

INTUMESCENT FLAME RETARDANT POLYAMIDE 11 NANOCOMPOSITES

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Abstract

Current polyamide 11 and 12 are lacking in fire retardancy and high strength/high heat resistance characteristics for a plethora of fabricated parts that are desired and required for performance driven applications. The introduction of selected nanoparticles such as surface modified montmorillonite (MMT) clay or carbon nanofibers (CNFs), combined with a conventional intumescent flame retardant (FR) additive into the polyamide 11/polyamide 12 (PA11/PA12) by melt processing conditions has resulted in the preparation of a family of intumescent polyamide nanocomposites. These intumescent polyamide 11 and 12 nanocomposites exhibit enhanced polymer performance characteristics, i.e., fire retardancy, high strength and high heat resistance and are expected to expand the market opportunities for polyamide 11 and polyamide 12 polymer manufacturers.

The objective of this research is to develop improved polyamide 11 and 12 polymers with enhanced flame retardancy, thermal, and mechanical properties for selective laser sintering (SLS) rapid manufacturing (RM). In the present study, a nanophase was introduced into the polyamide 11 and combining it with a conventional intumescent FR additive via twin screw extrusion. Arkema RILSAN® polyamide 11 molding polymer pellets were examined with two types of nanoparticles: chemically modified montmorillonite (MMT) organoclays, and carbon nanofibers (CNFs); and Clairant's Exolit® OP 1230 intumescent FR additive were used to create a family of FR intumescent polyamide 11 nanocomposites.

Transmission electron microscopy (TEM) was used to determine the degree of nanoparticles dispersion. Injection molded specimens were fabricated for physical, thermal, and flammability measurements. Thermal stability of these intumescent polyamide 11 nanocomposites was examined by TGA. Flammability properties were obtained using the Cone Calorimeter at an external heat flux of 35 kW/m² and UL 94 Test Method. Heat deflection temperatures (HDT) were also measured. TEM micrographs, physical, thermal, and flammability properties are presented. FR intumescent polyamide 11 nanocomposites properties are compared with polyamide 11 baseline polymer. Based on flammability and mechanical material performance, selective polymers including polyamide 11 nanocomposites and control polyamide 11 will be

cryogenically ground into fine powders for SLS RM processing. SLS specimens will be fabricated for thermal, flammability, and mechanical properties characterization.

1. Introduction

Flame retardant (FR) additives such as inorganic metal oxides/hydroxides or halogens with or without phosphorous and nitrogen containing materials are required in conventional methods to modify flammable thermoplastic materials as FR products [1]. Large amounts of FR additives (>30%) are necessary in those methods to make FR thermoplastics. In many cases a reduction of mechanical properties, such as toughness, melt flow, etc. and/or release of smoke and toxic emissions, occurs when the modified thermoplastic is burning.

The incorporation of nanoparticles has been shown to be an effective method for developing FR thermoplastic polymer by twin-screw extrusion (a melt blending process). Small amounts of nanoparticles (<7%) are required to make nanocomposites to exhibit similar enhanced flammability properties when compared with the modified thermoplastic processed by conventional methods [2-13]. However, unlike the conventional FR thermoplastics, the resulting nanocomposites exhibit enhanced mechanical properties such as high strength/modulus, moisture resistance, higher heat deflection temperature, etc. Therefore, nanotechnology can be used to develop novel FR thermoplastic structural components with high performance characteristics.

Our previous studies [14-15] indicated that low amounts ($\leq 5\%$) of nanoparticles enhance the mechanical properties (such as tensile strength, flexural strength, and Young's modulus) but are somewhat lacking in flame retardancy to those FR thermoplastics with conventional FR additives. Large amounts of nanoparticles (>7%) would yield relatively good enhancement of flame retardancy, but the mechanical properties of the resulting polymer nanocomposites would be compromised.

Thus the major technical objective of this research program is the enhancement of the FR properties of the polyamide 11 nanocomposites while maintaining the mechanical properties of the polyamide 11 by incorporating selected nanoparticles (nanoclay and carbon nanofiber) and conventional intumescent FR additives into the Rilsan® polyamide 11 by melt processing conditions. It is anticipated that if synergism occurs between the nanoparticles and conventional FR additives in the polyamide 11 resin, the FR and thermal properties of the resulting polymer nanocomposites are expected to be better than the sole addition of nanoparticles. Various weight loadings of clay (5 to 7.5%) and carbon nanofiber (5 to 7.5%) and along with intumescent FR (20 to 30%) were melt-blended with polyamide 11 via twin-screw extrusion. The resulting pellets were injection molded into different test specimens.

Transmission electron microscopy (TEM) was used to examine the extent of dispersion of nanoparticles. Flammability properties were studied by conducting cone calorimetry of the specimens at 35kW/m^2 and UL 94. Thermal properties of the samples were analyzed using thermogravimetric analysis (TGA). Heat deflection temperatures were measured according to ASTM D648-06 Method B. Most data were compared with those of PA11 clay nanocomposites (PA11N) that we previously reported [14-15].

2. Experimental

2.1 Materials

Polymer Resin Polyamides (PA) are versatile thermoplastic engineering polymeric materials noted for outstanding properties such as high tensile strength, good resistance to flow under pressure (creep), excellent abrasion, chemical and heat resistance, and a low coefficient of friction. Polyamides such as PA6 and PA66 are high melting, moderately crystalline polymers (T_m 220-265°C) while PA11 and PA12 are intermediate melting materials (<200°C) and are less susceptible to moisture as compared to PA6 and PA66. Paul et al. [16] have examined the structure and properties of nanocomposites based on PA6, PA11, and PA12. Their studies were focused solely on nanoclays whereas our studies are directed to examining/comparing nanoclay and other nanoparticles to determine enhanced polymer characteristics such as flame retardancy and improved thermal/mechanical properties for the resulting PA11N.

Arkema's RILSAN® polyamide 11 (PA11) was selected for this study since it is an attractive polyamide used in quite a variety of applications. RILSAN® PA11 thermoplastic [17] is a polymer developed by Atofina Chemicals, Inc. (now known as Arkema, Inc.) in 1942. Derived from a series of complex chemical operations, RILSAN® PA11 is one of the few polymers that is produced from 'green' raw materials – castor beans. RILSAN® PA11 resin has earned a preferred material status in the most demanding applications due largely to their unique combination of thermal, physical, chemical, and mechanical properties. This results in an outstanding "cost performance ratio." Processing ease is another major benefit of RILSAN® polyamide 11 resins. Supplied in powder or pellet form RILSAN® PA11 resin can be processed by injection molding, extrusion, blown film extrusion, extrusion blow molding or rotomolding. The ease of processing of Rilsan® has led designers to select them for industries as diverse as aerospace, offshore drilling, electrical cables, automotive, and pneumatic and hydraulic hose.

Nanoparticles Two types of nanoparticles, nanoclay and carbon nanofiber, were used. Southern Clay Products' montmorillonite (MMT) nanoclay, Cloisite® 30B (a natural MT modified with an organic modifier, MT₂EtOT: methyl-tallow-bis-2-hydroxyethylquaternary ammonium at 90 meq/100g) was selected [18]. Achieving exfoliation of organomontmorillonite in various continuous phases is a function of the surface treatment of the MMT clays and the mixing efficiency of the dispersing equipment. Surface treatment of MMT is conveniently accomplished with the exchange of inorganic counterions, e.g., sodium etc., with quaternary ammonium ions. The second type of nanoparticles used was Pyrograf®-III PR-19-PS carbon nanofiber (CNF) from Applied Science, Inc. CNF is a form of vapor-grown carbon fiber, which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons [19-22]. In properties of physical size, performance improvement, and product cost, CNF complete a continuum bounded by carbon black, fullerenes, and single-wall to multi-wall carbon nanotubes on one end and continuous carbon fiber on the other end [22].

Fire Retardant Additive Clariant's Exolit® OP 1230 is an intumescent flame retardant additive based on metal phosphinate. It is a white powder with high P content (~24%), non-toxic, hydrophobic, and exhibits good thermal stability. It had been mixed with polyamide 66 and the resulting products showed enhanced FR properties [23].

2.2 Measurements

Morphological Microstructures Analysis The cross-sections of the PA11 nanocomposites were investigated by TEM to examine the dispersion of nanoclay, carbon nanofibers, and intumescent FR additives within the PA11 polymer matrix. Uniform distribution of the nanoparticles/FR additives within the polymer matrix is essential to yield the best enhancement of material properties of the polymer matrix.

Thermal Stability Testing Thermal stability of the PA11 baseline and PA11N were examined by thermogravimetric analysis (TGA) using the Perkin Elmer TGA 7. Weight changes in sample materials are measured as a function of temperature or time in TGA. The sample is heated by a furnace with nitrogen while the loss or gain of sample weight is monitored by a sensitive balance. Weight, temperature, and furnace calibrations were carried out within the range of the TGA (100-900°C) at scan rates of 10°C/min and 20°C/min.

Flammability Testing The tests described herein were conducted in accordance with ASTM E1354 standard test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. The method is based on the observation that the net heat of combustion of most materials is directly related to the amount of oxygen released per kilogram of oxygen consumed. Specimens in the test are burned in ambient air conditions with a predetermined external heat flux that can be set from 0 to 100 kW/m² (35 kW/m² was adapted in our study). Burning is generally induced by a spark ignition source. The primary measurements are oxygen concentration and exhaust gas flow rate. Additional measurements include the mass loss rate of the specimen, the time to sustained flaming and smoke obscuration. Results of the test are expressed in terms of time to ignition; peak, average and total heat release rates, mass loss and mass loss rate; effective heat of combustion; visible smoke development; and release rates of carbon monoxide and carbon dioxide. Three specimens were tested for each formulation. Heat release rate data will be discussed in detail.

An additional test was UL 94, a standard test for flammability of plastic materials in industry that serves as a preliminary indication of plastics acceptability for use as a component of a device or appliance with respect to its flammability behavior. UL 94 is not intended to reflect the hazards of a material under actual fire conditions but is considered as a preliminary step toward obtaining plastic recognition and subsequent listing in the "Plastics Recognized Component Directory" (formerly known as "Yellow Cards"). The materials are tested in a vertical setting to determine the UL94 V-0 rating. UL 94 Vertical burning test involves a 1/2" x 5" specimen which is held at one end in the vertical position. A burner flame is applied to the free end of the specimen for two 10 second intervals separated by the time it takes for flaming combustion to cease after the first application. Five specimens are tested for each formulation.

Heat Deflection Temperature (HDT) Heat deflection temperature is defined as the temperature at which a standard test bar deflects a specified distance under a load. It is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. An Atlas HDV2 DTUL/ Vicat tester is used. The bars are placed under the deflection measuring device. A load of 1.80 MPa is placed on each specimen. The specimens are then lowered into a silicone oil bath where the temperature is raised at 2°C/minute until they deflect 0.25 mm for ASTM D648 test procedure. The temperature at the specified load and deflection is recorded.

3. Results and Discussion

3.1 Processing and Characterization of the Polymer Nanocomposites

Blending Nanoclays/FR Additive/PA11 Polymer Chemically treated pillared clay Cloisite® 30B and intumescent fire retardant additive Exolit® OP1230 were used. The individual clay layers are separated by alkyl ammonium ion incorporation (d spacing increased) allowing for anticipated intercalation of solid organic resins when the clay is melt blended with the resins. Clays were blended with the PA11 resin to intercalate and eventually exfoliate the clay. Twin screw extrusion mixing enhances the exfoliation rate. The degree of exfoliation is examined by TEM.

A 30 mm Werner Pfleider corotating twin screw extruder which is configured for a wide variety of materials was used. The extruder L/D can be varied from 21 to 48, with options of multiple feeds and vents. The energy profile of the screw is adjusted to optimally meet the needs of the target product. Table 1 shows the nanoparticles and FR additive selected at various wt% loading levels with the PA11 resin. For the clay a relatively long residence time is preferred for the screw profile allowing high shear characteristics for complete separation of the nanoclay platelets with the polymer matrix being uniformly dispersed into the clay galleries. Approximately 10 lbs of each formulation were produced. Separate volumetric feeders were used for the base resin and the nanoparticles. The PA11 was dried in a desiccant drier before compounding. Injection molded specimens of each blend were prepared and examined by TEM. Figure 1 shows the TEM micrographs of polyamide 11 with 25% FR and 5% Cloisite® 30B. It is evident that exfoliation of Cloisite® 30B in PA11 polymer was achieved. The micro-sized FR intumescent FR additives were also uniformly dispersed in the PA11 polymer.

Blending CNF/FR Additive/PA11 Polymer PR-19-PS CNF possesses a diameter of about 130 nm and a length of several microns. It can be classified as MWNT. It was blended with PA11 polymer along with FR additive in three different loading levels via twin screw extrusion (Table 1). For the CNF, the screw was configured to allow separation of the CNF without fracturing them. Figure 2 shows the TEM micrographs of polyamide 11 with 20% FR and 7.5% CNF. The CNF was also well dispersed in the matrix.

Table 1 Composition of Different Formulations of PA11 Nanocomposites

Formulation	PA11 (wt%)	Clay (wt%)	CNF (wt%)	FR (wt%)
1	100	0	0	0
2	70	0	0	30
3	75	5	0	20
4	70	5	0	25
5	72.5	7.5	0	20
6	75	0	5	20
7	70	0	5	25
8	72.5	0	7.5	20

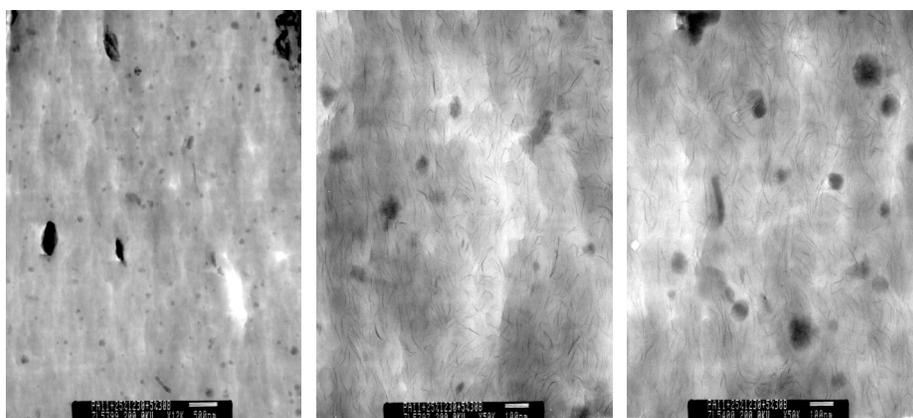


Figure 1 TEM micrographs of polyamide 11 with 25% intumescent fire retardant additive and 5% Cloisite 30B polymer showing exfoliation of nanoclay in PA11 was achieved. The intumescent FR additive (micron-sized black particles) was uniformly dispersed in the PA11 polymer.

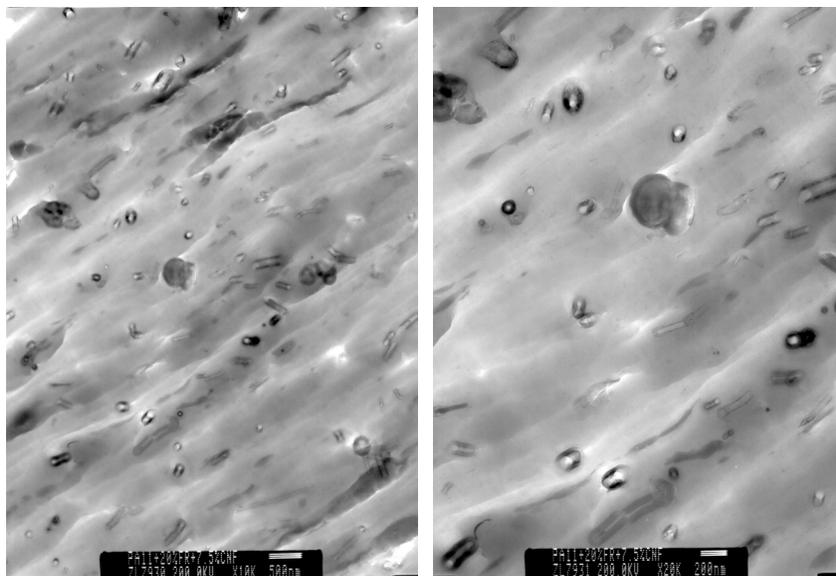


Figure 2 TEM micrographs of polyamide 11 with 20% FR additive and 7.5% PR-19-PS CNF.

3.2 Thermal Stability of the Polymer Nanocomposites

TGA was performed on all eight formulations under nitrogen using scan rates of 10°C/min and 20°C/min. The test could not be performed under air since the intumescent FR additives would expand at high temperature under an air environment resulting in erratic results. Since lower and higher scan rates showed similar trend of curve shifts with the lower scan rate exhibiting a better separation of curves, only the TGA data obtained using the scan rate of 10°C/min is shown. Figure 3 compares the thermogravimetric analysis result of polyamide 11 with only 30B and polyamide 11 with both 30B and FR at 10°C/min. The decomposition temperature of polyamide 11 with 5%30B and 25%FR is higher than that without FR and shows that the presence of FR materials can enhance the thermal stability of the polymer. The data also show that the formulations with clay only had the same or higher thermal stability than the composition with the FR additive alone, while the compositions with both the clay and FR additive showed a much higher stability. These data confirm that synergism exists between the clay and FR additive in the polyamide 11 matrix.

Figure 4 shows the TGA results of polyamide 11 with CNF and FR additive. The sample with 7.5% CNF and 20% FR had the highest decomposition temperature while the PA11 baseline sample had the lowest decomposition temperature. The data showed that the increased loading of either CNF or FR enhances the thermal stability of the material since the sample with 5% CNF and 20% FR had a lower decomposition temperature than the other two samples which contained increased amounts of either CNF or FR additive. The addition of CNF slightly increased the thermal stability of the polyamide 11 while the combination or synergy of CNF and FR additive yielded better FR enhancement and similar to nanoclay formulations.

It should be noted that for the formulations with both nanoparticles and FR additive, the compositions with highest decomposition temperatures in TGA had the lowest PHRR in

cone calorimetry (section 3.3). Thus combining TGA with UL 94 is proposed as a good screening tool for selecting those candidates for submission for cone calorimetry analysis.

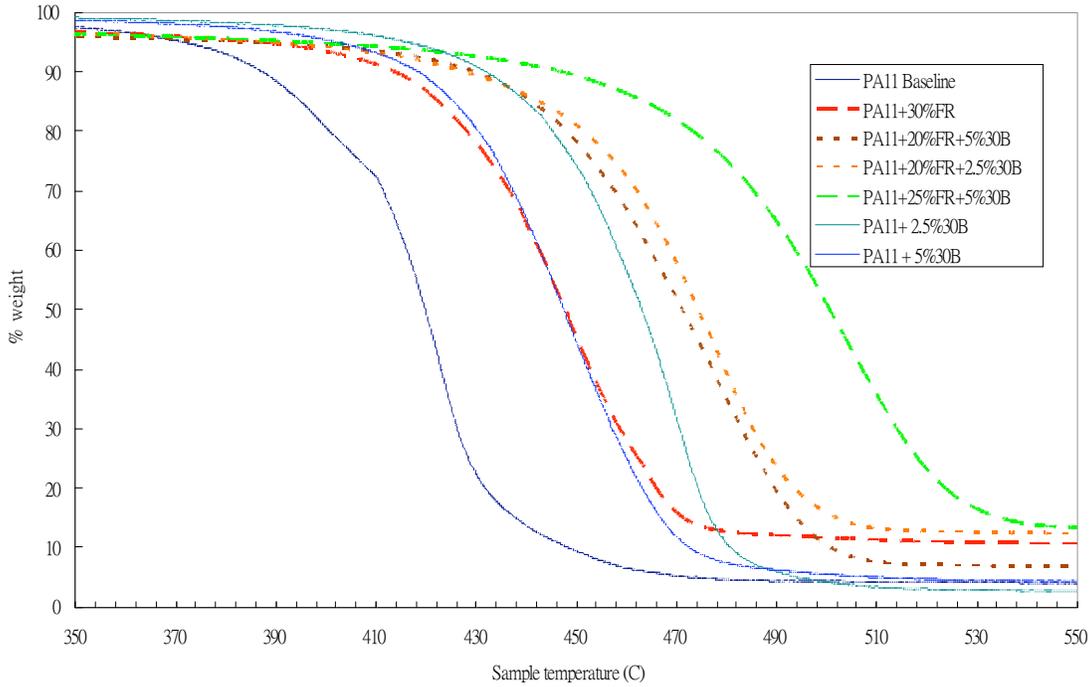


Figure 3 Thermogravimetric analysis of PA11 clay nanocomposites with and without fire retardant additive at 10°C/min.

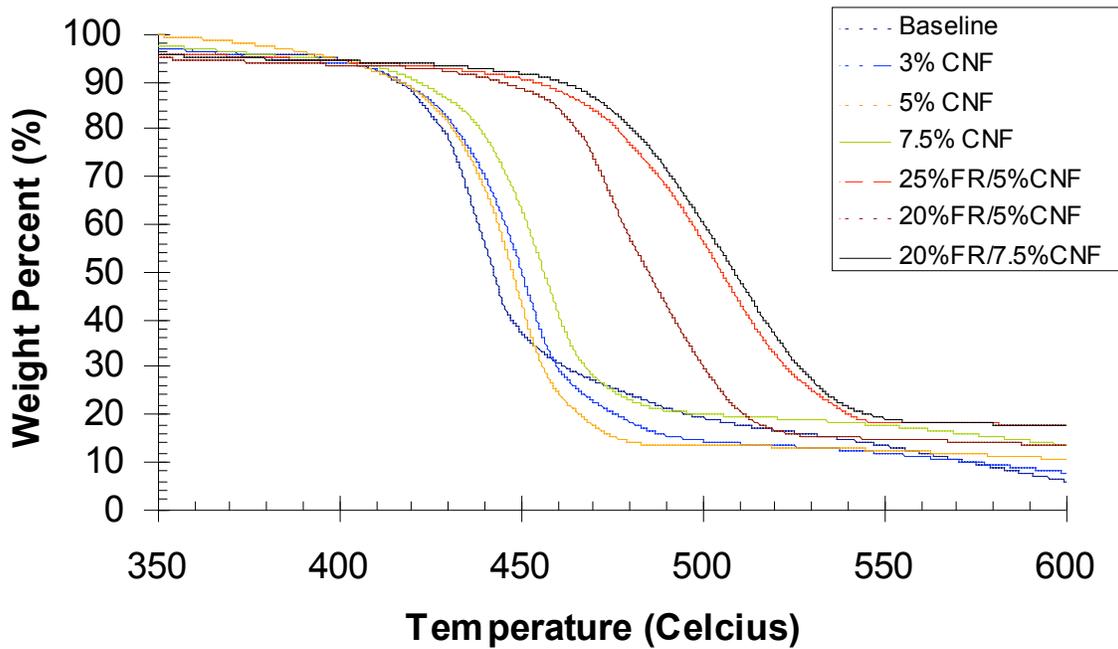


Figure 4 Thermogravimetric analysis of PA11 CNF nanocomposites with and without fire retardant additive at 10°C/min.

3.3 Flammability Properties of the Polymer Nanocomposites

Cone Calorimetry Eight sample sets were examined with no additional conditioning/drying prior to cone calorimeter testing. Cone Calorimeter experiments were conducted on a FTT Dual Cone Calorimeter at a heat flux of 35kW/m^2 with an exhaust flow of 24 L/s using the standardized cone calorimeter procedure (ASTM E-1354-02d). All samples were tested without frame and grid, with the back side of each sample wrapped in aluminum foil. Data collected from all samples have an error of $\pm 10\%$ based on a specimen surface area of 100 cm^2 .

Overall data are shown below in Table 2. Two general trends can be noted from the data. First, the peak heat release rate (PHRR) of samples with both nanoparticles and FR (of lower wt% loading) were all lower than that with the FR only. Second, PHRR decreased as the loading level of nanoparticles increased, with the same loading level of FR. These observations match our expectation since larger amount of nanoparticles generally yields better enhancement on the flammability properties. The average HRR of all samples was also lowered significantly by the addition of nanoparticles. The total heat release was reduced as well. However, the total smoke release was increased substantially, comparing to the baseline material, which was mainly due to the addition of the FR additive.

Table 2 Overall Cone Calorimeter Data: FR-Polyamide-11 Nanocomposite Samples

Sample ID #	Sample Description	Time to ignition (s)	Peak HRR (kW/m^2)	Time to Peak HRR (s)	Average HRR (kW/m^2)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)
PA11 Control	No FR, No Clay	126	1589	243	636	34.5	99.1	121.8	1208
PA11 30% FR	FR only	129	887	268	515	34.1	94.8	96.0	2120
PA11 20% FR	w/ 5% Clay	142	544	175	254	33.1	89.0	99.5	2587
PA11 20% FR	w/ 7.5% Clay	148	480	236	282	34.8	92.9	100.4	2740
PA11 25% FR	w/ 5% Clay	136	446	180	223	37.2	96.3	105.6	2938
PA11 25% FR	w/ 5% CNF	209	355	353	238	30.3	86.4	81.3	2462
PA11 20% FR	w/ 5% CNF	189	313	455	123	31	87.9	87	2372
PA11 20% FR	w/ 7.5% CNF	176	288	451	109	28.7	82.3	80.8	2256

An interesting observation is worthy of discussion and involves an anomaly of nanoparticle behavior. It is usually expected that when the loading level of FR additive is increased with constant wt% loading of nanoparticles, the PHRR should decrease. This is true for the clay FR nanocomposites, however, it is the opposite for CNF compositions. This anomaly may be due to some physical effects during the test and requires further investigation.

The peak heat release rate (PHRR) of PA11 and PA12 nanocomposites with various weight loadings of different nanoparticles are shown in figure 5. It shows that synergism existed between the nanoparticle and fire retardant additive. These FR intumescent PA11 nanocomposites (FR-PA11N) had lower PHRR than the PA11 with only the fire retardant additive and that with only the nanoparticle (of same loading level). Among all the PA11-clay nanocomposites such as PA11 + 25%FR + 5% 30B, PA11 + 20%FR + 7.5% 30B, and PA11 + 10% 30B, all exhibited the lowest PHRR. For the PA11-CNF nanocomposites, the synergism between CNF and FR additive gave a substantial enhancement of PHRR over the formulations with only the CNF. However, different loading levels of particles are expected to have different effects on the mechanical

properties of the polymer nanocomposites. The mechanical properties of these compositions are under investigation.

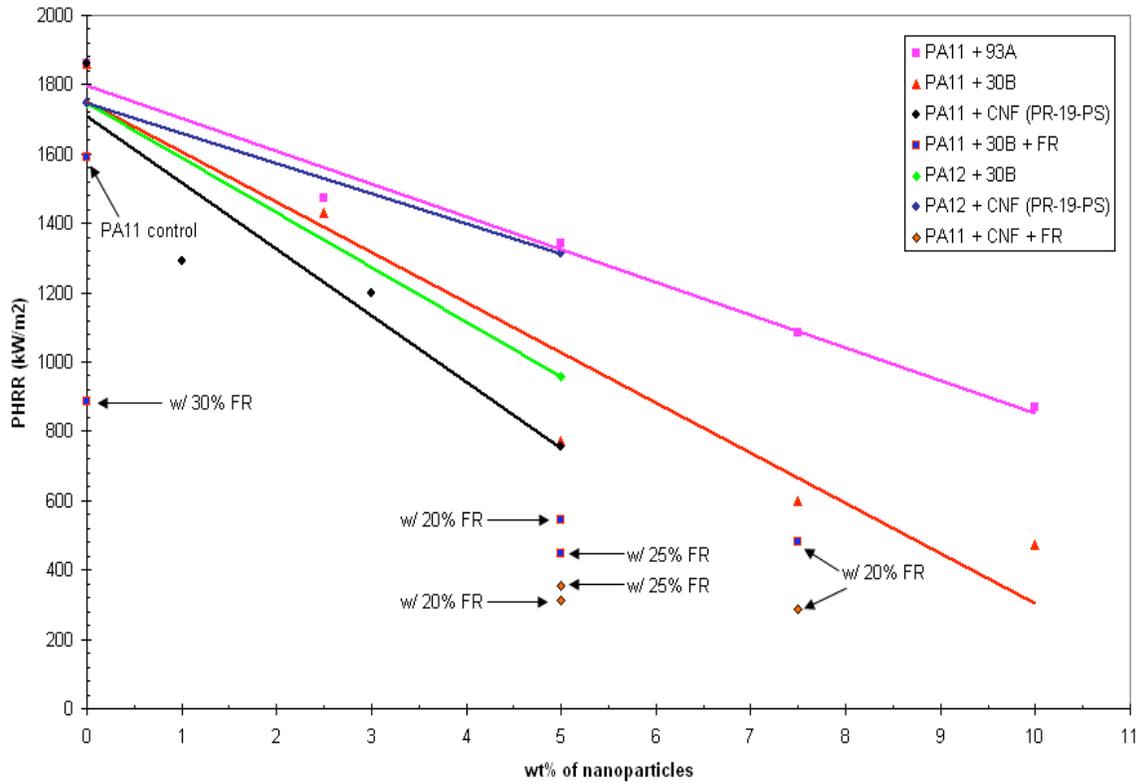


Figure 5 Peak heat release rate of PA11 and PA12 of various weight loading of nanoparticles. 93A = Southern Clay Products’ Cloisite® 93A organoclay; 30B = Southern Clay Products’ Cloisite® 30B organoclay; CNF = Applied Science, Inc’s PR-19-PS carbon nanofibers.

UL 94 The materials were tested as “received with no additional conditioning/drying” before UL 94 testing. The test was performed in our lab and the UL 94 testing requirements and procedures were followed as stringently as possible. Our lab is not certified for UL 94 and the results serve as a screening tool. Five specimens were tested for each formulation. The testing was performed in a fume hood with a preset airflow of 90-105 ft/min. Fume hood sash was pulled down as much as possible to prevent airflow from the outside environment. The erratic exhaust airflow from the fume hood and the surrounding made the reproducibility of the testing challenging. The burner is lit during the time of this experiment to keep the applied flame constant between each specimen. Table 3 shows the results of the testing.

Table 3 UL 94 Results of Cloisite 30B and PR-19-PS Samples

Sample (% PA 11 resin / % Nanoparticle / % FR 1230)	Duration of flaming combustion after the first burner flame application (t ₁)	Duration of flaming combustion after second burner flame application (t ₂)	Whether or not flaming drips ignite cotton placed below specimen	Whether or not specimen burns up to holding clamp
Baseline (PA 11)	18.78	N/A	Yes	N/A
Baseline (PA 11)	23.66	N/A	Yes	N/A
Rating	N/A			
70 / 0 / 30	0.00	0.00	No	No
70 / 0 / 30	0.00	1.75	No	No
70 / 0 / 30	0.00	3.06	No	No
70 / 0 / 30	0.00	1.30	No	No
70 / 0 / 30	0.00	2.62	No	No
Rating	V-0			
Cloisite 30B				
70 / 5 / 25	2.00	6.10	No	No
70 / 5 / 25	1.65	12.97	No	No
70 / 5 / 25	2.75	5.41	No	No
70 / 5 / 25	2.50	7.20	No	No
70 / 5 / 25	2.80	10.44	No	No
Rating	V-1			
72.5 / 7.5 / 20	1.12	2.57	No	No
72.5 / 7.5 / 20	1.25	5.71	No	No
72.5 / 7.5 / 20	1.54	7.69	No	No
72.5 / 7.5 / 20	1.25	5.47	No	No
72.5 / 7.5 / 20	2.50	5.91	No	No
Rating	V-0			
75 / 5 / 20	3.34	16.40	No	No
75 / 5 / 20	4.37	20.66	No	No
75 / 5 / 20	4.22	8.84	No	No
75 / 5 / 20	3.72	40.72	No	No
75 / 5 / 20	7.32	13.13	No	No
Rating	V-1			
PR19PS CNF				
70 / 5 / 25	0	3.07	No	No

70 / 5 / 25	0	4.57	No	No
70 / 5 / 25	0	2.93	No	No
70 / 5 / 25	0	4.5	No	No
70 / 5 / 25	0	3.27	No	No
Rating	V-0			
75 / 5 / 20	2.06	2.77	No	No
75 / 5 / 20	0	6.77	No	No
75 / 5 / 20	0	4.87	No	No
75 / 5 / 20	0	2.92	No	No
75 / 5 / 20	0	2.97	No	No
Rating	V-0			
72.5 / 7.5 / 20	0	3.37	No	No
72.5 / 7.5 / 20	0	3.77	No	No
72.5 / 7.5 / 20	0	3.07	No	No
72.5 / 7.5 / 20	0	3.87	No	No
72.5 / 7.5 / 20	0	3.52	No	No
Rating	V-0			

Note: To obtain a UL 94 V-0 rating, one of the criteria conditions is that the afterflame time for each individual specimen t_1 (afterflame time after first flame application) or t_2 (afterflame time after second flame application) has to be ≤ 10 s. For V-1 rating the afterflame time for each individual specimen t_1 or t_2 has to be ≤ 30 s.

Only two baseline specimens (100% PA 11) were tested because its classification is clear. Both specimens burned for more than 10 seconds after first flame application. Moreover, drips from the specimens ignite the cotton placed below. Therefore, it is safe to conclude that baseline PA11 did not pass the UL 94 V-0 test. There were some other distinct observations that can be made from the testing:

1. The addition of FR OP1230 and/or the nanoparticles greatly reduced the combustion of the polymer after the first burner flame application and also prevented the system from dripping
2. PA11 with 30% of fire retardant material and no nanoclay performed best in terms of combustion time
3. Of three formulations with nanoclay, only one (72.5% PA11, 7.5% 30B, 20% FR) passed the requirement of V-0 rating
4. All three of PR19PS CNF formulations passed the V-0 requirements

The results clearly indicated the enhancement of PA11 systems with FR additive and nanoclay. The system with 70% PA11 and 30% FR additive performed the best. The composition of FR additive and nanoclay were varied and compared with PA11/FR system. In terms of total flaming time for 5 specimens of each formulation, only the system with 7.5% 30B/20% FR 1230 passed the V-0 requirement. The formulation with 5% 30B/25% FR 1230 failed the requirements by a small margin while the formulation with 2.5% 30B/25% FR 1230 clearly failed the requirement. The nanoclay out-performed the FR additive in improving fire-resistance by comparing the results for 7.5%30B/20%

FR and 5% 30B/25% FR. Just by increasing the nanoparticle by 2.5% and reducing the FR by 5%, better results were obtained. It is recommended that another formulation, specifically 10% 30B/20% FR should be tested to confirm the trend. The same trend was also observed with carbon nanofiber samples. Increased loadings of CNF result in improved fire retardancy. However, the difference was not as clear as with the Cloisite 30B formulations. The 72.5/7.5/20 formulations for Cloisite 30B and PR-19-PS with 20 % of fire retardant additive both passed the requirements for V-0 test. The CNF formulation has no combustion at the first flame application and has a lower total combustion time than the Cloisite 30B formulation. Therefore, PR19PS with fire retardant additive out-performs its Cloisite 30B counterpart.

The results of UL 94 test were quite consistent with the cone calorimetry data. Those formulations which passed the V-0 requirement had the lowest PHRR. One exception was the polyamide 11 with 25% FR additives and 5% nanoclay. It had a slightly lower PHRR than the one with 20% FR and 7.5% nanoclay but it only passed the V-1 requirement. However, as mentioned above, it only failed the V-0 requirement by a small margin. Out of the five tested specimens, three of them passed the requirements and the remaining two only burned for less than a few seconds longer than the requirement. These variations might be due to the experimental apparatus.

3.4 Heat Deflection Temperature of the Polymer Nanocomposites

Based on the results of cone calorimetry, six formulations (PA11 baseline, PA11/20%FR/5%30B, PA11/20%FR/7.5%30B, PA11/20%FR/5%CNF, PA11/25%FR/5%CNF, and PA11/20%FR/7.5%CNF) were chosen for the heat deflection temperature (HDT) testing. The specimens had the same weight loading of fire retardant additive but different amounts of nanoclay. Figure 6 shows that the polyamide 11 with additive had substantial increases in heat deflection temperature compared to the polyamide 11 baseline. It also shows that higher weight loading of nanoclays gave higher HDT, which agreed with our prediction based on the results of TGA. Further experimental investigation is needed in order to analyze the effect of the fire retardant additives in the systems. More testing is also needed to compare these systems to the polyamide 11 composites with only nanoclays since the heat deflection temperatures of these polymer nanocomposites were not measured.

All three formulations with FR additives and CNF were chosen for the test because they had the lowest PHRR. HDT testing is still in progress. However, it is expected that they all would have higher HDT than the baseline polyamide 11 and the FR additive and nanoclay formulations.

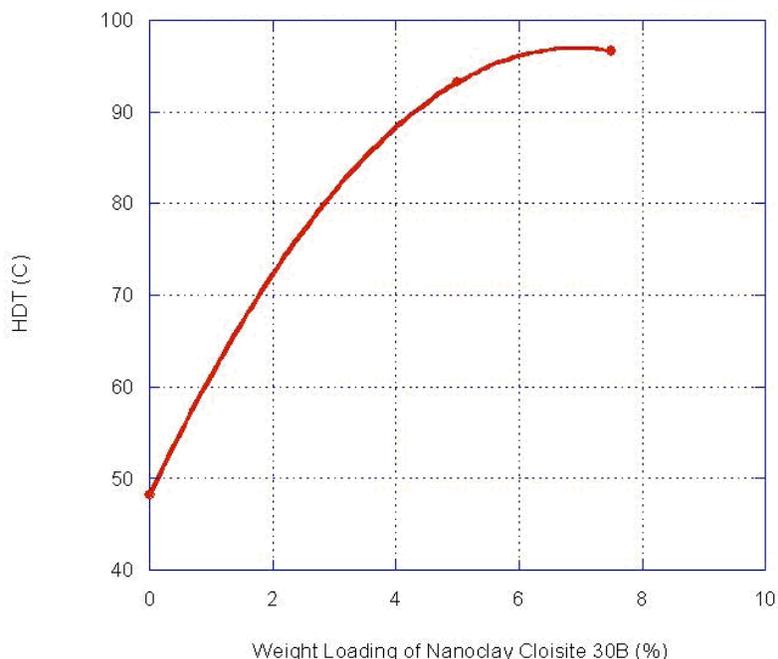


Figure 6 Heat deflection temperature of PA11N with 20% FR additive and various loading of nanoclay.

4. Summary and Conclusions

A total of eight polymer blends of polyamide 11 polymer with MMT nanoclay / carbon nanofiber and intumescent fire retardant additive were compounded separately via twin screw extrusion. Injection molded specimens of PA11 baseline and FR-PA11N were fabricated for physical, mechanical, thermal, and flammability properties measurements. Some results were also compared with PA11 clay nanocomposites. Transmission electron microscopy (TEM) was used to examine the dispersion of the nanoparticles in the polyamide 11 resin. Thermal stability of PA11N was analyzed using thermogravimetric analysis. Flammability properties were measured by cone calorimeter at a radiant heat flux of 35kW/m² and UL 94 test. Heat deflection temperatures were also measured.

The following conclusions were drawn from this study:

1. The TEM analysis has shown that good dispersion of the nanoclays / carbon nanofibers in the polyamide 11 resin systems was achieved.
2. The peak heat release rate of the FR-PA11-nanoclay or FR-PA11-CNF polymers decreases as the amount of nanoclay or CNF increases. The PHRR of these polymers is also lower than that of FR-PA11 composite.
3. Further experimental investigation is needed in order to evaluate and compare the effect of different amounts of the nanoclay or CNF and fire retardant additives on PHRR of the polymer systems, respectively.
4. For the FR-PA11-nanoclay polymers, only the formulations with 20% FR and 7.5% clay passed the UL 94 V-0 requirement. For the FR-PA11-CNF polymers, all three formulations passed UL 94 V-0 requirement.

5. All systems of polyamide 11 with both nanoparticles and FR additive have higher decomposition temperatures than those compositions with solely nanoparticles or FR additive alone.
6. Some trends and relationships were observed between the results of cone calorimetry and those of TGA and UL 94. The combined use of TGA and UL 94 testing can facilitate the selection of key candidates for cone calorimetry analysis. This would reduce the number of candidates for cone calorimetry analysis which is costly.
7. The heat deflection temperature is increased substantially by the addition of nanoclays and fire retardant additive. The HDT of the FR-PA11-CNF nanocomposites will be determined.
8. More data are needed to investigate the effect of different loadings of the intumescent fire retardant additive on the heat deflection temperature of the polymer systems.
9. In general, nanoclay and CNF enhanced the thermal stability of the polyamide 11.
10. Synergism was established in terms of thermal and flammability properties that occur between the nanoparticles (nanoclay and CNF) and the intumescent FR additive.
11. Mechanical properties data of the FR-PA11N are needed to complete the evaluation of these nanocomposites.
12. Microstructural analyses of pre- and post-test FR-PA11N specimens would provide a more fundamental understanding of material behavior during combustion.
13. Future studies of FR-PA11 composites with other nanoparticles (e.g. nanoalumina, Multi-wall carbon nanotubes) as well as other intumescent FR additives are proposed.

5. References

1. G.N. Nelson and C.A. Wilke, Ed., *Fire and Polymers III. Materials and Solutions for Hazard Prevention*, American Chemical Society, Washington, D.C., 2001.
2. E. Giannelis, *Adv. Mater.* 8, 29 (1996).
3. J.W. Gilman, T. Kashiwagi, *SAMPE J.*, 33 (4), 40 (1997).
4. J.W. Gilman, *Appl. Clay. Sci.* 15, 31 (1999).
5. J. Zhu, A.B. Morgan, J. Lamelas, C.A. Wilke, *Chem. Mater.* 13, 3774 (2001).
6. M. Zanetti, G. Camino, R. Mulhaupt, *Polym. Degrad. Stabil.* 74, 413 (2001).
7. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, Jr., E. Manias, E. P. Giannelis, M. Wuthernow, D. Hilton, S.H. Phillips, *Chem. Mater.* 12, 1866 (2000).
8. T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Awad, J. Douglas, *Macromol. Rapid Commun.*, 23, 761 (2002).
9. J.H. Koo *et al.*, *Proc. SAMPE 2003*, SAMPE, Covina, CA, 2003, p. 954.
10. F. Yang, R.A. Yngard, G.L. Nelson, "Nanocomposites 2002," San Diego, CA, Sept 23-5, 2002.
11. T. Kashiwagi *et al.*, "Nanocomposites 2002," San Diego, CA, Sept 23-25, 2002.
12. A.D. Pool, H.T. Hahn, *Proc. SAMPE 2003*, SAMPE, Covina, CA, 2003.

13. A.B. Morgan and C.A. Wilke, Ed., *Flame Retardant Polymer Nanocomposites*, Wiley, New York, 2007.
14. J.H. Koo et al., *Proc. SAMPE 2005 ISSE*, SAMPE, Covina, CA, 2005.
15. S. Lao, J.H. Koo et al., *Proc. SAMPE 2005 ISTC*, SAMPE, Covina, CA, 2005.
16. T. D. Fornes, D.R. Paul, *Macromolecules*, 37, 7698 (2004).
17. Polyamide 11 technical data sheet, Arkema, Inc., France.
18. Cloisite® 30B technical data sheet, Southern Clay Products, Gonzales, TX.
19. G.G. Tibbetts, *J. Crystal Growth* 1984; 66:632.
20. M.L. Lake, J-M. Ting. In *Carbon Materials for Advanced Technologies*, T.D. Burchell, Ed., Pergamon, Oxford: England, 1999.
21. G.G. Tibbetts, M.L. Lake, K L. Strong, B.P. Rice, *Composites Science and Technology* 67, 1709-1718 (2007).
22. B. Maruyama, K. Alam, *SAMPE J.*, 38 (3), 59 (2002).
23. A. Beard, T. Marzi, Addcon 2005, Hamburg, Germany, 20-21 Sept 2005.

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