ADVANCEMENT IN THE STUDY OF 3D PRINTABLE FLAME RETARDANT POLYAMIDE 11 NANOCOMPOSITES

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ABSTRACT

Several studies have examined the viability of flame retardant (FR) polyamide 11 (PA11) composites with varying levels of success. A comparison on these studies can provide insight into which additives are most effective for enhancing the flammability and mechanical properties of PA11 composites. A FR PA11 review study found that studies that have used tandem composites of multiwalled carbon nanotubes (MWNT) along with nanoclay yielded PA11 composites with desirable UL94 V-0 ratings, as well as high performance in mechanical properties. In this investigation, the tandem MWNT/nanoclay composites were examined along with alumina nanofibers and a new FR additive. The new materials were fabricated with twin-screw extrusion into 1.75 mm filament for the purpose of fused filament fabrication (FFF) additive manufacturing. Characterization for the study included TGA, MCC, UL 94, and tensile testing.

1. INTRODUCTION

1.1 Background

Rislan®, commonly known as PA11, is a high-performance bioresin produced by Arkema [1,2]. PA11 has excellent properties including scratch resistance, low density, high chemical resistance, and lower water absorption than other members of the polyamide family [3]. While PA11 has excellent chemical and mechanical properties, its high flammability can make it a safety hazard for certain applications. Many studies have succeeded in producing PA11 composites with improved thermal properties, however, these studies usually require large amounts of fillers which dramatically reduce the polymer's natural mechanical character.

1.2 Polyamide 11 Flame Retardant Study Review

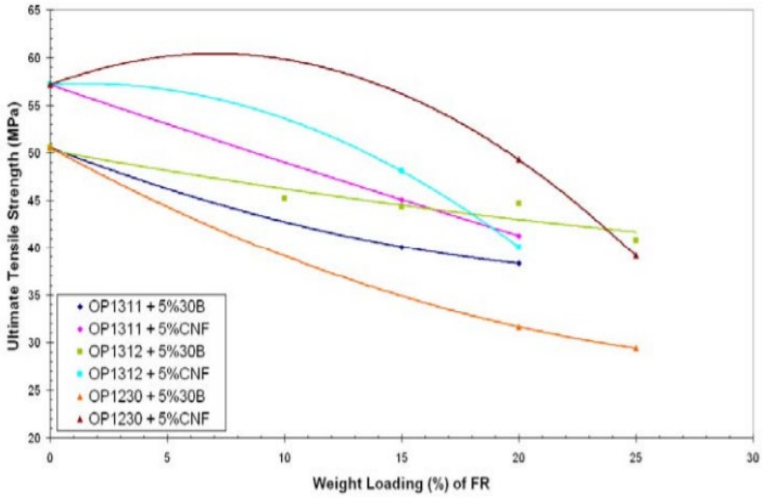
There have been several studies which investigated the viability of a FR PA11. Many of these studies have succeeded in creating a PA11 composite which achieved a UL 94 V-0 rating. These studies have consistently achieved a V-0 rating with FR loadings as low as 20 wt % [4,5]. Later studies were able to consistently achieve a V-0 rating with FR loadings as low as 15 wt % [6]. While it is clearly possible to achieve a PA11 composite with high flame retardant capabilities, it remains a goal to further optimize the formulation by decreasing FR filler amounts. This is important because higher loadings of FR diminish the desirable mechanical properties inherent of PA11. Additionally, previous PA11 studies incorporated various nanofillers, such as nanoclay and MWNT in an attempt to further enhance thermal properties as well as mechanical. The

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following PA11 studies were reviewed with the goal of creating an optimized FR PA11 composite using low loadings of FR.

S.C Lao et al experimented to produce a FR PA11 with enhanced mechanical properties. The study investigated twenty-six composites using variations of two nanofillers and three flame retardants [4]. The nanofillers used were carbon nanofiber (CNF) and Closite® 30B nanoclay. It should be noted that 30B is no longer commercially available. For FR, OP1230 OP1311 and OP1312 from Clariant were used. Comparative data of three formulations tested suggest that OP1312 performed better and achieved a V-0 rating with lower overall loading. The three formulations each used 20 wt% of their respective FR and 5 wt% of nanoclay filler. The formulations using OP1230 and OP1311 achieved a V-1 rating while the OP1312 formulation achieved a V-0 rating. This could be a result of better synergy between the OP1312 and the nanoclay. Additionally, of the formulations tested, OP1312 and 5 wt % 30B achieved the highest ultimate tensile strength and rupture tensile strength. Additional high performance combinations include OP1312 with CNF, which demonstrated high thermal stability, and OP1230 with CNF, which performed well in thermal stability and mechanical properties.



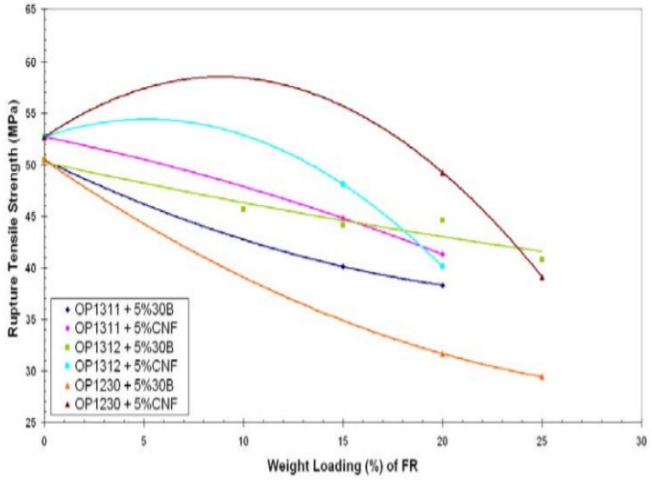


Figure 1: Ultimate tensile strength and rupture tensile strength comparison of PA11 composites [4].

Wu et al conducted further investigation into FR PA11, testing composites using OP1312 and Cloisite 30B nanoclay for improvement in the material's flammability properties [7]. In addition, Kraton FG1901 elastomer was investigated to determine if it could be a viable additive to offset some of the mechanical losses that come with the use of the FR. While the formulations studied did not achieve the desired V-0 rating, the tensile test results showed a strong improvement in mechanical properties with loadings as low as 5 wt %.

Table 1: Mechanical characterization of PA11 composites [7]

Sample ID	Formulation	Tensile Strength (MPa)	SD	Modulus (MPa)	SD	Elongation at Break (%)	SD
1	PA11	48.5	3.2	1,380	40.7	164	73.5
-	Kraton elastomer	34.5	-	-	-	500	-
2	80N_20FR	41.6	1.8	1,870	135	6.32	2.3
3	75N_20FR_5K	37.9	0.9	1,630	54.3	9.35	1.9
4	70N_20FR_10K	33.8	1.1	1,370	66.5	17.3	2.5
5	65N_20FR_15K	29.9	0.6	1,330	47.2	24.9	2.9
6	60N_20FR_20K	26.9	0.4	1,140	31.4	40.1	10.8
-	ALM FR PA11	46	-	1,345	-	38	-

The study examines the mechanical properties of 80 percent nylon and 20 % FR. It also looks at the effect of replacing 5, 10, 15, and 20 % of the nylon with elastomer. At a replacement of 5 wt % the elongation at break improved from 6.3 to 9.4 % and the modulus improved from 1380 to 1870 MPa. This came at the cost of a decrease in tensile strength from 41.6 to 37.9 MPa. Further additions of elastomer improved elongation at break to 40.1 MPa, while lowering the modulus and tensile strength to 1140 and 27 MPa.

When considering the elastomer's effect on flammability, its properties provide for a middle ground when compared to PA11. The study's TGA comparison of neat PA11 and neat elastomer demonstrated that the elastomer has slightly improved thermal stability reaching 445 and 478°C before 10 and 50 % decomposition. This compares to 403 and 438°C for PA11 [7]. However, elastomer has a higher peak heat release rate when it does reach its threshold temperature when compared to PA11. MCC results show a peak heat release of 1786 W/g for the elastomer and 1277 W/g for PA11.

In a second study, Wu et al investigated the synergy between MWNT and nanoclay in PA11 composites [6]. The study continued its use of OP 1312 FR, Cloisite 30B nanoclay, and Kraton FG1901 elastomer while incorporating Baytube C70 P multiwalled carbon nanotubes (MWNT). The study investigated six formulations, each with 15 wt% loading of OP 1312.

Table 2: UL 94 test results for PA11 composites [6]

Formulation	Average 1st burn flaming combustion duration (s)	Averaged 2nd burn flaming combustion duration (s)	Flaming Drip	UL 94 Rating
PA11	4	-	Yes	V2
15FR_10K_2.5NC_2.5MWNT	2	3	No	V0
15FR_15K_2.5NC_2.5MWNT	2	2	No	V0
15FR_20K_2.5NC_2.5MWNT	3	1	No	V0
15FR_10K_3.5NC_3.5MWNT	3	1	No	V0
15FR_15K_3.5NC_3.5MWNT	2	1	No	V0
15FR_20K_3.5NC_3.5MWNT	2	2	No	V0

Wu et al also examined the mechanical properties of the 15FR_20K_2.5NC_2.5MWNT and 15FR_15K_3.5NC_3.5MWNT formulations. Both formulations performed very well compared to previous PA11 FR studies, achieving an elongation at break of 30 and 17 %, respectively.

In another study, Fahy et al examined the effect of functionalized NAFEN alumina nanofibers in PA11 composites [5]. The study used OP1312 FR in loadings of 15 and 20 wt% and achieved a V-0 rating with formulations at 20 wt% FR. The study found that functionalized ANF had significantly improved dispersion within the PA11 matrix. This improved dispersion also resulted in the treated ANF providing an improved thermal stability to the composites when compared to formulations without ANF. While the tensile testing didn't directly indicate an improvement in mechanical properties in the tested formulations, the mechanical was however improved from previous studies in which similar formulations had used nanoclay instead of ANF.

In summary, the FR PA11 review strongly suggested the use of MWNT/clay formulations in future studies. MWNT and nanoclay combined were the only combination achieving a V-0 rating at FR loadings below 20 wt%.

1.3 FFF Printing

Fused filament fabrication (FFF) is a form of additive manufacturing (AM) technology. FFF works by heating filament which is extruded in a controlled manner layer-by-layer to construct desired products. Developed in the 80s by S. Scott Crump, FFF has since emerged as an important facet of modern manufacturing. FFF's simple design allows it to have a highly versatile range of capabilities. If it can be extruded into filament and subsequently melted, it is theoretically a candidate for FFF 3D printing. There are of course limitations, as printing at higher temperatures can be a difficult obstacle to overcome. Due to value of such capabilities, high temperature FFF printing is the subject of continued research. Both the versatility of FFF printing and its emergence as a highly capable form of manufacture make it an excellent candidate for research prototyping.

2. EXPERIMENTATION

2.1 Materials

The Rislan® PA11 was acquired from Arkema. Prior to fabrication the polymer was dried at 50°C for 24 hours. The additives used for the PA11 composite were Exolit® OP 1400 flame retardant received from Clariant, Nafen™ alumina nanofibers (ANFs) provided by ANF Technology, Baytube C70 P MWNT, Kraton elastomer, and BYK Cloisite® 20A nanoclay. 20A nanoclay was chosen in lieu of 30B because 30B is no longer commercially available.

2.2 Formulation Selection

The formulation matrix was designed to optimize the PA11 composites of previous studies. The use of FR severely reduces the mechanical properties of PA11. Analysis of previous studies demonstrate the efficacy of using nanoclay/MWNT, ANF, and elastomer to improve flammability and mechanical properties of FR PA11. In addition, a new FR, OP1400, which has a higher phosphorus content compared to OP1312 was chosen in attempt to decrease the necessary FR loadings required to achieve a V-0 flammability rating.

Table 3. PA11 formulation matrix

Formulation	PA11 (wt%)	FR (wt%)	n-clay	n-alumina	MWNT	Elastomer
1	73.5	12.5	2	0	2	10
2	73.5	12.5	2	2	0	10
3	71	15	2	0	2	10
4	71	15	2	2	0	10
5	71.5	12.5	2	2	2	10
6	66	15	2	0	2	15

2.3 Materials Fabrication

The Thermo Scientific Process 11 parallel twin-screw extruder was used to fabricate the PA11 composites. The Process 11 is effective at materials fabrication due to its capability of compound mixing during the extrusion process. The Process 11 is a tabletop extruder, and therefore the materials passing through do not have a long residence time within the barrel. To improve the compounding effect, each formulation was extruded into a filament, pelletized, and extruded an additional time. To achieve the consistent filament diameter necessary for FFF 3D printing, the extruded filament was passed through a water bath before being collected with a spool winder.

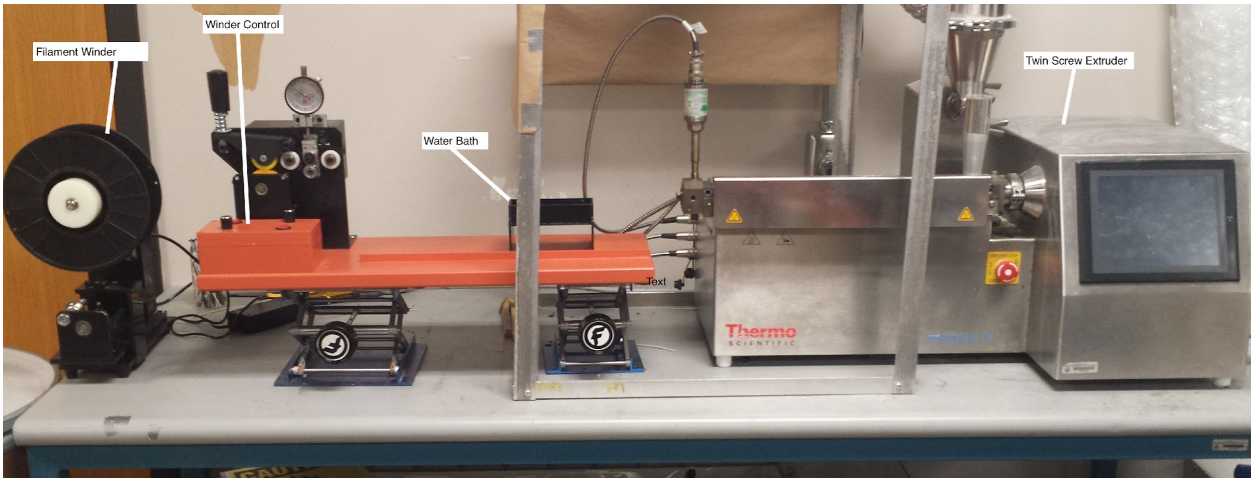


Figure 2. Process 11 twin-screw extruder.

2.4 FFF Additive Manufacturing

The 4M CraftBot FFF printer was used to print the standardized UL 94 and ASTM D618-14 type IV test bars. The printer maintained a bed temperature of 85°C and a head temperature of 240°C during the printing process. The samples were printed in a +45°/-45° raster pattern with a layer height of 0.18 mm. Due to variabilities with the extrusion process, the filament diameter varied depending on the formulation. Infills of 90-100% were used depending on filament thickness, with thicker filament using a lower infill; without these adjustments the thicker filament would overfill and print incorrectly. An 18 loop rim was printed as a foundation to prevent curling. Eight samples were printed for each selected formulation, including five UL 94 samples and three tensile samples.

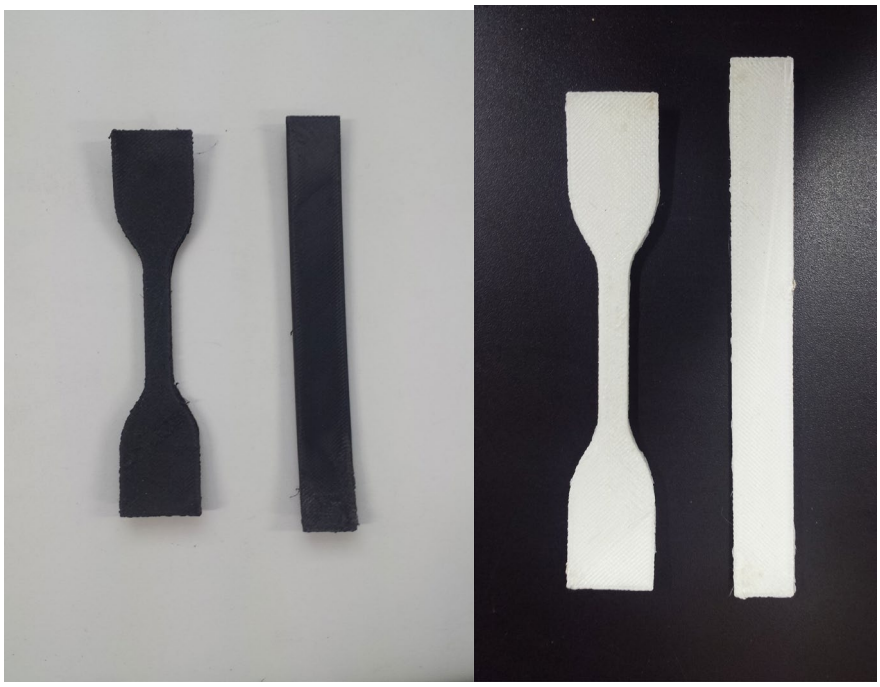


Figure 3. Photographs of FFF printed PA11 nanocomposite test bars.

2.5 Materials Characterization

Microscale Combustion Calorimetry (MCC2) is an instrument manufactured by Govmark, Inc. The MCC was used to investigate combustion properties in accordance with ASTM D7309-2007 standards. The MCC works by raising a small sample into a pyrolysis chamber where it slowly pyrolyzes as the temperature is raised from 100 to 750°C at a rate of 1°C/s. The aerosol enters a combustion chamber where the temperature is set at a constant 900°C. Oxygen levels are internally calculated to provide heat release as a function of temperature. Testing was performed in triplicate.

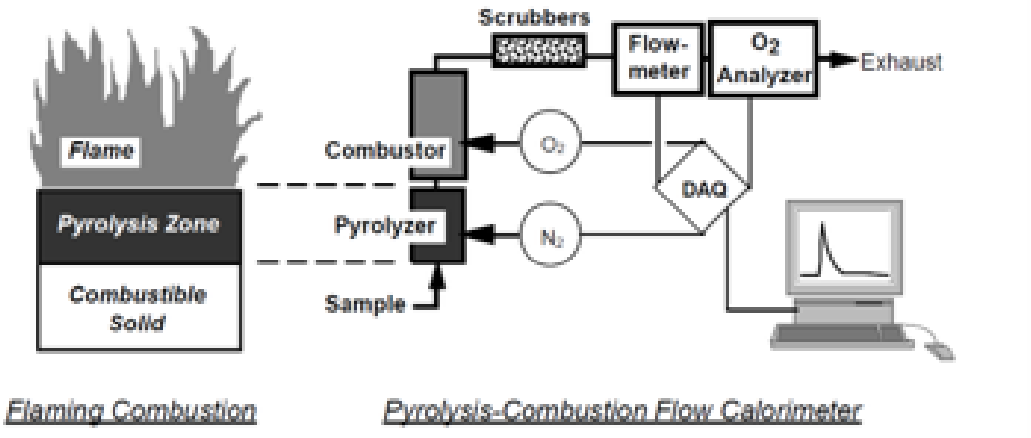


Figure 4. Illustration of Micro-Combustion Calorimeter [1].

Thermogravimetric analysis (TGA) of all samples was performed using a TGA-50 from Shimadzu Scientific Instruments. The samples were heated in a nitrogen environment from room temperature to 1000°C at a heating rate of 20°C/min. The air flow rate was 50 ml/min.

UL 94 is a standardized plastics flammability test developed to test the safety of materials exposed to flame. One variation of the UL 94, the vertical UL 94 test, is performed when a 20-mm flame is directed at the bottom of a standardized test bar. The sample is held vertically from above and at a 45-degree angle from the torch. The flame burns the sample for two ten-second periods. At the end of each ten seconds, the torch switches off. Time is then recorded until the material self-extinguishes. During the process the test specimen is observed to determine if dripping or flaming drips occurs. A safety rating is determined by collected data with V-0 being the safest rating. It should be noted that the lab and therefore the results are not officially certified for UL 94.

Mechanical properties testing was performed using an Instron Tension Tester 5966. A crosshead type extensometer was used to grip the 3D printed test bars. Testing was done in triplicate at room temperature with a crosshead speed of 5 mm/m.

3. RESULTS

3.1 Thermal Properties Analysis

TGA analysis results shown in Figure 5 summarized in Table 4 show a strong improvement in thermal stability for all PA11 formulations when compared to neat PA11. Thermal decomposition for 10% mass of PA11 occurs around 428°C and the temperature at 50% mass loss occurs at 454°C. Formulation 2, which contained 12.5 wt% FR, 2 wt% of both nanoclay and ANF, and 10 wt% showed the highest improvement in onset thermal degradation with a T10 of 467°C. All formulations had a temperature at 50% mass loss right at 500°C. Formulations 4 and 5 both had high residue masses of 12 and 12.5 wt%.

Overall thermal stability of the tested materials can be observed in Figure 5. All tested composites are translated to the right at higher temperatures. Further, at high temperatures it is clear that the PA11 nanocomposites have a higher mass remainder compared to the neat PA11. This is indicative of the FR property of enhancing thermal stability at higher temperature.

Table 4. Decomposition temperatures of PA11 formulations

Formulation	**T_{dec} at 10 wt% mass loss (°C)**	**T_{dec} at 50 wt% mass loss (°C)**	**Residue mass at 1000°C (wt%)**
Neat PA11	428	454	2.3
1	461	500	10.4
2	467	500	10.3

3	461	500	11.1
4	465	499	12
5	465	499	12.5
6	462	500	11.7

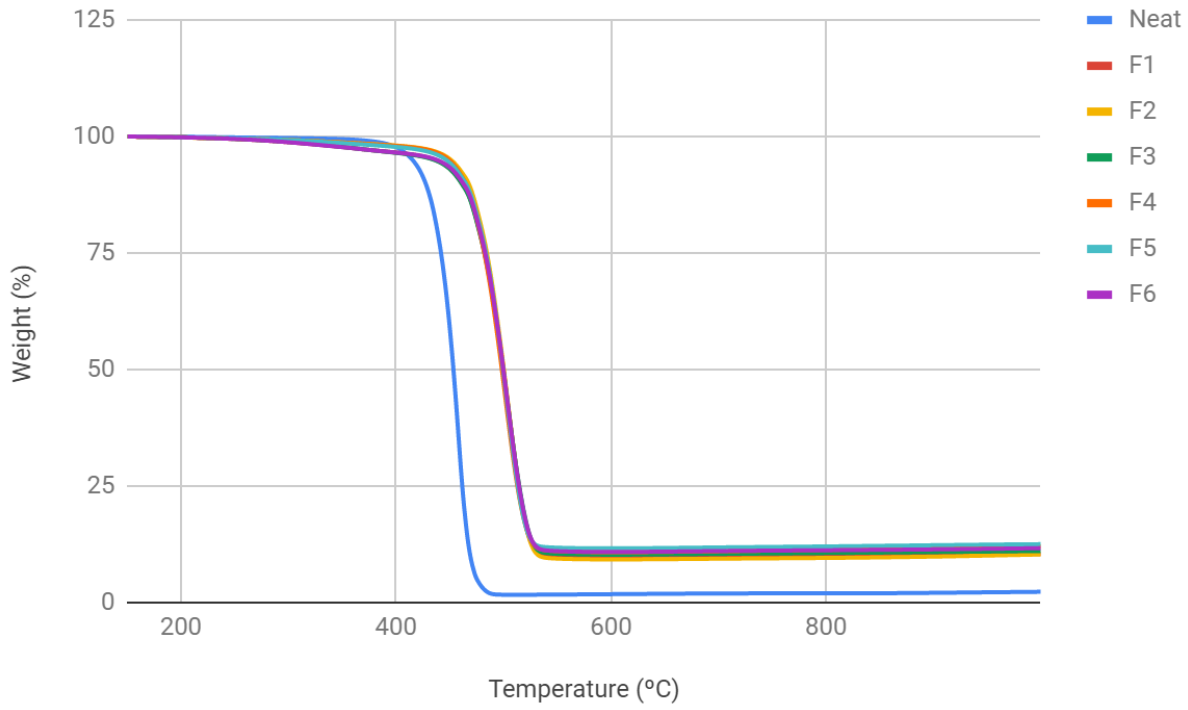


Figure 5. TGA curves of neat PA11 and its FR formulations.

Table 5 summarizes the heat release data gathered from MCC analysis. The peak heat release rate for PA11 was 2738 W/g. Each tested composite had a significant improvement in peak heat release rate ranging from 1420 W/g for F3 and 1504 W/g for F5.

Figure 6 shows the MCC graphs for all formulations. The composite formulations were all translated to the right compared to the neat PA11 with a difference of about 50 degrees between temperatures at peak heat release. This reinforces the TGA results suggesting large improvement in thermal stability. In addition, the curves of the composites are wider, which demonstrates a slower more controlled heat released compared to sharper curve of neat PA11.

MCC and TGA results were considered when selecting which composites to print and perform follow up flammability and mechanical testing. Formulations 3 and 4 demonstrated the strongest improvements in peak heat release rate while Formulation 5 had the highest residual mass as indicated by the TGA analysis.

Table 5. MCC heat release data for PA11 nanocomposites

Formulation	**Peak HRR (W/g))**	**SD**
Neat PA11	2738	223
1	1443	81
2	1494	25
3	1420	37
4	1435	16
5	1504	40
6	1459	79

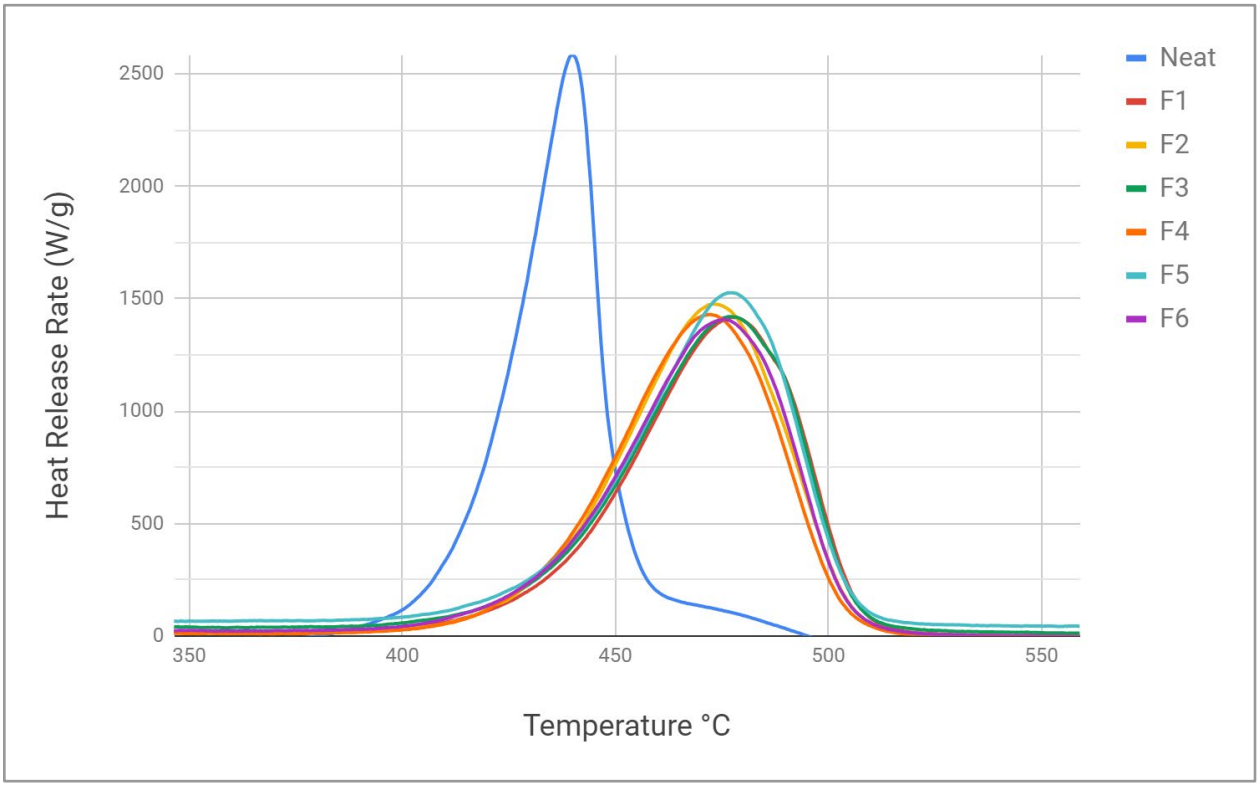


Figure 6. Heat release rates of PA11 composites.

Table 5 shows the results of the UL 94 tests. Most test specimens did not last long enough for a second flame exposure. Residual flames lasted for long periods, averaging about one minute. This frequently resulted in the sample burning severely to the point that it fell from its clamp as a

burning clump sometimes igniting the cotton indicator. Figure 7 shows the aftermath of the UL 94 testing. Of the tested samples, none achieved a UL 94 rating.



Figure 7: UL 94 test specimens after flame exposure with unexposed specimen for reference.

Table 6. UL 94 test data

Formulation	Average t1 (s)	Average t2 (s)	Flaming Drip	UL 94 Rating
3	77.9	-	Yes	Fail
4	53.1	-	Yes	Fail
5	62.1	-	Yes	Fail

3.2 Tensile Results and Analysis

Table 7 shows the results of the Instron tensile testing. Overall the strongest performance for mechanical was for Formulation 4, which contained 2 wt% of ANF and nanoclay. It performed best across the board with a tensile stress of 19.3 MPa, an E-modulus of 235 MPa and load at break of 394 N. Formulations 3 and 5 maintained similar results with the differences being a higher E-modulus in F5 of 208 MPa compared to 177 MPa for F3. The slightly improved modulus might be explained by the higher nanofiller loading of F5.

Table 6. Tensile test results for PA11 composites

Formulation	Tensile stress (MPa)	SD	Tensile Strain (mm/mm)	SD	E-Modulus (MPa)	SD	Load at break (N)	SD

3	17.8	0.42	0.19	0.3	177	13.5	347	8.9
4	19.3	0.8	.25	.04	235	36	394	35
5	17.4	2.1	.18	.05	208	26	342	49

4. CONCLUSIONS AND FUTURE WORK

The PA11 nanocomposites fabricated during this study demonstrated a strong improvement in thermal properties, such as thermal stability and heat release rate, however, these improvements were not translated into significantly improved flammability results as all tested formulations failed the UL 94 test. The results were unexpected based on similar FR PA11 nanocomposites which achieved the desired V-0 rating. The main differences between the formulations tested in this study and the ones which achieved a V-0 rating are the use of a new OP1400 flame retardant which uses a higher phosphorus content than the OP1312, and the use of a different nanoclay. The discontinued sale of Closite® 30B resulted in the use of commercially available 20A. Our study is a strong indication that the FR OP1400 and the 20A nanoclay do not synergize as effectively with PA11 when compared to the OP1312/30B composites of previous studies.

Future optimization studies should consider the use of OP1312 flame retardant with the commercially available Closite® 20A nanoclay. If the results are similar to the findings of Wu et al, it could indicate that the OP1400 FR is likely a poor choice for PA11 composites.

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