

FLAMMABILITY AND THERMAL PROPERTIES OF POLYAMIDE 11-ALUMINA NANOCOMPOSITES

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Abstract

Neat polyamides 11 and 12 lack high strength/high heat resistance and flame retardancy. The incorporation of selected nanoparticles is expected to enhance these properties to a level that is desired and required for performance driven applications. This enhancement may result in additional market opportunities for the polyamide 11 and 12 polymer manufacturers. The objective of this study is to develop polyamide 11 polymer nanocomposites with enhanced thermal, flammability, and mechanical performance for selective laser sintering (SLS) rapid manufacturing. Three types of nano-alumina (X-0 needle, X-25SR, and X-0SR) with different organic treatments were melt-compounded into polyamide 11 in three different weight loadings of the nanoparticles (2.5%, 5%, and 7.5%). Injection molded specimens were fabricated for thermal, flammability, and mechanical properties characterization. Although nano-alumina was uniformly dispersed in polyamide 11 and better thermal stability of the nanomodified materials was observed, the desired FR characteristics of the nanomodified polyamide 11 was not achieved. None of the materials passed the desired UL 94 V0 rating.

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 when using these 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 approach for developing FR thermoplastic polymer by twin-screw extrusion (a melt blending process). Small amounts of nanoparticles (<7%) are required to prepare nanocomposites that exhibit 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 improved, high performance characteristics.

The major technical objective of this study is to investigate the feasibility of enhancing the fire retardancy and flammability properties of nylon (polyamide) thermoplastic material by combining it with selected nanoparticles. It involved the incorporation of nanoparticles into nylon (polyamide) 11 (PA11) to form a nylon (polyamide) 11 nanocomposite (PA11N). These PA11N materials are expected to exhibit reduced flammability and improved thermal properties as compared to the baseline PA11 material. The effect of nanoparticles on the resin will also be examined. Three types of nano-alumina (n-alumina) with different organic surface treatments and shape, namely Dispal® X-0 needle, X-25SR, and X-0SR, were melt-blended, separately. These n-alumina were compounded with RILSAN® PA11 using twin-screw extrusion to form PA11N in three different weight loadings (2.5%, 5%, and 7.5%). A total of ten formulations (including the neat PA11) were produced. The resulting pellets were injection molded into different test specimens. Transmission electron microscopy (TEM) was used to examine the extent of dispersion of nanoparticles in the polymer. Flammability properties were studied by conducting UL 94 test. Thermal properties of the samples were analyzed using thermogravimetric analysis (TGA).

2. Experimental

2.1 Materials

Polymer Resin Polyamides (PAs) 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. Fornes and Paul [14] 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 and 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 a variety of applications. RILSAN® PA11 thermoplastic [15] 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 are 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. Three types of n-alumina with different organic surface treatment and shape were used. They were Sasol's Dispal® X-0 needle, X-0 SR, and X-25 SR. They

are synthetic alumina nanopartilces which are high purity, highly dispersible, colloidal Boehmite alumina powders manufactured by Sasol. These alumina powders are available in micron size but they become nano-sized in the dispersed phase. Figure 1 shows the high resolution SEM micrographs of as-received n-alumina.

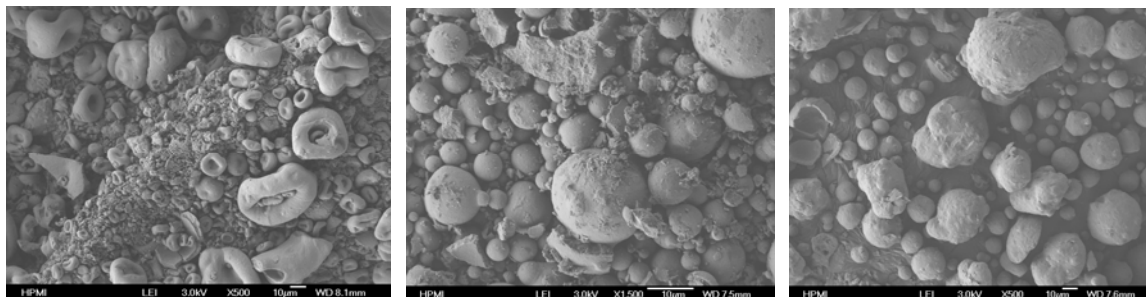


Figure 1 SEM micrographs of as-received n-alumina; X-0 needle (left), X0-SR (middle), and X25-SR (right).

2.2 Measurements

Morphological Microstructures Analysis The cross-sections of the PA11 nanocomposites were investigated by TEM to examine the dispersion of n-alumina within the PA11 polymer matrix. Uniform distribution of the nanoparticles 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 UL 94 is 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 UL 94 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.

3. Results and Discussion

3.1 Processing and Characterization of the Polymer Nanocomposites

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. 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. Figures 2 to 4 show TEM micrographs of PA11 with 5% X-0 needle, 5% X0-SR, and 5% X25-SR, respectively, which are indication that good dispersion of the nanoparticles in the polyamide matrix were achieved.

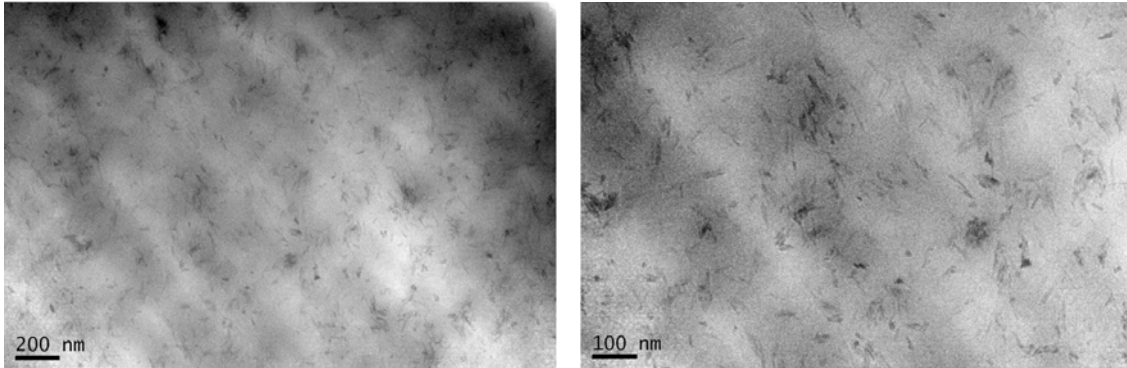


Figure 2 TEM micrographs of polyamide 11 with 5% X-0 needle n-alumina.

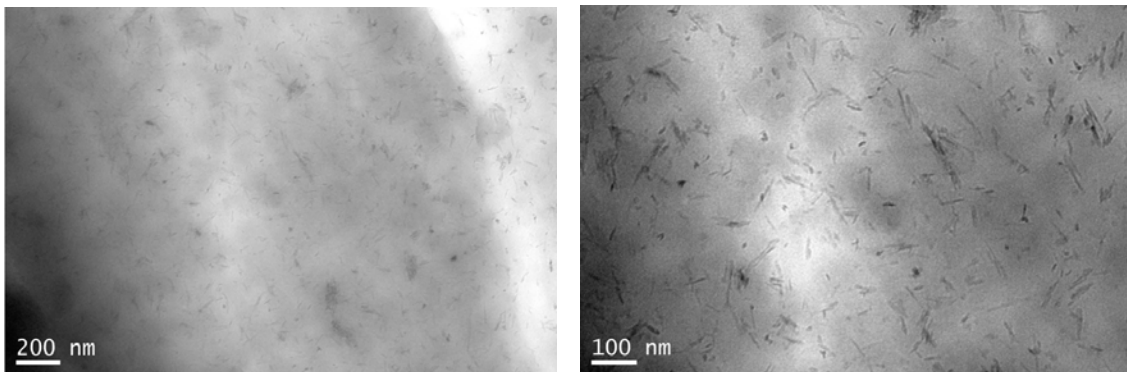


Figure 3 TEM micrographs of polyamide 11 with 5% X0-SR n-alumina.

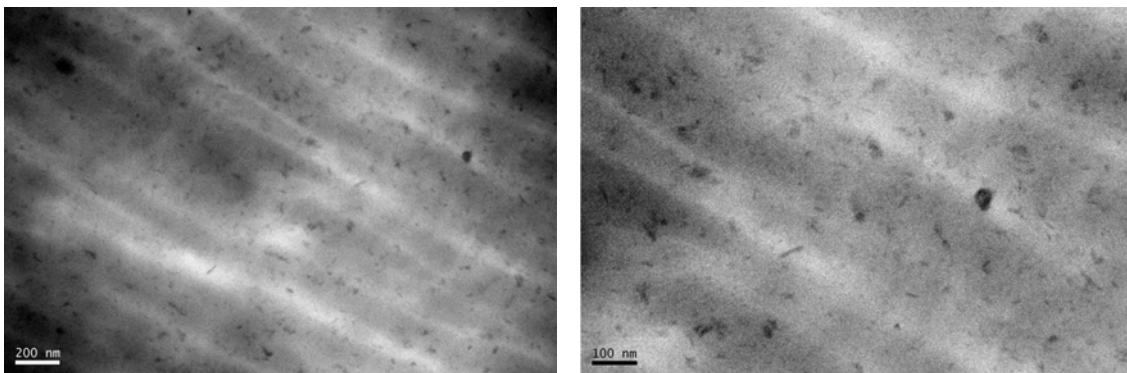


Figure 4 TEM micrographs of polyamide 11 with 5% X25-SR n-alumina.

3.2 Thermal Stability of the Polymer Nanocomposites

TGA was performed on the nine polymer blends and control under nitrogen using a scan rate of 10°C/min. Table 1 shows the decomposition temperatures of the PA11 nanocomposites as well as the neat nylon 11. All PA11 n-alumina nanocomposites had substantial increases in decomposition temperatures (from 26 to 46°C) compared to the neat nylon 11. There was not a clear trend of thermal properties enhancement among different types of n-alumina or different weight loading. However, the lowest weight loading of each type of n-alumina appeared to provide the best improvement in decomposition temperature. Figures 5 to 7 showed the TGA plots of nylon 11 and the nanocomposites with 2.5%, 5%, and 7.5%, respectively, of each type of the n-alumina. It has been clearly shown that in all loading levels of n-alumina, the PA11/n-alumina polymer nanocomposites have better thermal stability than the neat PA11 polymer.

Table 1. Decomposition Temperatures of PA11/n-Alumina Nanocomposites

Samples	Decomposition Temperature (°C)	ΔT (°C)
PA11	421	---
PA11/2.5% X-0	467	46
PA11/5.0% X-0	459	38
PA11/7.5% X-0	464	43
PA11/2.5% X0-SR	457	36
PA11/5.0% X0-SR	453	32
PA11/7.5% X0-SR	458	37
PA11/2.5% X25-SR	455	34
PA11/5.0% X25-SR	447	26
PA11/7.5% X25-SR	448	27

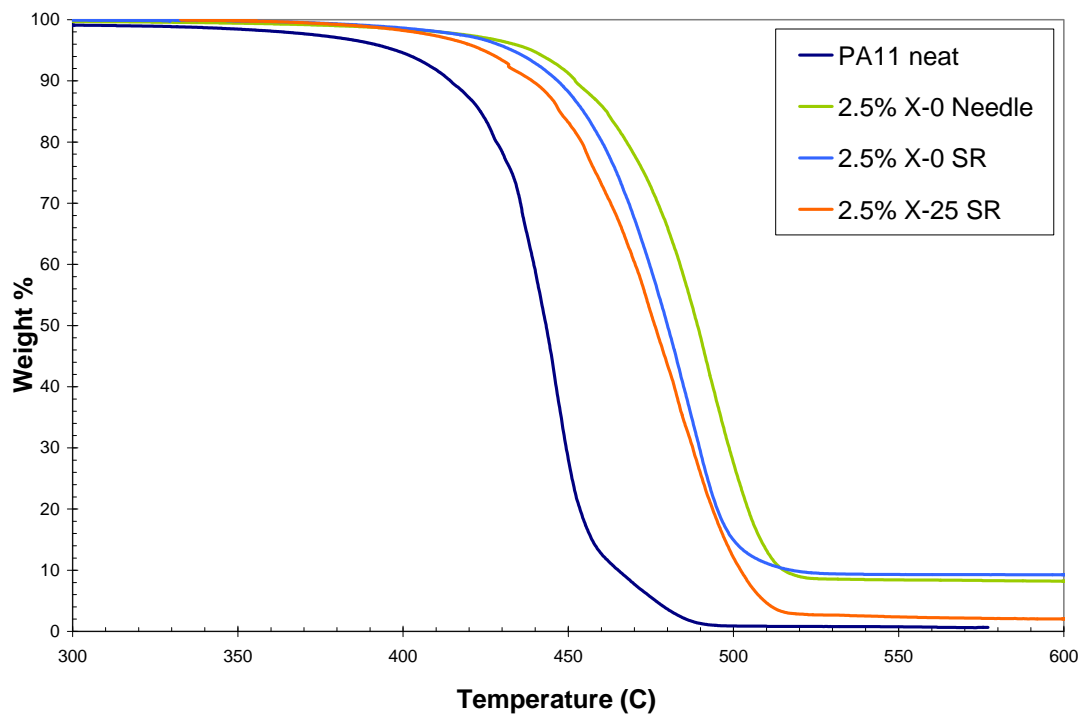


Figure 5 TGA of polyamide 11 with 2.5% n-alumina at 10°C/min in nitrogen.

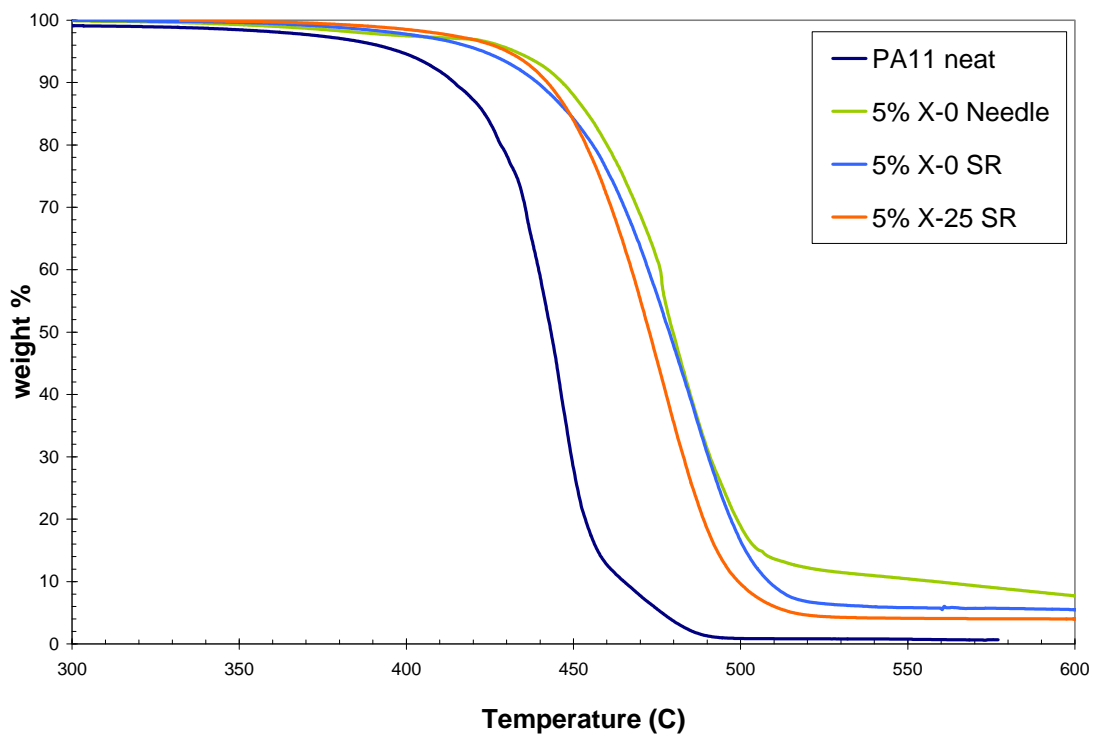


Figure 6 TGA of polyamide 11 with 5% n-alumina at 10°C/min in nitrogen.

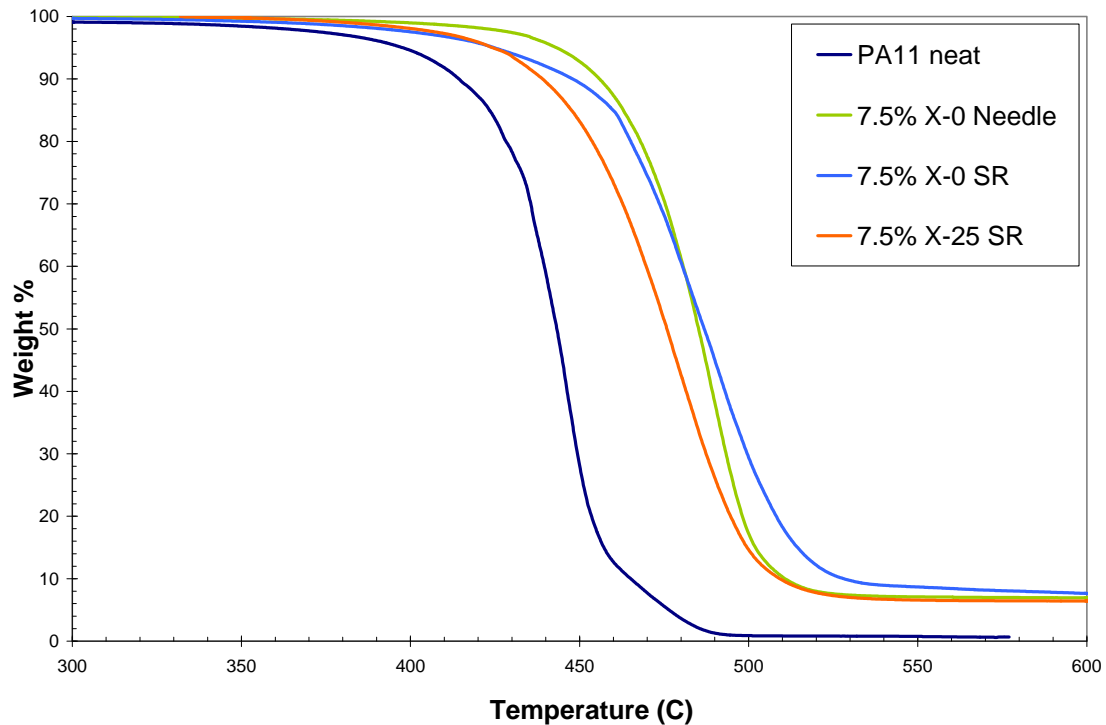


Figure 7 TGA of polyamide 11 with 7.5% n-alumina at 10°C/min in nitrogen.

3.3 Flammability Properties of the Polymer Nanocomposites

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.

As shown in Table 2, the addition of n-alumina to the PA11 material increased the FR properties of the nylon 11 by reducing dripping and flaming combustion time. Though all formulations of the PA11N failed the V-0 and V-1 ratings, the X-0 needle formulations performed the best in terms of average burn time and resistance to dripping. The X-0 SR performed the worst, with several samples completely burned, and the X-25 SR was the middle performer.

Table 2. UL 94 Results of PA11/n-Alumina Nanocomposites

Samples	1 st Burn Drip	2 nd Burn Drip	Drip Rank (1 = best)	UL 94 Rating
PA11	Yes	Yes	3	Failed
PA11/2.5% X-0	Yes	Yes	1	V-2
PA11/5.0% X-0	Yes	Yes	1	V-2
PA11/7.5% X-0	Yes	Yes	1	V-2
PA11/2.5% X-0 SR	Yes	Yes	3	Failed
PA11/5.0% X-0 SR	Yes	Yes	3	Failed
PA11/7.5% X-0 SR	Yes	Yes	3	Failed
PA11/2.5% X-25 SR	Yes	Yes	2	V-2
PA11/5.0% X-25 SR	Yes	Yes	2	Failed
PA11/7.5% X-25 SR	Yes	Yes	2	Failed

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.

X-0 needle Overall these samples exhibited the highest resistance to dripping compared to the other PA11N formulations. On average, they also had the lowest total flaming combustion time. The 5% weight loading achieved the lowest total flaming combustion time. All three weight loadings achieved a V-2 rating.

X-25 SR These samples exhibited less resistance to dripping than the X-0 needle, but performed comparably in terms of total flaming combustion time. Increasing the weight loading resulted in higher total flaming combustion times. This is because the drip resistance of the PA11N was increased, but allowed for flame propagation up the material. For the lower weight loadings, the flaming portion of the sample was allowed to drip and fall, not allowing enough time for the flame to propagate.

X-0 SR The PA11 samples with X-0 SR exhibited high total combustion times and several of the samples burned completely. Increasing the weight loading increased the total combustion times, and several samples did not withstand the first 10 second flame application.

4. Summary and Conclusions

A total of ten formulations of polyamide 11/n-alumina nanocomposites, including the neat PA11, were melt-compounded and injection molded to test specimens. TEM demonstrated that n-alumina surface treated particles are well dispersed in the polyamide 11 matrix. TGA showed that n-alumina improved the thermal stability of the nylon 11 substantially. The UL 94 test showed that all formulations did not pass the ideal V-0 rating. All of them exhibited flammable dripping that ignited the cotton under the specimens during the test. The X-0 needle formulations performed the best, followed by X-25 SR, and the X-0 SR performed the worst in performance. The addition of selective flame retardant additives or anti-dripping agents will be incorporated into the system

together with the n-alumina for enhanced flammability properties. Additional tests, such as mechanical testing, cone calorimetry, heat deflection temperature, etc., will be carried out to fully characterize these polyamide 11/n-alumina nanocomposites so that they can be considered for use in consumer products. Additional research is ongoing.

5. References

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