COMBINED EFFECTS OF MONTMORILLONITE CLAY, CARBON NANOFIBER, AND FIRE RETARDANT ON MECHANICAL AND FLAMMABILITY PROPERTIES OF POLYAMIDE 11 NANOCOMPOSITES

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ABSTRACT

This paper is focused on the development of polyamide 11 (PA11) nanocomposites with enhanced fire retardant (FR) properties for application in selective laser sintering (SLS). Test specimens of PA11 containing various percentages of intumescent FR additive, montmorillonite (MMT) clay, and carbon nanofiber (CNF) were prepared via the twin screw extrusion technique. The combined effects of MMT clay, CNF, FR additives on the mechanical and flammability properties of these PA11 nanocomposites are studied. Izod impact testing, tensile testing, and SEM analysis of are used to characterize mechanical properties. UL-94 and SEM analysis of char surfaces are used to characterize the flammability properties of these materials. Results are analyzed to determine any synergistic effects among the additives to the material properties of PA11.

1. INTRODUCTION

Selective Laser Sintering (SLS) is a method of rapid manufacturing (RM) that involves the fabrication of parts through the building up of layers of a polymer powder. Each layer is very thin (0.076-0.152mm) and is added to the part when a computer-controlled laser heats and fuses the powder particles into a solid material, which is also fused to the solid layer that was previously fused below it (schematic is shown in Figure 1). This process allows for a part to be manufactured directly from a 3D CAD file. The 3D design is sliced into layers that are then fused together using an SLS machine. The SLS technique has developed significantly over the past several years and is used in the manufacturing of a modest variety of commercial and industrial parts and prototypes [1].

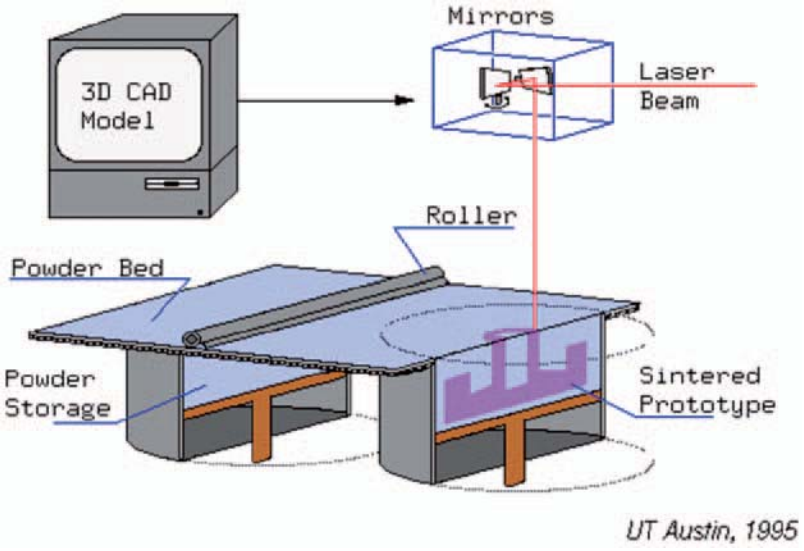

Figure 1: Schematic of SLS process.

Current polymers that are widely used in SLS are polyamide (PA) 11, PA12, and glass-filled PA12. Commercial manufacturing endeavors have been undertaken that make use of PA11 and PA12, such as Boeing's use of PA11 SLS manufacturing to produce air ducting systems for F18 Fighter jets [2] and Siemen's use of PA12 SLS manufacturing to produce hearing aid shells. Despite the successes in the application of these SLS manufactured PA11 and PA12 parts, these materials have number of poor characteristics that limit their applications. Both PA11 and PA12 have relatively poor thermal, flammability, and mechanical properties when compared to other commercially available thermoplastics. They are limited to a use temperature of roughly 71°C, with brief exposure to temperatures up to 121°C. In addition, both of these materials are quite flammable. The tensile strength and moduli of these PA polymers are also mediocre, especially when compared to traditionally manufactured polymers such as PEEK [3].

It is possible through the use of additives to modify and improve select properties of a polymer to better perform its designed function. Such additives, both micron-sized and nano-sized, have been successfully implemented to improve the flammability and select mechanical properties of PA11 [3-6]. In conventional methods, FR additives like inorganic metal-oxides or halogens are used to improve the flammability characteristics of polymers. In order achieve desirable FR properties the weight percentage of FR additives in these polymer mixtures is typically greater than 30%. However, the inclusion of FR additives also results in the degradation of the polymer's mechanical properties [7].

Nanomaterials have also been successfully used as additives to improve the properties of polymers. Nanomaterials are defined as materials with structured components that have at least one dimension in the nanometer-scale (10^{-9} meter). There are numerous varieties of nanomaterials being implemented into different polymers to improve the flammability of polymer materials: nanoclay, carbon nanofibers (CNFs), or multi-walled carbon nanotubes (MWNTs). These different materials have differing degrees of effectiveness, however they all offer material improvements at much lower weight percentages (<7wt%). In addition, the inclusion of nanomaterials typically results in improved mechanical properties as well [3,4].

While these additives are helpful when used separately, they are often most beneficial when used in combination with each other if they are compatible. It has been shown that combining conventional FR additives with nanomaterial additives can greatly increase the effectiveness of both, as well as reduce or reverse the negative effect of conventional FR on the mechanical properties of polymers [1]. In addition, two nanomaterial additives used at once have the potential to improve various polymer properties greater than the same amount of either nanomaterial would individually [5,6].

The purpose of this paper is to study the combined effects of a conventional FR, montmorillonite (MMT) nanoclay, and CNF into a PA11 polymer base. Focus will be placed on the mechanical and flammability properties of the resulting composites in comparison to neat PA11 and PA11 composites lacking the synergistic effects of multiple additives.

2. EXPERIMENTATION

2.1 Materials

2.1.1 Polymer The base polymer used for this study is Rilsan® PCG LV polyamide 11 (PA11) manufactured by Arkema. PA11 is a versatile thermoplastic polymer noted for its positive properties of abrasion, chemical, and heat resistance, good resistance to creep, and a low coefficient of friction. PA11 is an intermediate melting material with a melting temperature of less than 200°C.

2.1.2 Fire Retardant Additive Clariant manufactures different FR additives known as Exolit® OP grades for various types of plastics. The specific FR used in this study is OP1230. It is an intumescent FR additive based on metal phosphinate. It is a white powder containing phosphorus and other propriety FR. It is non-halogenated, hydrophobic, and exhibits good thermal stability. It was developed as a general purpose FR additive for plastics.

2.1.3 Nanoclay The nanoclay used in this study is Cloisite® 30B manufactured by Southern Clay Products. It is a natural montmorillonite clay modified with an organic modifier.

2.1.4 Carbon Nanofibers Carbon nanofibers are discontinuous graphite filaments with diameters less than 200nm and varying lengths manufactured by Applied Sciences, Inc. The specific grade used in this study is PR24XT-PS CNF.

2.1.5 Processing The materials used in this experiment were processed via co-rotating twin-screw extrusion, a melt blending process. Masterbatches of PA11/10% MMT and PA11/10% CNF were produced prior to the creation of the final PA11/MMT/CNF/FR blends. The specific operating conditions for the melt-blending process are shown in Tables 1-3. The individual specimens were produced through injection molding.

Table 1: Processing conditions for PA11/MMT masterbatches

Operating conditions					
Feeding rate (kg/h)	3				
Screw speed (rpm)	250				
Temperature profile (°C)	464	464	500	464	464
Torque (%)	19-20				

Table 2: Processing conditions for PA11/CNF masterbatches

Operating conditions					
Feeding rate (kg/h)	2				
Screw speed (rpm)	80				
Temperature profile (°C)	464	464	500	464	464
Torque (%)	20-21				

Table 3: Processing conditions for PA11/MMT/CNF/FR blends

Operating conditions					
Feeding rate (kg/h)	2				
Screw speed (rpm)	100 -130				
Temperature profile (°C)	464	464	500	464	464
Torque (%)	25				

2.2 Measurements

2.2.1 Izod Impact Test Notched Izod testing is a common qualitative measure of toughness of a material, measuring energy absorbed prior to failure under high triaxiality and high rate loading conditions. It measures the energy required to fracture a notched specimen at relatively high rate bending conditions. A pendulum with adjustable weight is released from a known height; a rounded point on the tip of the pendulum makes contact with a notched specimen [8]. The specific device used in our testing is the Shanta Engineering Izod/Charpy Impact Tester. The specimen layout and Izod tester is shown in Figure 2.

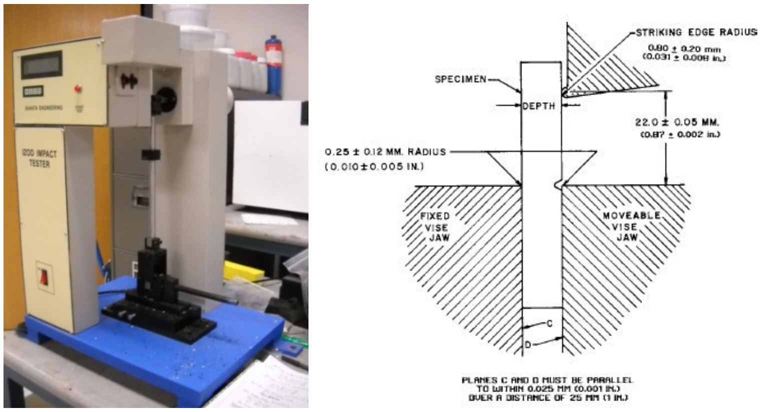

Figure 2: Shanta Engineering Izod/Charpy Impact Tester (left) and layout of Izod test specimen according to ASTM D256 [9].

2.2.2 Tensile Tests Tensile tests are performed for several reasons and the results of tensile tests are frequently included in material specifications to ensure quality. Tensile testing involves locking a specimen into a testing setup and applying a tensile load to specimen until it breaks. The data recorded through this testing can be used to determine numerous material properties [10]. In our application we are interested in the ultimate tensile strength, elongation at break, and tensile modulus. The specific device used in our testing is an Instron Tensile Tester.

2.2.3 Microstructural Analysis In order to better understand the microstructural mechanisms behind our mechanical test results, we will analyze the fracture surface of our post-test Izod and tensile specimens. This analysis will give us a greater qualitative understanding of how our various additives affect the structure and properties of our composite materials. Similarly, microstructural analysis will be conducted on burnt UL-94 specimens to understand the protective mechanisms. We used the Quanta 650 SEM/ESEM to perform fractural and charred surfaces analysis of our materials.

2.2.4 UL-94 Vertical Burn Test The test for flammability of plastic material used in parts for electronic devices and appliances is commonly known as UL-94. It is a flammability specification issued by the Underwriters Laboratories Inc [11].

The flammability specification UL-94 contains several small-scale flame tests procedures that define parameters for flame testing of plastics. In this specification, the behavior of plastic when exposed to fire is expressed quantitatively. The amount of material burned refers to the length of sample that burns in a specified period of time. We performed the vertical burn test, in which a flame is applied to the base of the specimen held in the vertical position and the extinguishing times are determined upon removal of the test flame, as well as whether the specimen produces flaming drips (see Figure 3 for test layout). Ratings for UL-94 range from V-2, which is the worst rating for a material that still passes, to V-0, which is the best rating [11].

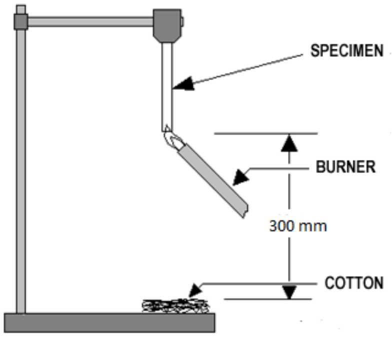

Figure 3: Testing layout for the UL-94 vertical burn test.

3. RESULTS

3.1 Mechanical Properties

3.1.1 Izod Impact Strength The results from Izod impact testing of our composites are shown in Table 4. Formulation 2, which includes 3.5% MMT, 3.5% CNF, and 0% FR, has the highest Izod impact strength. Formulation 6, which includes 3.5% MMT, 3.5% CNF, and 20% FR, has the lowest Izod impact strength. There are no significant differences between 3.5% MMT, 3.5% CNF and 2.5% MMT, 2.5% CNF. However, greater FR percentages tend to lead to lower Izod impact strength, as shown in Figures 4 and 5. The Izod impact strength of neat PA11 is remarkably high compared to the polymer blends, and for most formulations the decrease from neat PA11 is greater than 90%.

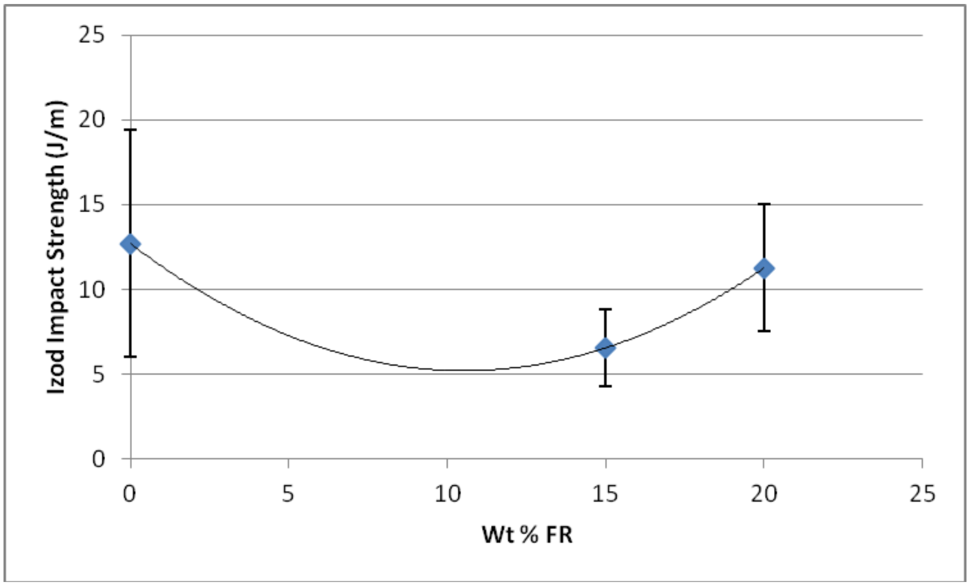

Figure 4: Izod impact strength for PA11/2.5% MMT/2.5% CNF composite as a function of weight percent FR OP1230.

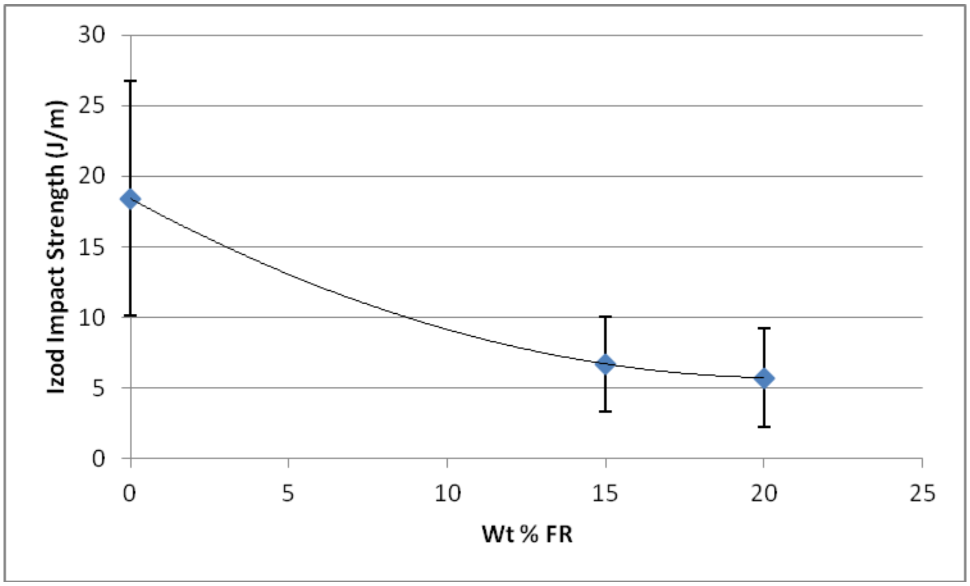

Figure 5: Izod impact strength for PA11/3.5% MMT/3.5% CNF composite as a function of weight percent FR OP1230.

Table 4: Izod Impact Strength of PA11 Composites

Formulation	MMT	CNF	FR	Izod Impact Strength (J/m)
Neat PA11	0%	0%	0%	113.7
#1	2.5%	2.5%	0%	12.7
#3	2.5%	2.5%	15%	6.6
#4	2.5%	2.5%	20%	11.3
#2	3.5%	3.5%	0%	18.4
#5	3.5%	3.5%	15%	6.7
#6	3.5%	3.5%	20%	5.7

3.1.2 Tensile Testing The results for tensile testing of our composites are shown in Table 5. Figure 6 shows tensile strength of PA11 composites as a function of weight percent FR OP1230. Polymer blends which include 2.5% MMT and 2.5% CNF have higher tensile strength but the differences between them are not considerable. The weight percentage of FR also seems to have minimal effect on the tensile strength of the materials. However, all materials have a lower tensile strength than neat PA11.

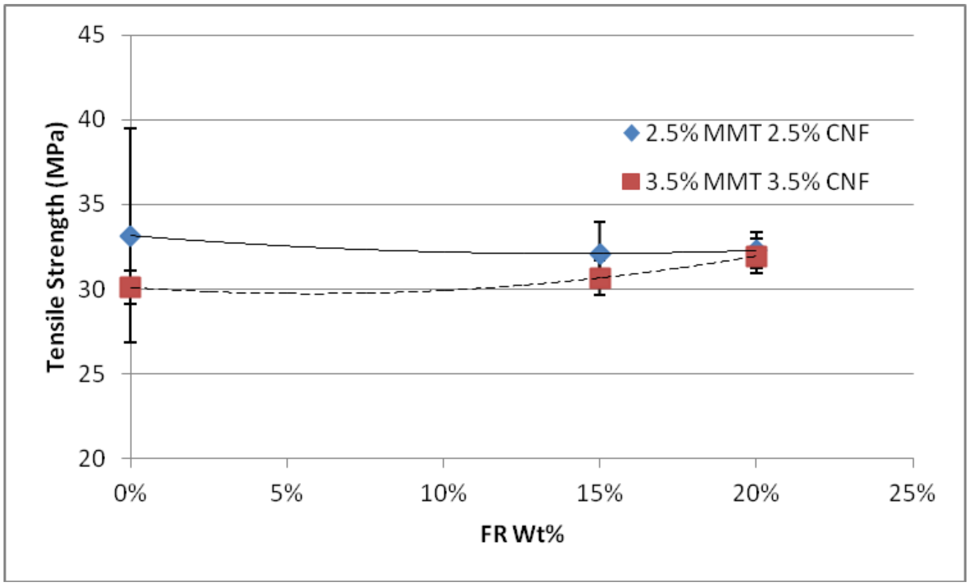

Figure 6: Tensile strength for PA11 composites as a function of weight percent FR OP1230.

Figure 7 shows that polymer blends with 3.5% MMT and 3.5% CNF generally have higher tensile modulus than those with only 2.5% MMT and 2.5% CNF. Formulation 5, which includes 3.5% MMT, 3.5% CNF, and 15% FR, has the highest tensile modulus. Formulation 3 which includes 2.5% MMT, 2.5% CNF, and 15% FR has the lowest tensile modulus. The weight percentage of FR OP1230 also seems to increase the tensile modulus, though the effect is not very significant. Compared to neat PA11, the polymer blends are more brittle but the tensile modulus is noticeably increased.

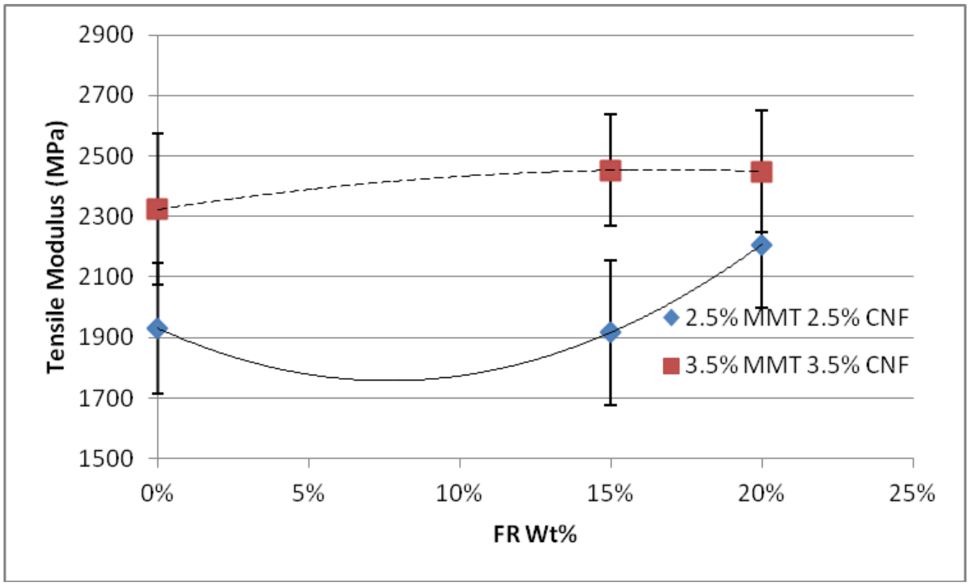

Figure 7: Tensile modulus for PA11 composites as a function of weight percent FR OP1230.

Figure 8 shows that formulation 3, which includes 2.5% MMT, 2.5% CNF, and 15% FR, has the highest elongation at break. Formulation 2, which includes 3.5% MMT 3.5% CNF and 0% FR, has the lowest elongation at break. The materials with higher concentrations of MMT and CNF tend to be more brittle and have lower elongation at break. There are mixed results on the effect of FR weight percent. For the 2.5% MMT 2.5% CNF compounds, FR increases elongation slightly, but for 3.5% MMT 3.5% CNF there is no significant change as a result of FR inclusion. All of the composites, however, show a significant decrease in elongation at break compared to neat PA11, which has more than 200 times higher elongation at break. Such a dramatic decrease in elongation is typical of nanocomposite materials.

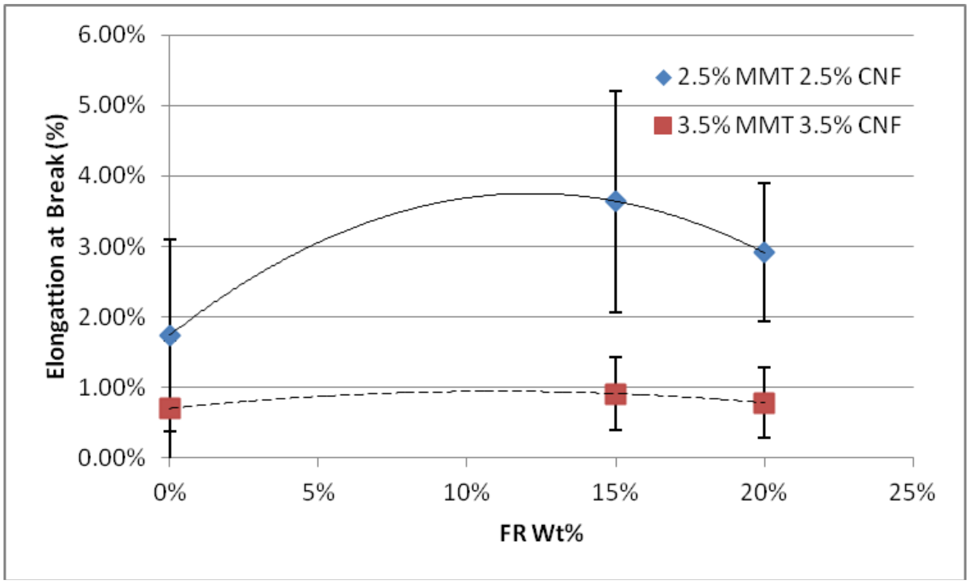

Figure 8: Elongation at break for PA11 composites as a function of weight percent FR OP1230.

Table 5: Tensile Testing Results for PA11 Composites

Formulation	MMT	CNF	FR	Tensile Strength (MPa)	Elongation at Break	Tensile Modulus (MPa)
Neat PA11	0%	0%	0%	41.8	234%	901
#1	2.5%	2.5%	0%	33.2	1.74%	1931
#3	2.5%	2.5%	15%	32.1	3.64%	1917
#4	2.5%	2.5%	20%	32.3	2.91%	2209
#2	3.5%	3.5%	0%	30.1	0.7%	2323
#5	3.5%	3.5%	15%	30.7	0.91%	2453
#6	3.5%	3.5%	20%	32.0	0.78%	2449

3.1.3 Fractural Surface SEM After completion of Izod impact testing, SEM images were taken of the fractural surface of the samples. The polymer material is insulating so the samples had to be coated prior to SEM analysis. Representative images from each formulation are shown in Figures 8-10 below. In Figure 8, the two materials are shown to have a relatively smooth fracture surface with strands of CNF protruding out from the surface. The second formulation has a higher concentration of CNF than the first (3.5% vs. 2.5%), which can be seen by the greater number of visible CNFs in the SEM image. The MMT clay is too small to be observed by the SEM used in this experiment. The protrusion of the CNFs from the fracture surface would seem to suggest that CNF would reinforce the material structure against fracture, but from the Izod results we know that these composites have much lower Izod resistance than the neat PA11. We have no definitive reason for this result based on the SEM, but it could be due to an effect from the MMT clay, which we are unable to observe. This could be due to the weak interfacial bonding between the CNF and PA11 polymer.

In Figure 9, the fracture surface of formulations 3 and 4 are shown to be quite rough when compared to those of the first two formulations. This could be due to the inclusion of micro-scale FR particles, which act as defects or weak points in the material structure that help to propagate the fracture. The FR particles themselves do not fracture, though, so they produce rough irregularities on the fracture surface. The Izod results agree with this analysis as the Izod resistance tends to decrease with the inclusion of FR. The protrusion of CNF can still be seen on the surface as well.

In Figure 10, the fracture surface of formulations 5 and 6 are shown to be similar to those shown in Figure 9, but with much greater CNF protrusion. This is to be expected as the weight percentage of CNF is higher in these formulations. The rest of the analysis is similar to that of Figure 9, where the FR particles create a rough surface and lower Izod resistance.

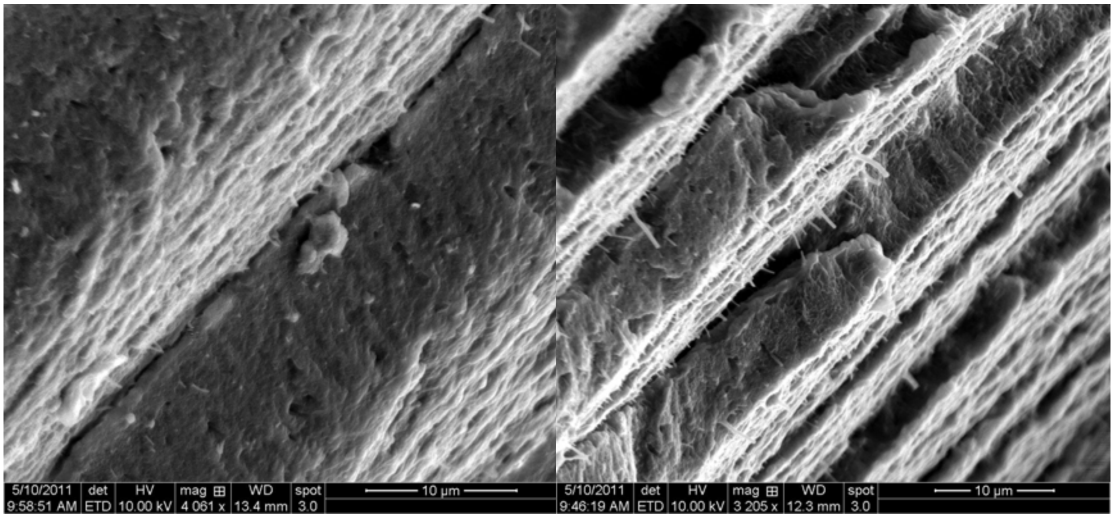

Figure 9: SEM images of the Izod fracture surface for formulations 1 (left) and 2 (right).

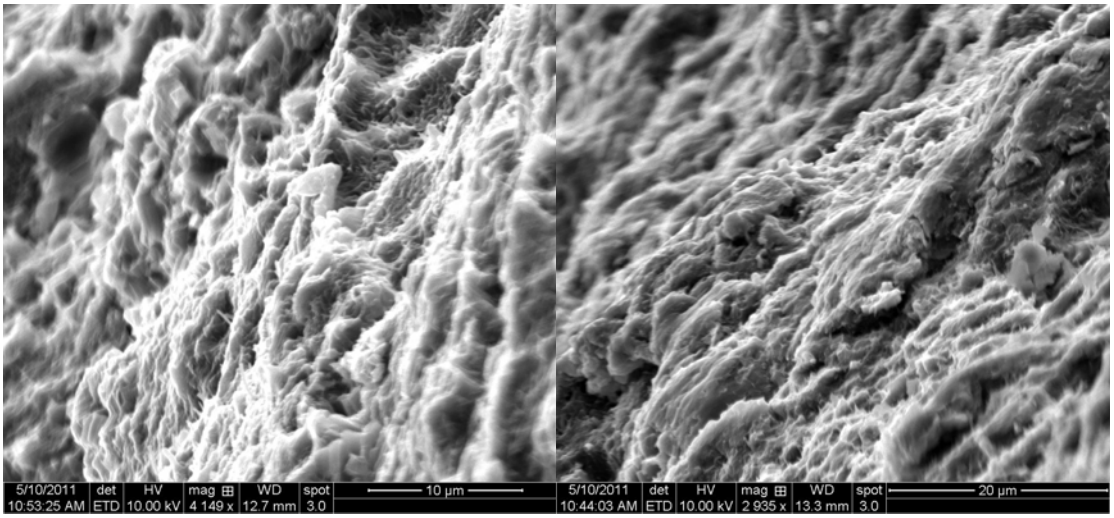

Figure 10: SEM images of the Izod fracture surface for formulations 3 (left) and 4 (right).

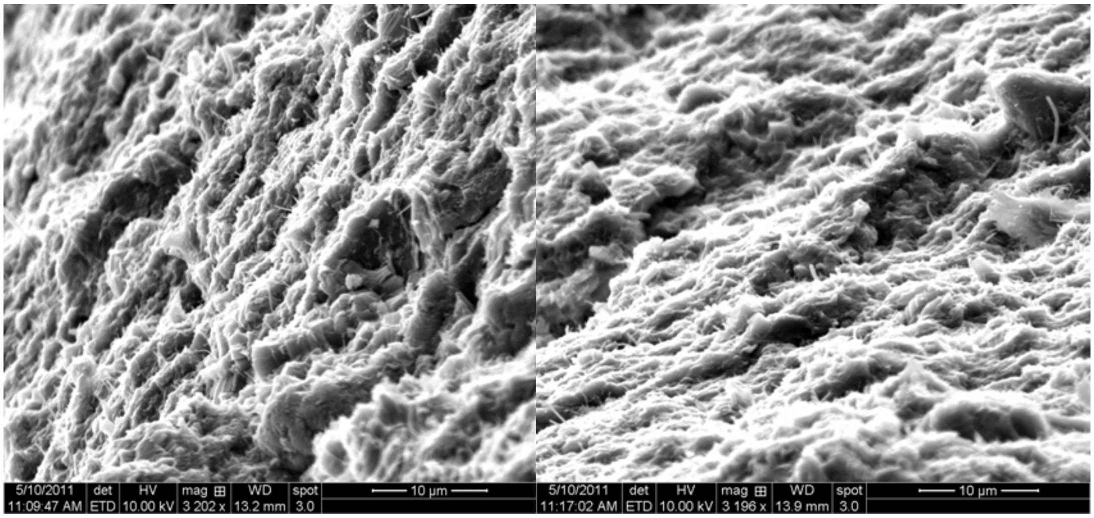

Figure 11: SEM images of the Izod fracture surface for formulations 5 (left) and 6 (right).

Flammability Properties

3.2.1 UL-94 Results The results for the UL-94 vertical burn test of our materials are shown in Table 6. The baseline PA11 material received a V-2 rating because it produce burning drips, but was still self-extinguishing in less than 30 seconds. The two formulations with MMT clay and CNF, but no FR additive failed the test. In the PA11/2.5% MMT/2.5% CNF formulation, the material burned quickly once ignited and produced numerous viscous drips. The PA11/3.5% MMT/3.5% CNF also burned readily once it was ignited, but it only produced drips on 6 out of 10 tests and the drips were very viscous. All of the formulations with FR additive passed the test with V-0 ratings. They all immediately self-extinguished and produced no drips during testing. Photos of the post-test specimens are show in Figure 7.

Table 6: UL-94 Vertical Burn Ratings for PA11 Composites

Formulation	MMT	CNF	FR	**UL-94 Rating**
Neat PA11	0%	0%	0%	**V-2**
#1	2.5%	2.5%	0%	**Fail**
#3	2.5%	2.5%	15%	**V-0**
#4	2.5%	2.5%	20%	**V-0**
#2	3.5%	3.5%	0%	**Fail**
#5	3.5%	3.5%	15%	**V-0**
#6	3.5%	3.5%	20%	**V-0**

The results for the formulations without FR additive are as expected. It is not unusual for nanomaterial additives alone to fail to improve a material's flammability rating and there are typically most beneficial when used to improve the effectiveness of conventional FR additives [3]. The results for the remaining formulations are quite promising. In previous tests, where MMT clay and CNF were combined with intumescent FR additives separately, such significant improvements in flammability properties were not observed with such low percentages of FR. In those experiments there were no formulations that were able to reach V-0 rating with only 15% FR, and there were several formulations that failed to reach it even at 20% FR [1]. These results suggest that there is a synergistic effect between MMT clay and CNF in improving the flammability of PA11 composites when combined with conventional FR additives.

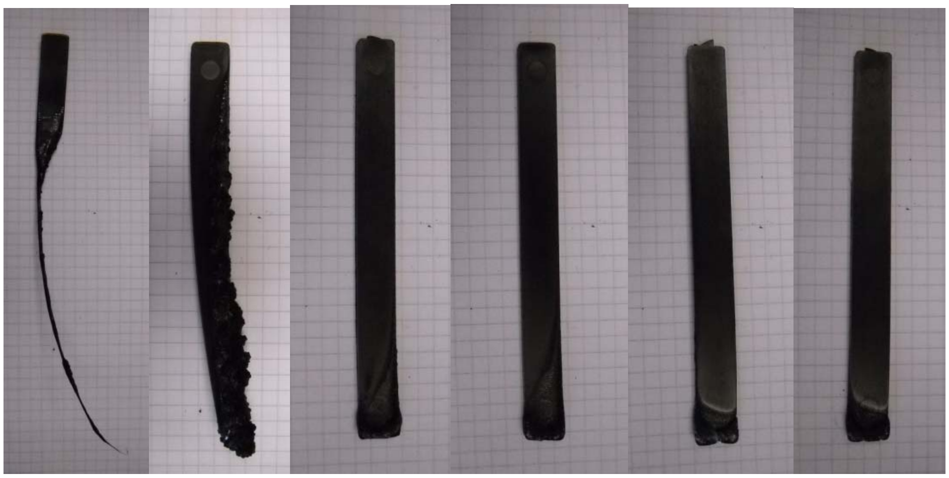

Figure 12: Post-test photos of UL-94 test specimens. Formulations 1 and 2 (left-most two photos) can be seen to have burned significantly while formulations 3-6 (in ascending order from left to right) show no significant burn damage.

3.2.2 Char Surface SEM After completion of UL-94 testing, SEM images were taken of burnt surface of the samples. The polymer material is insulating so the samples had to be coated prior to SEM analysis. Images of formulation 1 and 3 at 50x magnification are shown below. These formulations both have 2.5wt% of MMT and CNF, but formulation 3 has 15wt% FR and formulation1 has no FR. The char formation for these materials is very different because of the intumescent effect of the FR additive. The left side image shows the surface of burnt nylon. The right side image features lighter shaded puffy flakes that appeared when the material experienced combustion. These puffy flakes helped snuff out the ignition of formulation 3. The craters visible in the left side image are due to combustion gases building up in the char formation and escaping the material due to pressure differences when it is placed in the vacuum of the SEM instrument.

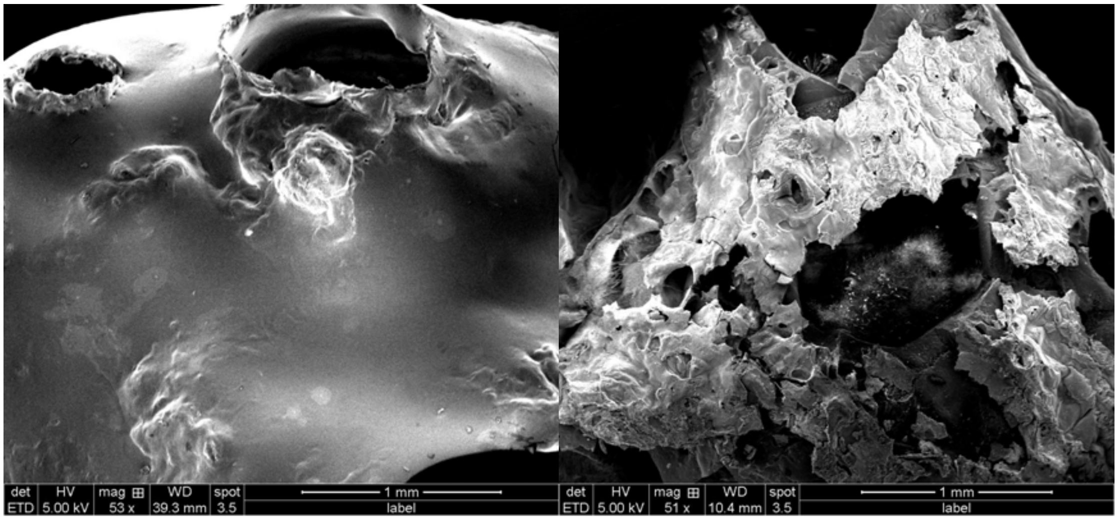

Figure 13: UL-94 char SEM images for formulations 1(left) and 3(right).

At the center of the right side image above for formulation 3, there is large agglomerate CNF. This agglomerate is focused in on in Figure 14 at 300x and 1000x magnification. As nylon was burnt away from UL-94 testing, the stronger CNFs were left behind to form these agglomerates. These agglomerates were present in all char surfaces that contained CNF.

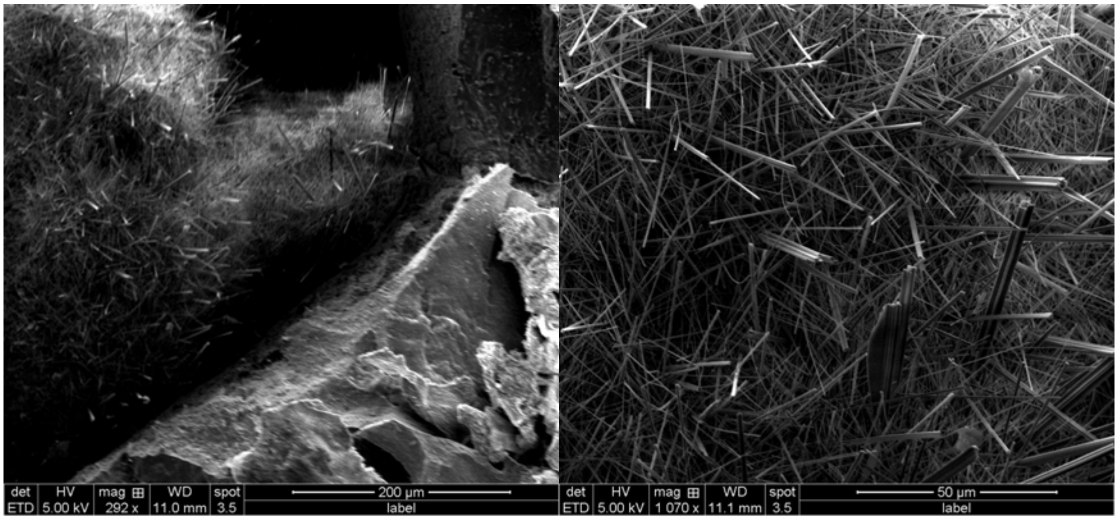

Figure 14: UL-94 char SEM images of formulation 3 in progressive magnification.

4. CONCLUSIONS

From tensile testing, the conclusion is that the lower MMT and CNF percentage, the higher the tensile strength. The differences are not very substantial though. Tensile modulus is higher when the polymer blend has more MMT and CNF. All the blends are very brittle compared to the neat PA11. On the other hand, all blends have higher tensile modulus. Neat PA11 has remarkably high elongation at break. Among the polymer blends, the blends which include 2.5% MMT and 2.5% CNF have higher elongation.

In general, mechanical properties of blended nanocomposites with synergistic effects exhibited similar properties to nanocomposites of just one nanomaterial additive.

From the SEM image, it is observed that formulation 2, which includes 3.5% CNF, has a higher concentration of CNF than the first one which includes 2.5% CNF. The MMT clay is too small to be observed by the SEM we used. For the further studies to observe MMT clay, TEM will be needed.

From the flammability tests, all the polymer blends were rated UL 94 V-0 except for formulations 1 and 2 which have failed the UL 94 test. Synergistic effect of MMT, CNF, FR additives was observed. Only 15% FR additives is needed with 2.5% MMT and 2.5% CNF to achieve UL 94 V-0 rating as compared to 20% FR additives needed for 5% CNF or 7.5% MMT used individually in PA11 polymer. Flammability properties of these polymer blends need to be further investigated using cone calorimetry.

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