POLYAMIDE 11-CARBON NANOTUBES NANOCOMPOSITES: PRELIMINARY INVESTIGATION

S. C. Lao[1,2], J. H. Koo[1,2*], W. Yong[1], C. Lam[1], J. Zhou[1], T. Moon[1,2], P. M. Piccione[3], G. Wissler[4], L. Pilato[4], Z. P. Luo[5]

[1]The University of Texas at Austin, Department of Mechanical Engineering-C2200, Austin, TX 78712-0292

[2]The University of Texas at Austin, Texas Materials Institute

[3]Arkema, Groupement de Recherches de Lacq, 64170 Lacq, France

[4]KAI, LLC, Austin, TX 78739

[5]Texas A&M University, College Station, TX 77843-2257

[*]Corresponding author: jkoo@mail.utexas.edu

Abstract

The objective of this research is to develop an improved polyamide 11 (PA11) polymer with enhanced flame retardancy, thermal, and mechanical properties for selective laser sintering (SLS) rapid manufacturing. In the present study, a nanophase was introduced into polyamide 11 via twin screw extrusion. Arkema Rilsan® polyamide 11 molding polymer pellets were used with 1, 3, 5, and 7 wt% loadings of Arkema's Graphistrength[TM] multi-wall carbon nanotubes (MWNTs) to create a family of PA11-MWNT nanocomposites.

Transmission electron microscopy and scanning electron microscopy were used to determine the degree and uniformity of dispersion. Injection molded test specimens were fabricated for physical, thermal, mechanical properties, and flammability measurements. Thermal stability of these polyamide 11-MWNT nanocomposites was examined by TGA. Mechanical properties such as ultimate tensile strength, rupture tensile strength, and elongation at rupture were measured. Flammability properties were also obtained using the UL 94 test method. All these different methods and subsequent polymer characteristics are discussed in this paper.

1. Introduction

Rapid Prototyping (RP) technology has allowed the product designer access to a vast arsenal of tools and technologies unprecedented in the history of manufacturing. The phenomenal pace of desktop computing with the market availability of 3D software and the development of RP technology allows product design to engage more freely with new ideas, to produce prototypes, and to carry out testing in a shorter time. RP has received much attention in recent years and has been embraced as a preferred tool for not only product development but, in some cases, "just-in-time manufacturing."

There are several different RP platforms, of which selective laser sintering (SLS) is the one that provides the widest commercial material capabilities [1-5]. The development of RP, defined as the creation of a 3D part directly from computer aided design (CAD) data without special tooling, has generated interest in moving to the next step where fully functional parts could be

created in the same way. The concept is widely known as rapid manufacturing (RM). A key objective in transitioning RM is the creation of an SLS RM capability for high-performance materials by leveraging existing commercial RP machines.

Rapid Prototyping is in the early stages of becoming a bona fide manufacturing process. Yet limitations in speed, materials, and accuracy create barriers to the acceptance of RM [1]. The ultimate vision for RM which is "tool-less" fabrication of a component with an appropriate material without human intervention has several interesting aspects. *Firstly*, it significantly alters the dominant engineering design heuristic of minimizing complexity since greater complexity or more extensive functional integration (usually associated with weight savings among other things) does not generally increase fabrication costs. *Secondly*, a RM process would allow a single facility to produce a wide variety of components that can be assembled into the final structure. *Thirdly*, neither tooling nor a large inventory of parts is necessary if you have the ability to build what you need when (or perhaps just before) you need it. *Finally*, possibly the most important benefit especially for military or aerospace applications area is the short lead time and cost saving for a new part or a modified part as compared to regular production which changes (or eliminates) another central tenet of traditional product development, that is, design freezing. In summary, this vision of RM has flexibility for affordable, low risk, agile, and earlier delivery of a product whose basic structure may be fixed but other modifications to the structure would undergo change(s).

In recent years an emerging vision of RM has occurred within the SLS industry. The SLS method involves the fabrication of a part by building up layers of powder whereby each thin layer (0.003" to 0.006") is added across a part build chamber as a computer controlled laser fuses particles into a layer region together to the previously fused regions. A three-dimensional (3D) computer aided design (CAD) file is sliced into layers with each of those layers becoming one of those fused regions. In this way, a 3D part is built from successive layers of small, uniform particles. The SLS process has been refined to support greater accuracy and duplication which sustains a modest array of manufacturing applications, such as ventilation ducts for aircraft crew. Yet these advances have been confined to special nylon (polyamide) materials as the precursor material used in SLS. In other words, the current embodiment of RM represents a small segment of utility since RM has been optimized for a narrow group of materials [nylon (polyamide) 11 and nylon 12]. RM has the capability for greater penetration in many market areas, especially the high performance advanced materials areas encompassing military and aerospace structures.

In SLS a part is built from layers of powder or uniform particles. As each thin layer is added across a part build chamber, a computer controlled laser fuses a region together and to previously fused regions. A 3D CAD file is sliced into layers with each of those layers becoming one of those fused regions. In this way, a 3D part is built from successive layers of small, uniform particles. The automated, layered fabrication of plastic components, for models, patterns and non-operational prototypes, using sliced CAD files was first conceived and commercialized in the United States with the method known as stereolithography in the late 1980's. This was followed by variations of the "rapid prototyping" method such as SLS (particulate powder layers), laminated object manufacturing (tape layers), fused deposition modeling (jetted polymeric material) and 3-D printing (powder layers w/ink-jet glue). It is important to note that both the cost per part [3] and material aspects [1,2,4] associated with SLS are both currently superior to other RP techniques.

Direct manufacturing successes include Boeing's use of PA11 SLS powder to manufacture air ducting systems for F18 fighter jets [5] and Siemen's use of PA12 SLS powder to manufacture hearing aid shells to fit individual user's ears. PA11 parts produced by Boeing's SLS technology are directly used in aerospace structures which meet stringent aerospace performance requirements, in contrast with prototypes or other designs typically associated with SLS processes. These parts are primarily environmental control system ducts (ECS).

Aerospace components are installed with relatively high numbers of parts in small volumes. This increases the number of interfaces and adds shape constraints both driving higher part complexity. ECS ducts typically define intricate shapes in order to route around other parts and aircraft systems within an aircraft. One of the major advantages of SLS technology is that part complexity does not increase fabrication cost. This coupled with the cost per part being independent from the number of parts produced means that SLS will continue to play a role in aerospace manufacturing.

Commercially available polymers for SLS include PA11, PA12, glass-filled PA12, and polystyrene from 3D Systems. The PA12 materials are typically used for design verification models and for limited functional prototypes. Polystyrene is used for investment casting patterns. The Boeing Company has developed laser sintering techniques using PA11 powders and has launched a manufacturing business [On Demand Manufacturing, Inc. (ODM), Camarillo, CA. ODM is now owned by RBM Products, Inc., Fountain, CO] to support large-scale production of functional parts for military aircraft. PA11 or PA12 materials are limited to a use temperature of about 71ºC with excursions to 121ºC, are flammable, and possess mediocre modulus and strength compared to high-performance thermoplastics such as PEEK.

The introduction of selected nanoparticles such as carbon nanofibers (CNFs) and MMT nanoclay into PA11 or PA12 by compounding has resulted in a family of intumescent polyamide nanocomposites. Small amounts of nanoparticles (<7%) are required to make polymer nanocomposites (PNCs) to exhibit enhanced flame retardant (FR) properties when compared with the modified thermoplastic processed by conventional methods [6-17]. However, unlike the conventional FR thermoplastics, the resulting PNCs exhibit enhanced mechanical properties such as high strength/modulus, moisture resistance, higher heat deflection temperature, etc. Therefore, nanotechnology can be considered as a unique technique to develop novel FR thermoplastic structural components with high performance characteristics.

Our previous studies showed that PA11-clay nanocomposites and PA11-CNF nanocomposites exhibited better mechanical, flammability, and thermal properties than neat PA11 polymer [18,19]. SLS parts of some of these PA11 nanocomposites had been fabricated successfully; however the few formulations fabricated might not have exhibited optimal properties that are necessary for the intended application [19]. Our present study is expanded to include the use of MWNT [20] in PA11 polymer and expected to result in superior property characteristics through the use of MWNT that are closely related to CNF. Pending the outcome of examining different wt% of MWNT in PA11 by twin screw extrusion and injection molding, a few, selected formulations will be chosen for SLS fabrication and complete characterization.

The PA11-MWNT masterbatch (containing 20wt% MWNT) provided by Arkema was diluted with Rilsan® BMNO PA11 to 1, 3, 5, and 7% using twin-screw extrusion. The resulting pellets were injection molded into different test specimens. The extent and uniformity of

dispersion of MWNT was examined by transmission electron microscopy (TEM). Flammability properties were studied by conducting UL 94 tests. Thermal properties were analyzed by thermogravimetric analysis (TGA). Tensile properties were obtained from the stress-strain behavior of the specimens and measured by automated tensile testing system.

2. Experimental

2.1 Materials

Polymer Nanocomposites Masterbatch Arkema's PA11-20wt% MWNT masterbatch was supplied by Arkema. Arkema's Graphistrength C100 MWNT [20] was melt-blended into Rilsan® BMNO PA11 via twin-screw extrusion.

Polymer Resin Arkema's Rilsan® BMNO PA11 was used. Rilsan® PA11 is one of the few polymers that are produced from 'green' raw materials – castor beans. It has earned a preferred material status in some demanding applications due largely to its unique combination of thermal, physical, chemical, mechanical properties, and ease of processing. This BMNO grade of PA11 possesses very similar properties to the grade of PCG LV which was used in previous studies [18,19] but has higher a viscosity than PCG LV and duplicates the one used in the PA11-MWNT masterbatch.

Nanoparticle Arkema's Graphistrength™ C100 MWNT within the masterbatch has outstanding mechanical properties combined with electrical and thermal conductivities. It can be used in a variety of applications such as high-strength thermosetting composites [20]. No surface treatment/functionalization was performed on the C100 MWNT. It is available in black powder form with an apparent density of 50 to 150 kg/m^3 and a mean agglomerate size of 200 to 500 µm. The C100 MWNT has a mean number of walls of 5 to 15, an outer mean diameter of 10 to 15 nm, and mean lengths of 0.1 to 10 µm.

2.2 Measurements

Morphological Microstructures Analysis The cross-sections of the PA11 nanocomposites were investigated by TEM to examine the dispersion of MWNTs in 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 blend.

Mechanical Testing In order to compare the mechanical properties of PA11 nanocomposites with the baseline material, stress-strain behavior was performed using an automated tensile testing system (Instron model 3345) in accordance with ASTM D638. Ultimate tensile strength, rupture tensile strength, tensile modulus, and tensile elongation at rupture were obtained from the stress-strain data.

Thermal Stability Testing Thermal stability of the PA11 baseline and PA11-MWNT nanocomposites were examined by thermogravimetric analysis (TGA) using the Perkin Elmer TGA 7. Weight changes in sample materials are measured as 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 [21]. 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. Five specimens are tested for each formulation.

3. Results and Discussion

3.1 Processing and Characterization of Polymer Nanocomposites

PA11-MWNT masterbatch was diluted to 1, 3, 5, and 7% using twin screw extrusion. A 30mm 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 4.6 kg (10 lbs) of each formulation were produced. Separate volumetric feeders were used for the masterbatch and the base resin. The PA11 was dried in a desiccant drier before compounding. Injection molded specimens of each blend were prepared and examined by TEM. Figures 1 and 2 showed the TEM micrographs of PA11 with 20% MWNT and PA11 with 7% MWNT, respectively. MWNTs were well dispersed in the polymer matrix although some aggregates of MWNTs of about 200nm in size were still observed. It is believed that better dispersion can be achieved by using optimized processing procedures or screw profile. Since individual MWNTs are observed throughout the TEM scanned specimens, these MWNTs appear to be well compatible with the PA11 even though there is no MWNT surface treatment/functionalization.
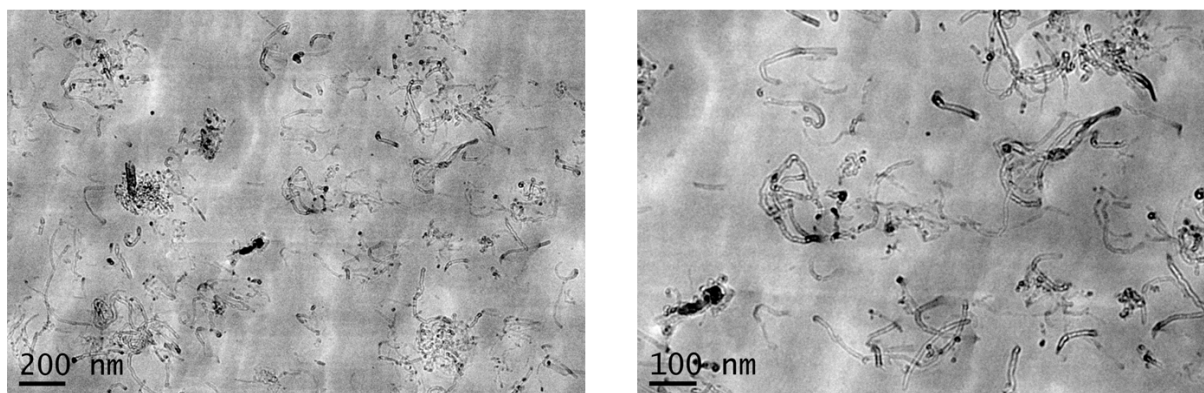

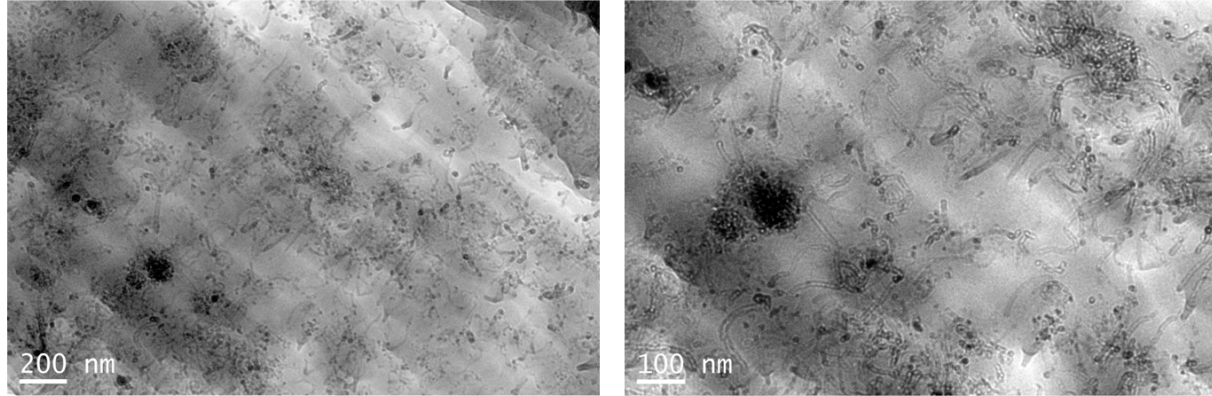**Figure 1.** TEM micrographs of polyamide 11 with 20% MWNT (PA11-MWNT masterbatch).

Figure 2. TEM micrographs of polyamide 11 with 7% MWNT.

3.2 Mechanical Properties of the Polymer Nanocomposites

Ultimate tensile strength, rupture tensile strength, tensile modulus, and tensile elongation at rupture of the PA11 MWNT nanocomposites are shown in Figures 3 through 6, respectively. Samples with 5 wt% MWNT were delayed in the extrusion sequence and not included in the present study. Table 1 shows a summary of the mechanical properties of the PA11 and PA11-MWNT nanocomposites. A general trend is observed and indicates that as the ultimate tensile strength, rupture tensile strength, and tensile modulus properties increase as the loading of MWNT increases. The ultimate tensile strength of PA11 neat and PA11-7%MWNT is 46$\pm$2 and 53$\pm$5 MPa, respectively. The rupture tensile strength of PA11 neat and PA11-7%MWNT is 34$\pm$4 and 53$\pm$5 MPa, respectively. The largest enhancement is tensile modulus of PA11 neat and PA11-7%MWNT is 1,284$\pm$28 and 1,669$\pm$45 MPa, respectively. There is a substantial decrease in tensile elongation at rupture of PA11 neat and PA11-MWNT, from 177$\pm$74 down to 6$\pm$2%. This observation is similar to our previous studies of PA11 with other nanoparticles (e.g. clay, CNF, etc.) [22].
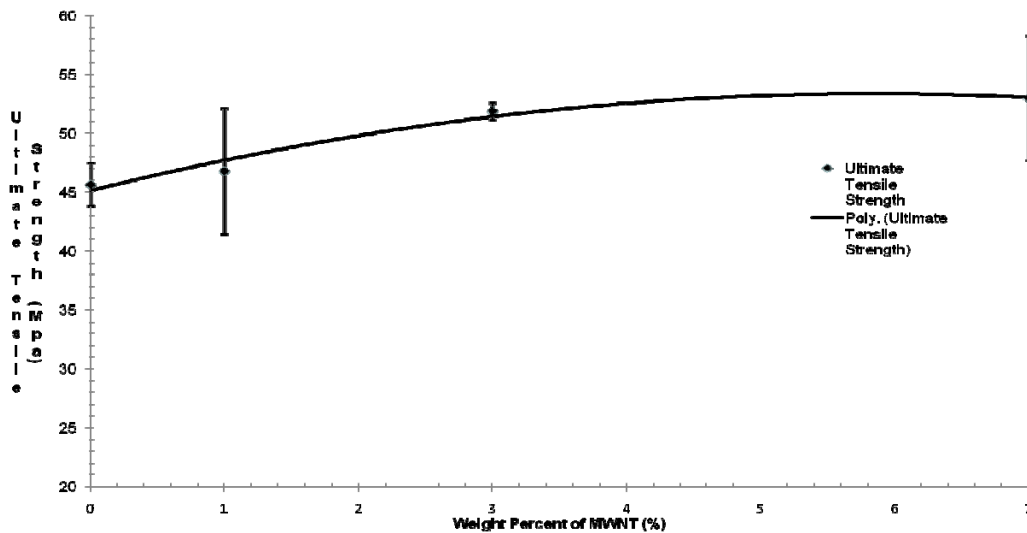
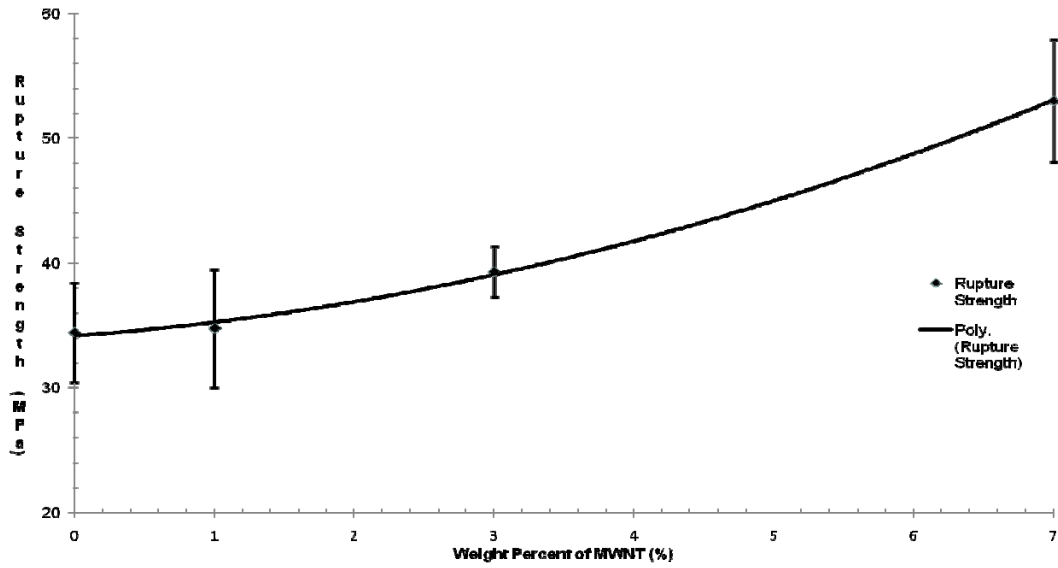**Figure 3.** Ultimate tensile strength of PA11 MWNT nanocomposites.

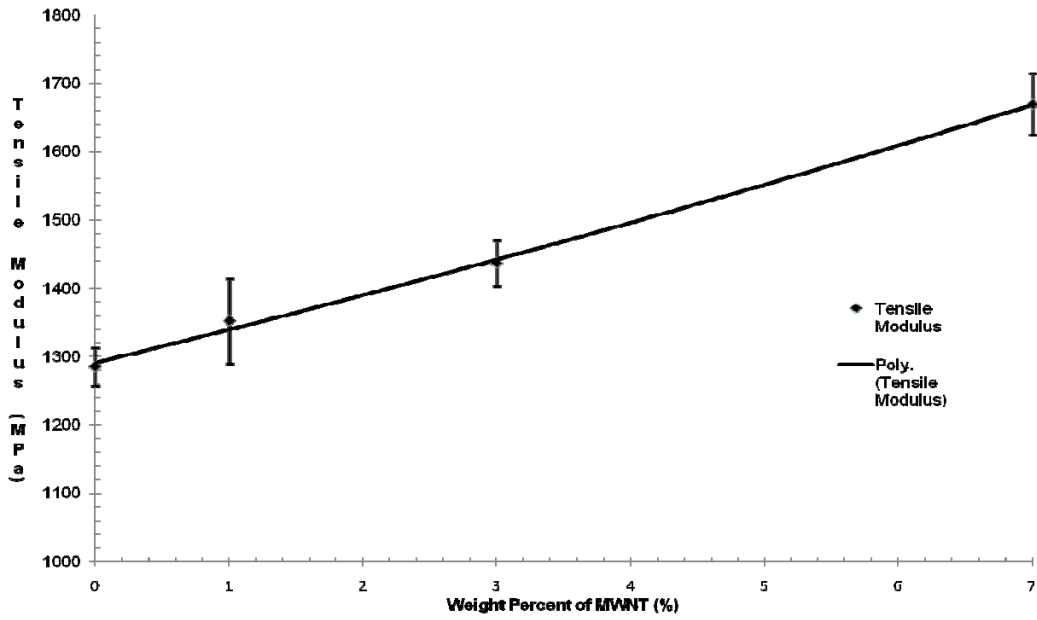**Figure 4.** Rupture tensile strength of PA11 MWNT nanocomposites.
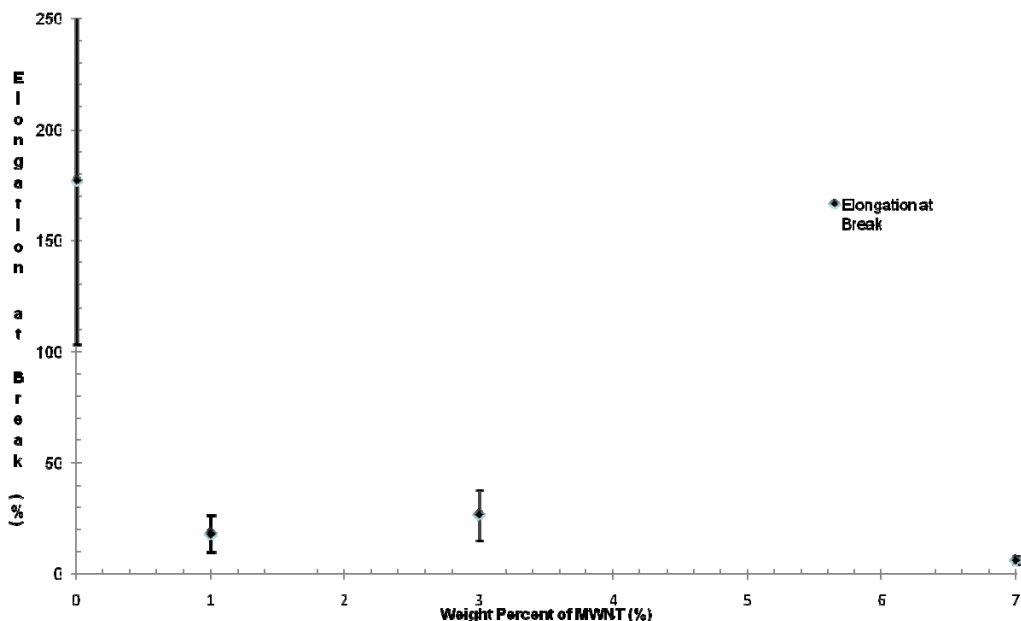

Figure 5. Tensile modulus of PA11 MWNT nanocomposites.

Figure 6. Tensile elongation at rupture of PA11 MWNT nanocomposites.

Table 1 Mechanical Properties of PA11-MWNT Nanocomposites

	Ultimate Tensile Strength (MPa)		Rupture Tensile Strength (MPa)		Tensile Modulus (MPa)		Tensile Elong. at Rupture (strain%)	
	Ave	Std Dev	Ave	Std Dev	Ave	Std Dev	Ave	Std Dev
PA11 neat	46	2	34	4	1284	28	177	74
PA11+1%MWNT	47	5	35	5	1352	62	18	8
PA11+3%MWNT	52	1	39	2	1436	33	26	11
PA11+7%MWNT	53	5	53	5	1669	45	6	2

3.3 Thermal Stability of the Polymer Nanocomposites

TGA was performed on all six formulations under nitrogen using scan rate of 10°C/min (Figure 7). A general trend of increased thermal stability is observed (higher decomposition temperatures) as the amount of MWNT is increased. Table 2 summarizes the 10% mass loss, onset, and 50% mass loss decomposition temperatures of the PA11-MWNT nanocomposites. The 10% mass loss, onset, and 50% mass loss decomposition temperatures of PA11-7%MWNT nanocomposite increase significantly from 418° to 440^oC, 425° to 457^oC, and 439° to 475^oC, respectively.
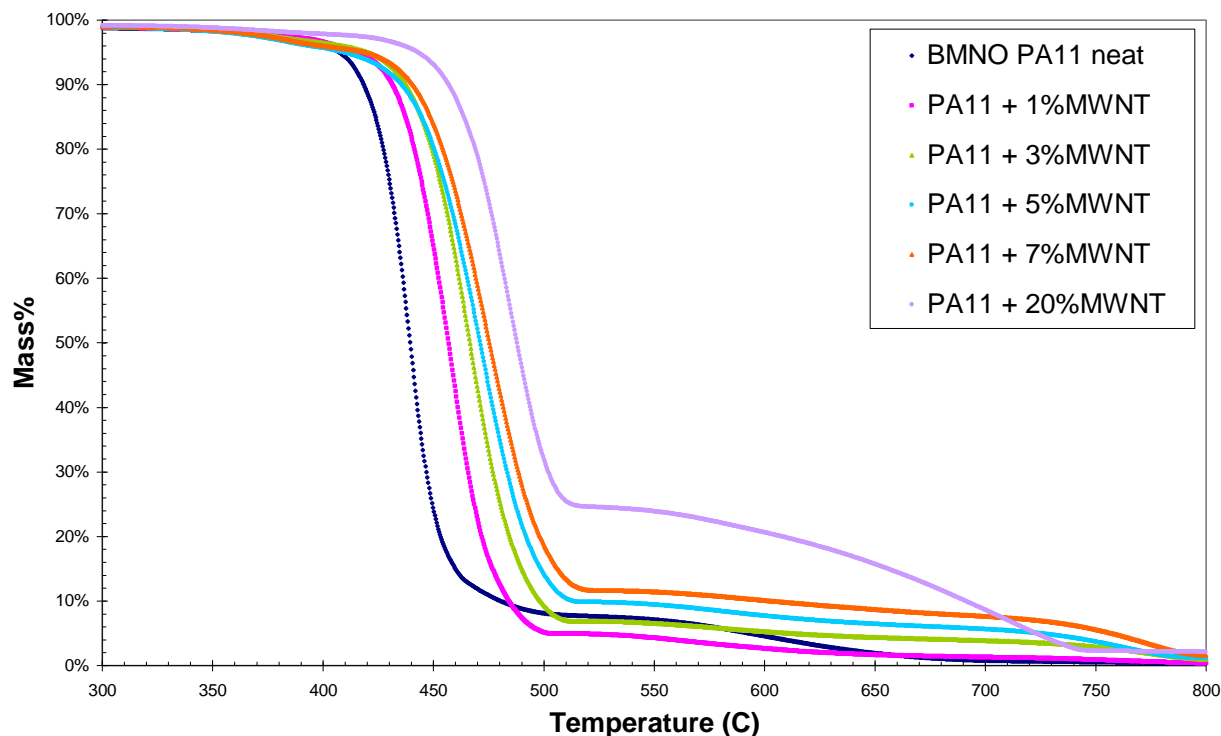
Figure 7. Thermogravimetric analysis of PA11 MWNT nanocomposites at 10°C/min in nitrogen.

Table 2 Summary of Thermal Stability of PA11-MWNT Nanocomposites

	Decomposition Temperatures (°C)		
Polymer Blend	at 10% mass loss	Onset	at 50% mass loss
PA11 neat	418	425	439
PA11+1% MWNT	431	438	457
PA11+3% MWNT	437	446	467
PA11+5% MWNT	434	450	471
PA11+7% MWNT	440	457	475
PA11+20% MWNT	456	472	488

3.4 Flammability Properties of the Polymer Nanocomposites

The materials were tested as "received with no additional conditioning/drying" prior to UL 94 testing. The test was performed in our lab with the UL 94 testing requirements and procedures followed as stringently as possible. Our lab is not certified for UL 94; the results serve as a screening tool. Five specimens were tested for each formulation (the one with 5% MWNT was lacking). 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 area 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.

Figure 8 shows photos of specimens before and after the test while Figure 9 shows a burning specimen during the test. All formulation specimens with MWNTs burned longer than 100 seconds after the first flame was applied and continued to burn. Therefore, none of the formulations passed any rating of the UL 94 test. However, it should be noted that the PA11 MWNT nanocomposites did not exhibit any dripping when they were burned, while the neat PA11 dripped copiously during the test.
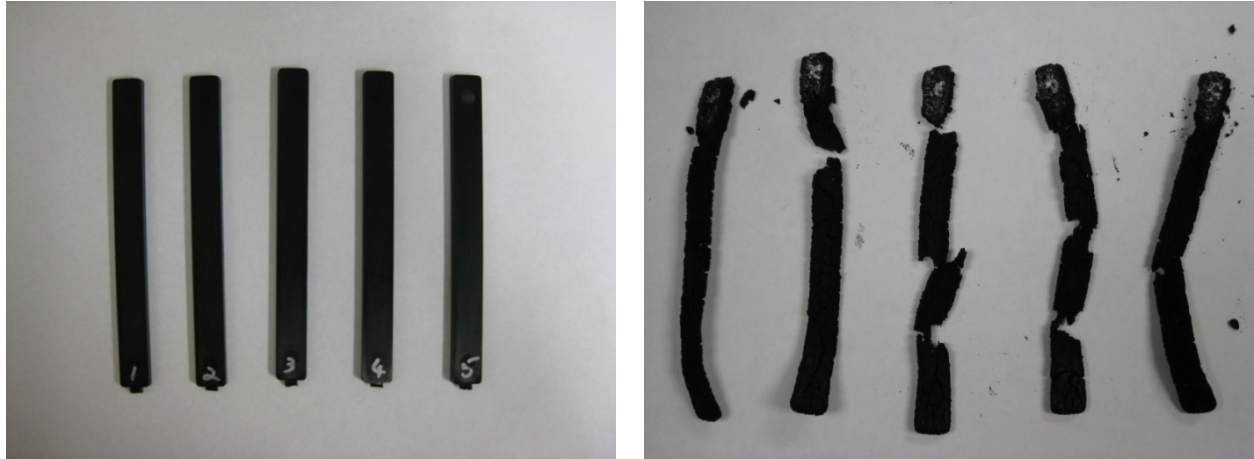

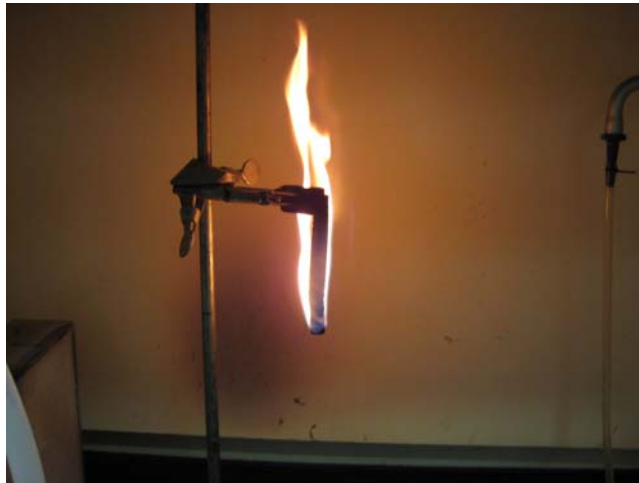**Figure 8.** UL 94 specimens (7wt% MWNT) before (left) and after (right) the burning test.

Figure 9. Flame burned all the way to the clamp in the UL 94 test.

4. Summary and Conclusions

A total of five formulations of PA11 MWNT nanocomposites were compounded separately via twin screw extrusion. Injection molded specimens of PA11 baseline and PA11-MWNT nanocomposites were fabricated for physical, mechanical, thermal, and flammability properties measurements. TEM showed that MWNTs were well dispersed into the PA11 matrix although it is possible that better dispersion can be achievable by using a more aggressive screw design. MWNTs enhanced the mechanical properties (except tensile elongation at rupture) as well as the

thermal stability of the PA11. However, all PA11 MWNT nanocomposites failed the UL 94 test. To make them truly fire retardant, a second additive such as conventional intumescent fire retardant additives to act as a synergist are proposed. It has been demonstrated that thermal and flammability can be enhanced substantially as long as synergism is established between the nanoparticles and conventional fire retardant additive in the polyamide matrix [22]. Furthermore, to improve the tensile elongation at rupture, an elastomeric component may be required. If, indeed, an elastomeric component is introduced, then its effect on the corresponding mechanical, thermal, and flammability properties must be determined.

5. References

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