon 6/66 are dried at different temperatures for various periods. Before and after weights are recorded. Table 5 shows weight changes at different conditions.

Table 5. Weight change of nylon 6/66 dried at different conditions

Condition 1	**Weight Loss Ratio for Each Step**	**Total Weight Loss Ratio**
70°C for 48 hours	2.70%	
80°C for 48 hours	0.18%	
105°C for 14 hours	0.05%	2.93%
Condition 2	**Weight Loss Ratio**	**Total Weight Loss Ratio**
80°C for 48 hours	2.58%	
105°C for 14 hours	0.02%	2.60%
Condition 3	**Weight Loss Ratio**	**Total Weight Loss Ratio**
105°C for 14 hours	2.59%	2.59%

Neat nylon 6/66 lost the most weight under condition 1. However, the material discolored significantly when dried at 105°C due to oxidation. Thus, the first two steps in condition 1 are used to pre-dry the material in this study.

3.2 UL94 Test

Five specimens of 63 wt.% nylon 6/66, 15 wt.% TPE, and 22 wt.% FR are tested to the UL94 procedures and results are recorded in Table 6, where t_1 and t_2 represent the first and second afterflame for each specimen, respectively. A picture of post-test specimens is shown as Figure 7.

Table 6. Afterflame periods of samples tested to UL94 flammability test

Specimen ID	**t_1 [s]**	**t_2 [s]**
1	1.4	2.2
2	2.8	0
3	2.2	0
4	3	0
5	5.9	0
Average	3.1	0.4
Standard Deviation	1.7	1.0

Figure 7. Post-test FFF printed UL94 samples ((material contains 63 wt.% nylon 6/66, 15 wt.% TPE, and 22 wt.% FR).

None of the five specimens experienced melt dripping or recordable afterglow periods. The afterflame period for each individual specimen was less than 10 s. The total afterflame period for any specimen was less than 50 s. The afterflame of any specimen did not reach the holding clamp and the cotton indicator did not ignite during the tests. The material passed the UL94 V0 rating according to Table 4.

3.3 MCC Test

The MCC test results are shown in Table 7.

Table 7. MCC results of different formulations

Sample ID	**Formulation in wt.%**	**HR capacity**	**Peak HRR**	**Total HR**	**Peak Temperature**
No.	Nylon 6/66-TPE-FR	[J/g-K]	[W/g]	[kJ/g]	[°C]
1	100-0-0	867.7±14.7	867.4±14.1	41.8±0.4	489.3±0.6
2	85-15-0	1,216.0±6.0	1,213.3±6.2	47.0±0.2	485.3±0.1
3	80-15-5	1,064.0±8.0	1,063.0±8.5	45.8±0.5	481.6±0.2
4	75-15-10	774.0±20.0	774.7±20.3	45.8±1.0	475.9±0.8
5	70-15-15	585.0±7.8	583.5±8.9	40.7±0.5	457.2±0.7
6	63-15-22	593.3±5.5	556.2±37.9	40.9±0.5	441.8±4.1

The HR capacity of neat nylon 6/66 (sample No.1) is averaged to be 867.7J/g/K. The addition of TPE increases the HR capacity, peak HRR, and Total HR of nylon 6/66 significantly, while the increase of FR reduces them all. The improvement on flammability properties of the material by adding FR becomes trivial as the FR loading increased from 15 wt.% to 22 wt.%. The addition of both TPE and FR decreases the peak temperature of nylon 6/66.

3.4 TGA Test

TGA results of samples tested in N_2 are shown in Figure 8. Temperatures of 10%, 50% weight loss and char yield are listed in Table 8. The nonoxidative thermal degradation of the studied materials can be divided into two stages:

1) Volatilization stage (up to 200°C)

In this stage, a small amount of weight is lost corresponding to the moisture departure. The weight loss increases as the FR loading in the material increases (*e.g.,* 0.7% for sample 85-15-0, 1.2% for sample 63-15-22). The trend matches results from other researchers [5]. However, the volatilization weight loss is significantly lower for nylon 6/66 due to the pre-dry procedure.

2) Major decomposition stage (Above 200°C)

In this stage, all samples start to lose weight significantly around 350°C. With further increasing temperature, a rapid weight loss is observed. At temperatures of above 500°C, the thermal decomposition of the material is nearly complete. A slightly earlier decomposition is observed along with the FR increase. For example, sample 85-15-0 and sample 63-15-22 starts to decompose at 370°C and 350°C, respectively. This effect is caused by the flame-retardant mechanism of the FR used in this study. The FR decomposes at a slightly lower temperatures than nylon 6/66 and forms a protective char layer. Overall, materials with increased percentage of FR reveals enhanced thermal stability and char yield.

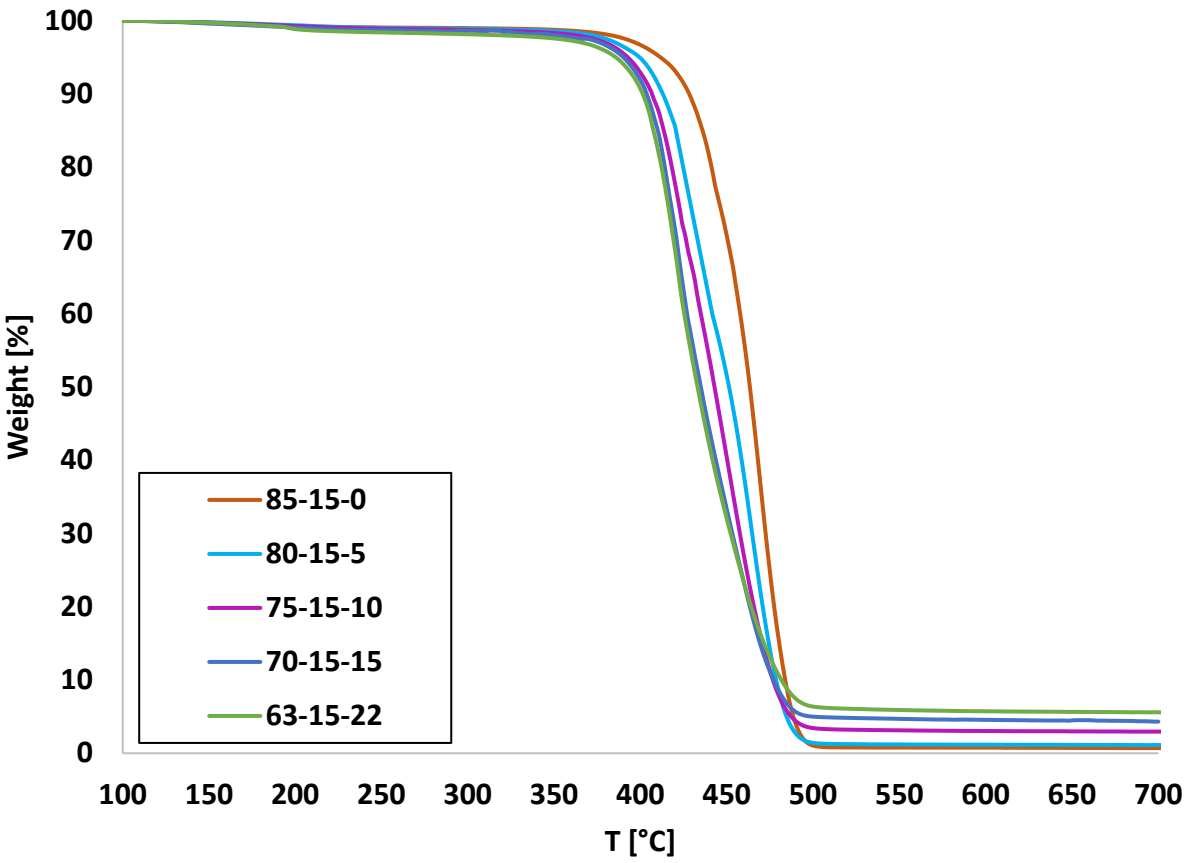

Figure 8. TGA results of samples tested in N_2 (Curves are labeled as nylon 6/66-TPE-FR in weight percentage).

Table 8. Decomposition temperature of samples tested in N_2

Label	$T_{10\%}$	$T_{50\%}$	Residue Mass at 1,000°C
Nylon6/66-TPE-FR	[°C]	[°C]	[%]
85-15-0	428.3	463.3	0.3
80-15-5	413	451.3	0.54
75-15-10	406.7	443	2.09
70-15-15	403.7	435	3.45
63-15-22	401.3	433	4.05

TGA results of samples tested in air are shown in Figure 9. The oxidative thermal degradation curves of the materials reveal similar trends to the nonoxidative thermal degradation curves shown in Figure 8 up to 500°C. Above 500°C, materials further degraded at a slower rate. This is due to the different thermal decomposition mechanism of nylon with the presence of oxygen. In air, the C-N bonds in the composites are broken into small fragments, which are then broken down to carbon dioxide, carbon monoxide, water, and hydrocarbons [6].

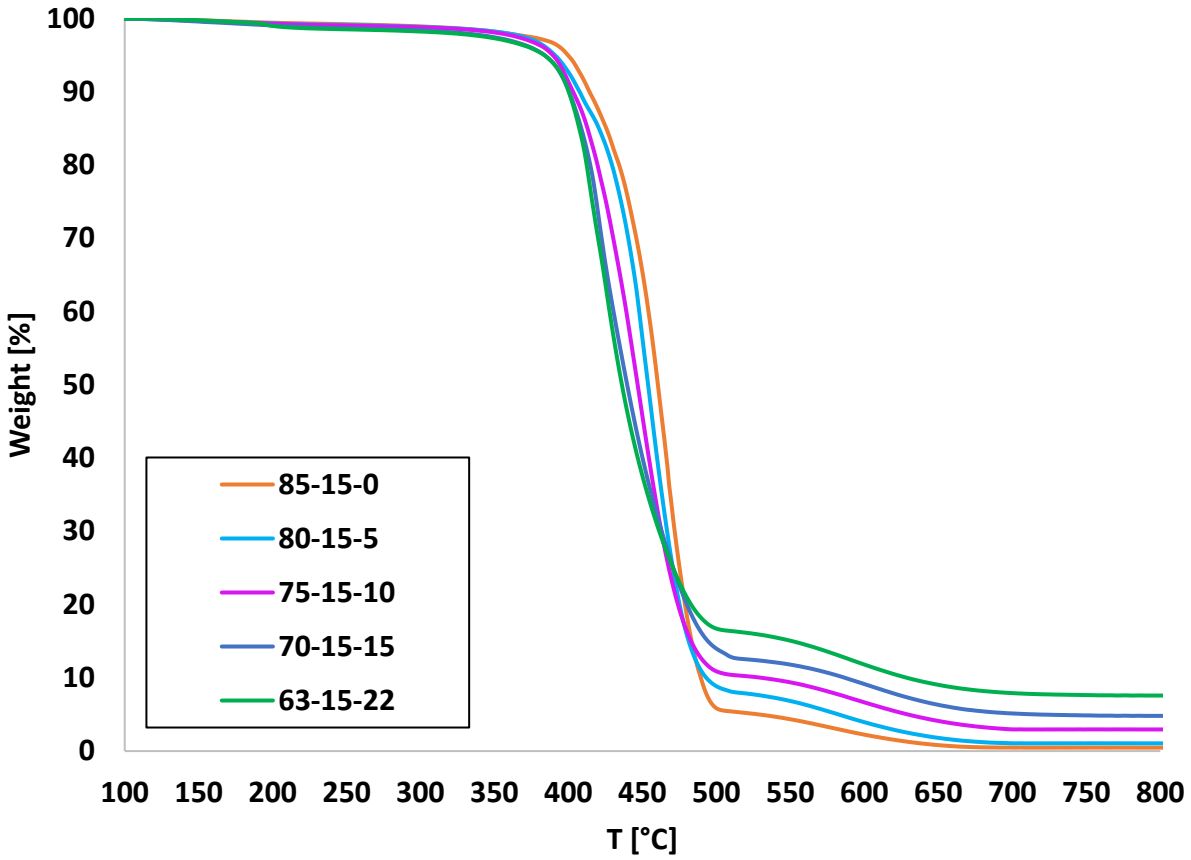

Figure 9. TGA results of samples tested in air (Curves are labeled as nylon 6/66-TPE-FR in weight percentage).

4. CONCLUSIONS

In this study, a 3D printable flame-retardant nylon is formulated and characterized. The developed composites passed UL94 V0 rating. The non-halogen FR introduced in this study improves the thermal stability and flammability properties of nylon 6/66 significantly, where it is found that 22 wt.% of FR is the maximum recommended load. It is noticed that the thermoplastic elastomer introduced in this study improves the processing stability of nylon 6/66. The following conclusions can be drawn:

- A pre-dry procedure is recommended before nylon 6/66 processing. The recommended drying profile is 70°C for 48 hours followed by 80°C for 48 hours.
- The addition of 15 wt.% of the TPE introduced increases the heat release capacity and peak heat release rate of nylon 6/66 by 40%, increases the total heat release by 12.7%, but decreased the peak temperature of the material by 4°C.
- The addition of 22 wt.% of the FR introduced decreases the heat release capacity and peak heat release rate of nylon 6/66/TPE mixture by over 50%, decreases the total heat release by 13% and reduces the peak temperature of the material by 44°C.

- The addition of 22 wt.% of the FR accelerates the decomposition of the nylon 6/66/TPE mixture by 20°C but increases the char yield of the material by over 12 times.

5. REFERENCES

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