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# RPPR Final Report

## as of 24-Aug-2018

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**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 1

**STEM Participants:** 1

**Major Goals:** The objective of this 6 month proposal was to synthesis and characterize polymer/MXene composites.

Here we chose to reinforce nylon-6 because it is an important polymer that was reinforced previously with another 2D material: clay.

A major goal of the proposed work was to reinforce nylon-6 with small amounts (< 10 wt.%) of Ti3C2Tz MXene flakes. The characterization was to include DSC, TGA and tensile testing.

**Accomplishments:** Two routes were attempted: solution-based processing and melt processing. In both case, the Ti3C2Tz flakes were successfully incorporated into the matrix resulting in a homogeneous composite with low filler loading. Solution-processing is limited by the scalability of MXene production and is dependent upon the use of strong acids or organic solvents due to nylon's high chemical resistance.

Melt processing is an attractive method as commercially available nylon-6 can be employed and simply allowed to mix in the presence of MXene. After 20 min. of mixing at 220 °C prior to extrusion, the resulting composites containing 5 wt.% Ti3C2Tz were ~ 30 % stiffer than neat nylon (1.6 GPa vs. 1.2 GPa). These results were obtained despite the fact that full dispersion was not achieved,

Somewhat surprisingly, the presence of Ti3C2Tz resulted in a composite that appeared to behave mechanically similar to dry nylon-6. The reason for this state of affairs is unclear at this time.

**Training Opportunities:** An undergraduate in our BS/MSc program carried out this work as part of his MSc thesis. He has been trained in many techniques such as DSC and TGA, polymer composite processing including extrusion, XRD, polymerization reactions, processing and dispersion of 2D materials (MXenes), mechanical testing, among others.

**Results Dissemination:** We are currently working on two papers based on the results obtained to date.

**Honors and Awards:** Nothing to Report

**RPPR Final Report**  
as of 24-Aug-2018

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:**

**Participant Type:** PD/PI

**Participant:** Michel W Barsoum

**Person Months Worked:** 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Funding Support:**

**Participant Type:** Co PD/PI

**Participant:** Caroline Schauer

**Person Months Worked:** 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Funding Support:**

**Participant Type:** Graduate Student (research assistant)

**Participant:** Michael Carey

**Person Months Worked:** 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Funding Support:**

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# Abstract

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Herein we report on the synthesis and characterization nylon-6 based composites reinforced with small amounts of  $\text{Ti}_3\text{C}_2\text{T}_z$  MXene flakes. Several synthetic routes were considered, namely solution based processing and melt processing. In both case, the  $\text{Ti}_3\text{C}_2\text{T}_z$  flakes were successfully incorporated into the matrix resulting in a homogeneous composite with low filler loading. Solution processing is limited by the scalability of MXene production and is dependent upon the use of strong acids or organic solvents due to nylon's high chemical resistance. Melt processing is an attractive method as commercially available nylon-6 can be employed and simply allowed to mix in the presence of MXene. After 20 min. mixing at 220 °C prior to extrusion, the resulting composites containing 5 wt.%  $\text{Ti}_3\text{C}_2\text{T}_z$  were  $\approx 30\%$  stiffer than neat nylon (1.6 GPa vs. 1.2 GPa). Somewhat surprisingly, the presence of  $\text{Ti}_3\text{C}_2\text{T}_z$  resulted in a composite that appeared to behave mechanically similar to dry nylon-6. The reason for this state of affairs is unclear at this time.

# 1 Introduction

Clay/polymer nanocomposites are known to offer improvements in a wide range of properties at low weight fractions of low-cost filler material, namely an increase in mechanical performance as well as improved thermal stability and gas permeation properties. These composites utilize smectite-type clays, including hectorite, montmorillonite, and synthetic mica as fillers which enhance the properties of the polymer matrix. These materials are all layered silicates, with each layer being constructed from tetrahedrally coordinated Si atoms in an edge-shared octahedral plane of either  $\text{Al}(\text{OH})_3$  or  $\text{Mg}(\text{OH})_2$ . These layers offer great mechanical properties in the direction parallel to the layer direction [1].

Recently, 2D materials have received a large degree of attention due to the unique properties they exhibit over their 3D counterparts, namely their large surface area to volume ratio and high degree of anisotropy. After the Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov of The University of Manchester, UK in 2010 for "*groundbreaking experiments regarding the two-dimensional material graphene*," there has been a large focus on graphene, making it without a doubt the most studied 2D material to date.

However, the rather plain surface chemistry of graphene as well as the manufacturing challenges associated with producing large scale defect free graphene [2] are major limitations in terms of specialized applications and general scalability. Due to the likeness to graphene, with the added advantages of stronger intermolecular forces, more complex inherent chemical structures, and surfaces which may be functionalized, MXenes are an attractive alternative to graphene. Additionally, MXenes are electronically conductive, unlike layered silicates.

## 1.1. Polymer Clay Literature

Polymers are used in majority as molded products, many of which have been successfully reinforced with glass fiber, talc, calcium carbonate, carbon black as well as other inorganic fillers. This filler content is generally between 20 and 40 wt% in composites, sometimes exceeding 50 wt% in thermosetting resins. These materials are not mixed homogeneously on a microscopic scale and are therefore composed of different phases with a small interfacial area which in turn limits the interaction between the polymeric matrix and the filler material. In 1980 Takayanagi *et al.* proposed a *molecular composite* with the simple concept of utilizing a filler of molecular size to further improve the mechanical properties of the resultant composite by maximizing the interfacial area between the matrix and the filler. This concept was shown to be effective through the use of a nylon matrix loaded at 5 wt% of aramid fiber with a diameter of 30 nm [3]. This was pushed to the next logical step by Okada's team at the Toyota Central Research & Development Labs in 1987 by considering the employment of nanoscale platelets (rather than fibers) as filler material [4], namely smectite type clays particularly montmorillonite (MMT), the structure of which is shown below in Figure 1. These materials were identified as great potential candidates as they are composed of several layers of approximately 1 nm thick silicate layers with a cross sectional area of  $100 \text{ nm}^2$ , much smaller than conventional filler

materials. Additionally, MMT is a ubiquitous clay mineral which undergoes intercalation and swelling in the presence of water and organic cations [5].

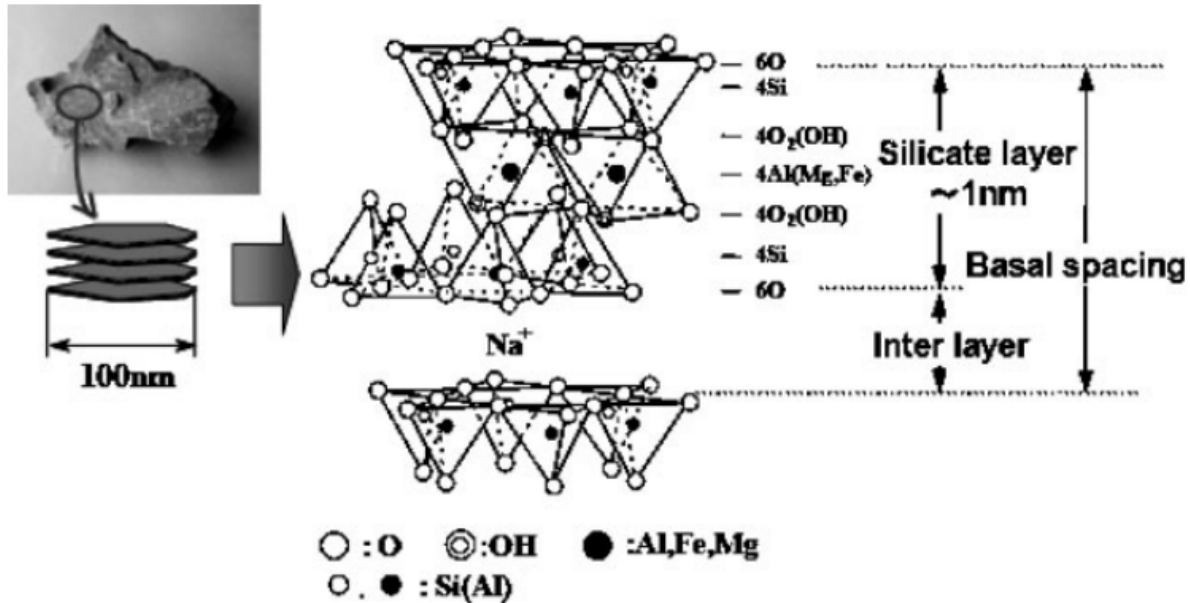


Figure 1: Structure of montmorillonite. Adapted from [4].

Polymerizations in the presence of MMT have been studied since 1964, however the major component was clay, and the focus of these studies was not to improve the properties of the polymer but rather to gain insight into scientific phenomena such as free radical initiated polymerization in the presence of clay surfaces [6, 7, 8]. In 1975, Fujiwara *et al.* attempted to synthesize a composite with nylon-6 and MMT with the specific interest of reinforcing nylon-6 (JPS51109998A). However, the major component of the composite was clay, and these composites were ceramic-like powders which were incapable of being injection-molded and of little practicality in terms of processing and by extension, applications. Okada *et al.* were convinced that in order to obtain the greatest performance of the polymer from the incorporation of silicates the upper limit of clay content lies at approximately 7.5 wt %, based on the idea of minimizing the interaction or agglomeration of silicate sheets. Additionally the author's note that if only all apexes touch, the upper limit of the silicate content is 1.5 vol. % (3.8 wt.-%), clearly indicating that a small amount of clay material is of key importance for polymer clay nanocomposites.

The first successful synthesis of a nylon-6 clay hybrid (NCH) was achieved by Okada *et al.* in 1987. Nylon-6 was chosen as it was a typical engineering polymer in the automotive industry that was commonly reinforced by glass fiber at high filler content (approximately 30 wt. %) [9]. This work was the first of its kind to recognize and successfully achieve the key step in the synthesis of these composites, namely the exfoliation of the clay material in conjunction with

making the clay similar to the polymer. For this particular work this was achieved by performing a cation exchange of montmorillonite with 12-aminolauric acid, thereby obtaining what the author's termed 12-montmorillonite [10].

The cation exchanged clay was then mixed with  $\epsilon$ -caprolactam in a mortar, ranging from 2 - 70 wt. % of the clay. The mixture was then heated at 250-270 °C for 6 h in order to polymerize. It is noted that in this system the clay can act as a catalyst. In order to expedite the ring-opening of  $\epsilon$ -caprolactam, a small amount of 6-aminocaproic acid is added, which brought the 12-montmorillonite content down to below 8 wt. %. The resulting composite material was coined as NCH - nylon clay hybrid as the term nanocomposite was not among the lexicon of the day. Compared to glass fiber, the size and morphology of montmorillonite in NCH can be seen in Figure 2.

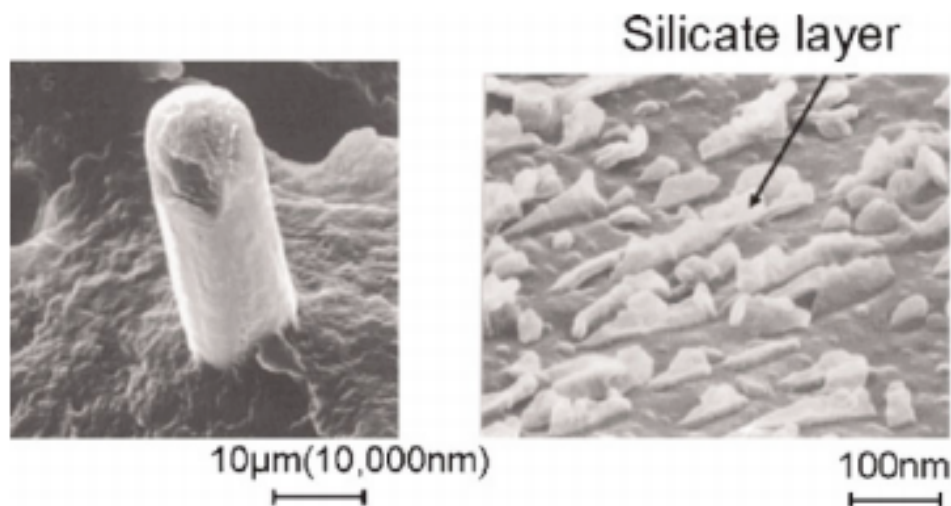


Figure 2: Size and morphology comparison of glass fiber and montmorillonite in NCH. Reprinted from [4].

The amount of clay in synthesized NCHs was estimated from weight-loss by thermogravimetric analysis (TGA). Additionally, the nylon - 6 end groups, amino ( $\text{NH}_2$ ) and carboxyl ( $\text{COOH}$ ) were analyzed via titration. Molecular weight was determined via gel permeation chromatography (GPC) with m-cresol as a solvent and end group analysis. X-ray diffraction was done on the NCH as well as the cation exchanged clay. It can be seen in Figure 3 that with increasing polymer content the non-basal peaks of the 12-montmorillonite become diminished, indicating a loss of order in the non-basal directions. That is, the 12-montmorillonite sheets have been dispersed in the nylon - 6, a key step to gaining meaningful improvements in properties.

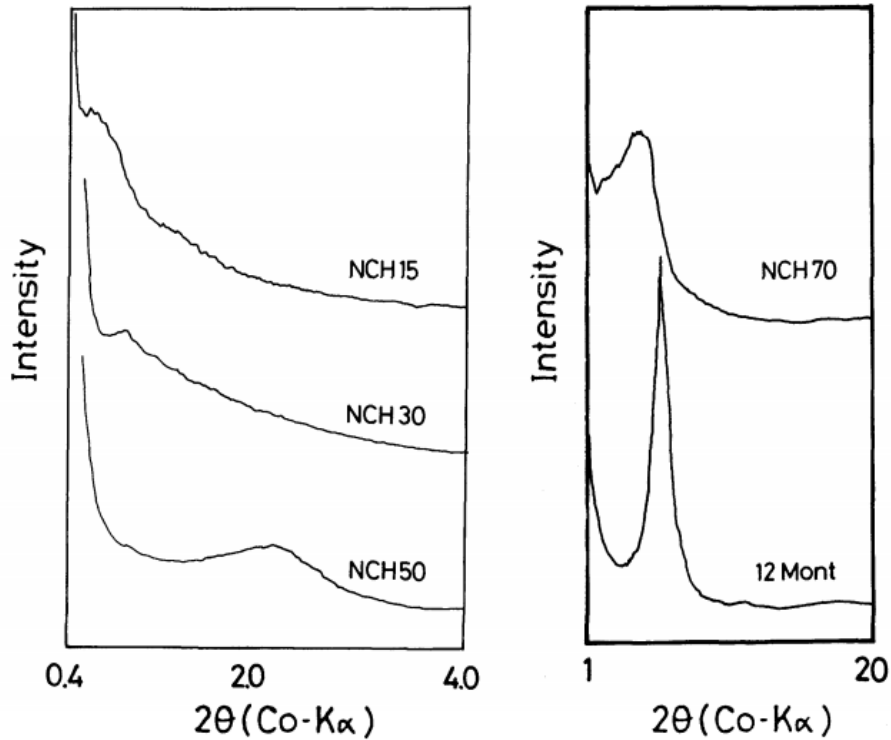


Figure 3: XRD scans of nylon clay hybrids with 12-montmorillonite content of 15, 30, 50 and 70 wt. %. It can be seen that the non-basal peak of the clay material is reduced in the NCH samples. Adapted from [10].

Addition of only several wt. % of clay improved strength, modulus and the heat distortion temperature, all of which become saturated at 5 wt. % clay. Upon increasing the content to 8 wt. % few improvements are observed. Additionally, anisotropic behavior was seen in the coefficient of thermal expansion, indicating anisotropy in the orientation of molecules.

Since this pioneering work by Okada *et al.*, a number of other nanocomposites have been synthesized including aliphatic [11, 12, 13, 14] and aromatic nylons [15], polyimides [16, 17, 18], polyolefins (such as poly(propylene) [19, 20, 21, 22], polyethylene [23], polystyrene [24, 25], and ethylene-propylene-elastomers [26], rubber [27, 28, 29, 30, 31, 32] and thermosetting resins such as epoxy [33, 18] and phenol resins [34] along with nanocomposite hydrogels [35, 36, 37, 38, 39], liquid crystal-clay composites [40, 41] and block co-polymers [42].

## 1.2. MXene Literature

MXenes are a group of early transition metal carbides and/or nitrides produced from the etching of the A layers from  $M_{n+1}AX_n$  phases, where M is an early transition metal, A is mainly a group IIIA or IVA element, X is carbon or nitrogen, and  $n=1, 2, \text{ or } 3$  [43, 44, 45]. Currently there are  $\approx 100$  different pure MAX phases [46]. Currently the MXene family includes among many others,  $Ti_3C_2$ ,  $Ti_2C$ ,  $Nb_2C$ ,  $V_2C$ ,  $(Ti_{0.5}, Nb_{0.5})_2C$ ,  $(V_{0.5}, Cr_{0.5})_3C_2$ ,  $Ti_3CN$ , and  $Ta_4C_3$  [44, 45]. Due to the nature of  $n$  ranging from 1 to 3, single MXene sheets consist of 3, 5, or 7 atomic layers for  $M_2X$ ,

$M_3X_2$ , and  $M_4X_3$ , respectively. Figure 4 depicts this structural trend and its relation to MXene [47].

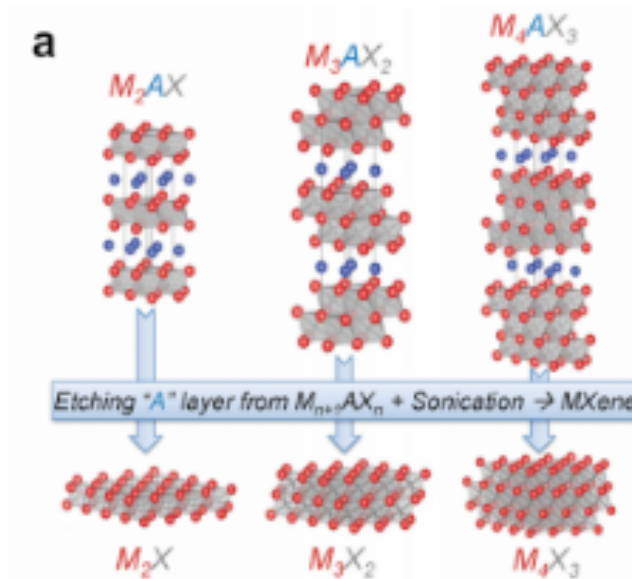


Figure 4: Schematic of MAX (top) to MXene (bottom) transformation, that readily occurs when MAX powders or thin films are immersed in HF or LiF/HCl solutions. Adapted from [47].

MXenes that are synthesized via wet etching, more specifically by acidic solutions containing fluoride ions (typically concentrated HF) have a mixture of -OH, -O, and -F terminations. This is represented by the chemical formula of  $M_{n+1}X_n(OH)_xO_yF_z$ . This is typically shortened to  $M_{n+1}X_nT_z$  for brevity's sake. As it stands today, MXenes with no surface terminations have not been synthesized.

Additionally, many of the most recent computational studies have included the consideration of surface terminations [48, 49]. This is generally done by simply considering a specific surface termination (for example, pure -OH, -O, or -F). Computational studies of this sort have predicted the properties of MXenes [50, 51, 52, 53, 54, 55, 56, 57, 58, 59], [60, 61, 62, 63, 64].

Post processing treatments to obtain specific surface terminations has only scarcely been reported to date, but it is possible [65]. Surface terminations and flake stacking of  $Ti_3C_2T_z$  and  $V_2CT_z$  were recently studied by electron energy-loss spectroscopy in transmission electron microscopy (TEM) [66, 67], neutron scattering, and nuclear magnetic resonance (NMR) spectroscopy [68, 69]. These studies have shown that the true surface of MXene is a random distribution of the aforementioned terminations.

Herein we explored different methods of incorporating low mass fractions (< 10 wt.%)  $\text{Ti}_3\text{C}_2\text{T}_z$  MXene into polyamide-6 in order to investigate the relationship between processing conditions and mechanical properties of composite properties.

## 2 Experimental Approaches

### 2.1 Solvent Casting

The initial efforts of this project focused on a solvent based approach due primarily to the limited, small scale production of delaminated, colloidal  $\text{Ti}_3\text{C}_2\text{T}_z$  suspensions. This method additionally allowed for small amounts of polymer and relatively small amounts of solvents to be used in initial studies. The fundamental principle employs a wet chemistry approach by dissolving the as-received nylon-6 pellets in a corresponding solvent (such as formic acid or 1,1,1,3,3,3-Hexafluoro-2-propanol), incorporating the d- $\text{Ti}_3\text{C}_2\text{T}_z$  and after allowing to mix, casting the solution and allowing the solvent to evaporate.

#### 2.1.1 Production of $\text{Ti}_3\text{AlC}_2$ MAX Phase

Powdered  $\text{Ti}_3\text{AlC}_2$  was produced by the ball milling of commercial TiC, Al and Ti powders in a ratio of 2:1.05:1 molar ratio with zirconia milling balls for 24 h. This mixture was then separated from the milling balls, placed in an alumina boat and heated in a tube furnace at a rate of 5 °C/min under continuous argon flow to 1350 °C. After a holding time of 2 h, the sample cooled at a rate of 5 °C/min. This lightly sintered brick was then milled into fine powders which were passed through a 400 mesh sieve to achieve a particle size of < 38 μm.

#### 2.1.2 Production of $\text{Ti}_3\text{C}_2\text{T}_z$ Delaminated MXene Colloidal Suspensions

One gram of the sieved  $\text{Ti}_3\text{AlC}_2$  powder was immersed in a 10 mL mixture of 12 M HCl acid and 1.09 g lithium fluoride for a LiF/ $\text{Ti}_3\text{AlC}_2$  molar ratio of 8.3:1. This mixture, housed in a polypropylene bottle along with a PTFE coated magnetic stir bar was placed in an oil bath at 35 °C and allowed to mix for 24 h. After this etching period, the reaction vessel was removed, wiped clean of any residual oil, and the contents of the bottle were divided into two centrifuge tubes so that approximately 5 mL of liquid was in each tube. In order to separate the sediment, these tubes were balanced and then placed in the centrifuge at 3500 rpm (or 2301 rcf) for 2 minute. The supernatant was then discarded and replaced with 6M HCl, for a total volume of about 40 mL in each centrifuge tube. This kept the amount of sediment around 0.5 g in 40 mL in each centrifuge tube to ensure effective washing. The HCl was used to dissolve the salts produced during the etching process.

The tubes were again centrifuged for 2 minutes at 3500 rpm. After decanting the supernatant and refilling with 40 mL of 6M HCl. This procedure was repeated 2 more times for a total of 3 acid washes. After the third wash, the tubes were filled with distilled water, and repeated until a pH of 5-6 was measured by pH paper. When this was achieved the tubes were centrifuged for 20 minutes at 5000 rpm (6533 rcf). The supernatant was discarded and in each tube 5 mL of distilled water was added. After dispersing with a vortex mixer, the contents of

each tube were combined into one, and the mixture was placed into a sonicating bath with a temperature maintained at 20 °C for 1 h with high purity argon bubbling through the solution.

Following sonication, the solution was again split into two centrifuge tubes and the contents were centrifuged for 1 h at 5000 rpm. The supernatant was decanted and stored in glass vials, and the sediment was discarded. In order to determine the concentration of  $\text{Ti}_3\text{C}_2\text{T}_z$  in the suspension, 3.0 mL of solution was vacuum filtrated overnight and the resulting film was dried at 110 °C in vacuum for 24 h before weighing to determine a concentration of 12.6 mg/mL for the delaminated suspension.

### 2.1.3 Synthesis of Solvent Cast Composites

With the concentration of the MXene colloidal suspension known, nylon-6 pellets purchased from Sigma Aldrich were dissolved in a solvent, (most commonly formic acid 98%) to form ~20% solutions of nylon-6. The pellets were allowed to mix into solution for 24 h to ensure complete dissolution. A volume of the delaminated suspension of MXene was measured and added to the polymer solution that corresponds to 10% by weight (targeted). Again, the solution was allowed to mix for 24 h before dispensing the solution into a polystyrene weighing boat and allowing it to dry into a film. Once dried, these films could be cut into smaller pieces for characterization.

### 2.1.4 Characterization of Solvent Cast Composites

Solvent cast films were cut into small sections and characterized by thermogravimetric analysis (TGA) under Ar flow at 10 °C/min from room temperature to 800 °C and held for 0.5 h. This method allows for the final mass to be taken as the amount of  $\text{Ti}_3\text{C}_2\text{T}_z$  present in the original sample. With a targeted MXene loading of 10 wt. %, by TGA, a load of 9.7 wt. % was determined, indicating that the employed synthetic method involved little loss of either polymer or MXene and a targeted load could be met with good agreement. **Error! Reference source not found.** shows the weight loss curves as a function of temperature for as received neat nylon 6 pellets and solvent cast composites loaded at 9.7 wt. %  $\text{Ti}_3\text{C}_2\text{T}_z$ .

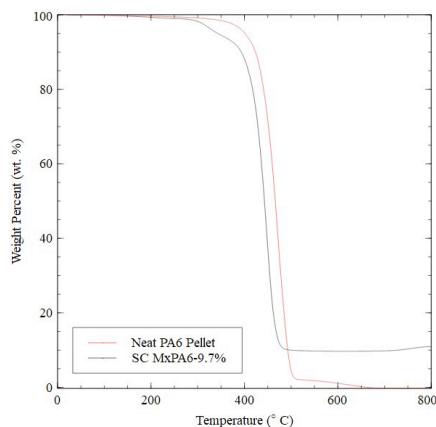


Figure 5: Thermogravimetric analysis of solvent cast MXene composite loaded at 9.7% vs. as received nylon-6 pellet. Also shown is the curve for neat nylon.

A differential scanning calorimeter, DSC, was utilized in order to determine the degree of crystallinity and enthalpies of melting and crystallization for both neat nylon 6 as well as nylon 6 MXene composites produced via the solvent cast method. The temperature was allowed to equilibrate at -50 °C, then ramped at 10 °C/min to 300 °C and held isothermally before ramping down to 22 °C at 10 °C/min. Enthalpic values are obtained by the integration of the crystallization and melting peaks using the software packages provided by the manufacturer of the DSC. Using the enthalpies of crystallization and melting, the percent crystallinity of each sample can be measured using the following equation:

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \quad (1)$$

where  $\Delta H_m$  is the latent heat of melting, and  $\Delta H_c$  is the latent heat of crystallization, both of which are experimental values determined from the area under the curve of the melting and crystallization curves, respectfully.  $\Delta H_m^0$  is a reference value for the heat of melting of a 100% crystallized polymer which for nylon-6 is 230.1 J/g [70]. However, Eq. (1) is only valid for neat polymers, and must be modified for composites by accounting for the fractional load occupied by the filler material. This is done by including the fraction of filler in the sample,  $f$ .

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{(1 - f)\Delta H_m^0} \times 100 \quad (2)$$

Table below summarizes the enthalpies of heat and crystallization as well as the percent crystallinity for the solvent cast composite sample and the as received nylon-6 pellet.

*Table 1: Differential Scanning Calorimetry results for neat and composite specimens*

Sample ID	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$\chi_c$ (%)
Neat PA6	223.75	-129.2	175.55	78.66	90.33
Solvent Cast MxPA6-9.7	221.87	-55.42	191.49	70.17	60.44

## 2.2 Melt Processing

The solvent cast method, while simple in its approach and therefore a good initial place to begin this investigation, has its drawbacks. Due to the chemical resistance of polyamides, scaling up this procedure would require large amounts of strong acids and/or organic solvents such as m-cresol or HFIP. This is neither cost effective nor environmentally friendly, therefore melt processing technique were tried. While injection molding was not available, a benchtop extruder was used to combine nylon-6 pellets with MXene multilayer powders and allowed to mix for a period of time before extruding a filament of composite material.

### 2.2.1 Production of $\text{Ti}_3\text{AlC}_2$ Phase

The synthesis  $\text{Ti}_3\text{AlC}_2$  phase was the same as above (See Section 2.1.1.).

### 2.2.2 Production of Multilayer $\text{Ti}_3\text{C}_2\text{T}_z$

In order to scale up the production of these samples to meet the volume requirements of the machinery involved, the method of MXene production required modification, namely the use of multilayer (ML)  $\text{Ti}_3\text{C}_2\text{T}_z$  rather than delaminated (d)  $\text{Ti}_3\text{C}_2\text{T}_z$  MXenes. This method requires fewer steps, but does not fully exfoliate the MXene sheets, however, much larger amounts (~10 g, rather than ~500 mg of d- $\text{Ti}_3\text{C}_2\text{T}_z$ ) can be made in a single batch. Due to the large amount of shear that occurs during the continuous mixing in the extruder within a viscous polymer melt, the working hypothesis was hoped that these forces would exfoliate and disperse the MLs within the nylon matrix.

One gram of the sieved  $\text{Ti}_3\text{AlC}_2$  powder was immersed in a 10 mL mixture of 10% hydrofluoric acid and 1.09 g lithium chloride for a  $\text{LiCl}/\text{Ti}_3\text{AlC}_2$  molar ratio of 5:1. The mixture was allowed to mix for 24 h at RT. After this etching period, the reaction vessel was removed and the contents of the bottle were divided into two centrifuged tubes so that approximately 5 mL of liquid was in each tube. In order to separate the sediment, the tubes centrifuged at 3500 rpm (or 2301 rcf) for 2 minutes. The supernatant was then discarded into a waste container and replaced with 6M hydrochloric acid, for a total volume of about 40 mL in each centrifuge tube. This kept the amount of sediment around 0.5 g in 40 mL in each centrifuge tube to ensure effective washing. The tubes were centrifuged for 2 minutes at 3500 rpm. After decanting the supernatant and refilling with 40 mL of 6M HCl, this procedure was repeated 2 more times for a total of 3 acid washes. After the third wash, the tubes were filled with distilled water, and repeated until a pH of 5-6 was measured by pH paper. When this was achieved the tubes were centrifuged for 20 minutes at 5000 rpm (6533 rcf). The supernatant was discarded and in each tube 5 mL of distilled water was added. This solution was vacuum filtered and the resulting sediment was dried in vacuum overnight at 110 °C. After drying, powders were made by crushing the sample with a mortar and pestle.

### 2.2.3 Extrusion of Neat and Composite Filament

A SJZS-10 Laboratory Micro Twin Screw Extruder from Long River Industry and Trade Company (Wuhan, China) was used to continuously mix and extrude neat and composite samples. Multilayered  $\text{Ti}_3\text{C}_2\text{T}_z$  powder and nylon-6 pellets in a ratio that would correspond to 5 wt. % MXene were loaded into the hopper of the extruder. This extruder was equipped with four heating zones; an initial warming zone, set to 180 °C, two middle zones that were set to 250 °C and a dye temperature zone at 210 °C. The filament that was extruded was attached to a torque motor and allowed to spool. Specimens were allowed to mix continuously in the extruder for a period of time before extruding. One run used a mixing time of 20 minutes, while another allowed for 5 h of mixing.

## 2.2.4 Tensile Testing of Extruded Filaments

The monofilament made via the extrusion method was cut into small sections and prepared as tabbed tensile specimens according to ASTM D3822. Sample diameters were measured by digital image correlation, with five measurements being taken along the gauge length and averaged. Samples with excessive deviation in diameter were discarded.

Tensile tests were conducted on a 3300 series Instron with a 100 N load cell. A total of ten samples were tested, five neat and five composite. A strain rate of 7.62 mm/min was used. Tensile results shown in Figure 6 indicate that composite specimens loaded with 5 wt. %  $\text{Ti}_3\text{C}_2\text{T}_z$  behaved like nylon-6 that had been dried or had just recently been molded/extruded.

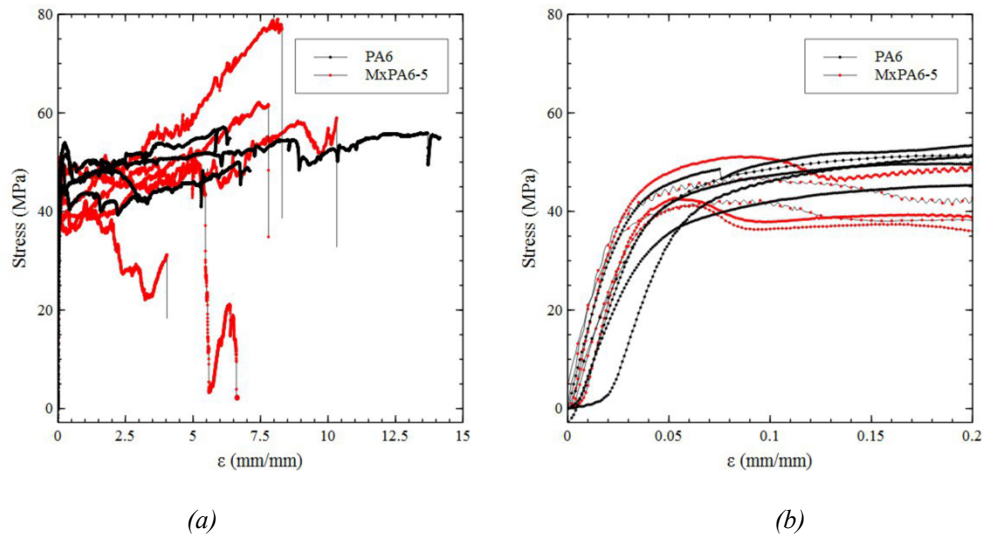


Figure 6: a) Full and, b) low strain region of engineering stress-strain plots for neat nylon and 5 wt.% MXene loaded samples, mixed for 20 min. before extruding. Unique "dry-like" behavior of 5 wt.% MXene loaded samples can be seen in b by the presence of a "knee."

Both the neat and composite tensile specimens were kept in the same conditions (temperature, relative humidity, etc.) so this difference can be attributed to the presence of the MXene. Numeric tensile results are summarized below in Table 2. The average modulus of elasticity for the neat nylon-6 was 1256 MPa, while the average for the composite material was 1645 MPa. This corresponds to a 31 % increase. A two-tailed t-test at 97.5% confidence leads to the conclusion that the differences between these means is significant.

The MXene containing nylon-6 had an UTS of 59 MPa, while the nylon-6 had an average UTS of 53 MPa, which corresponds to be a  $\approx 10$  % increase, but the difference in these means is not significant according to a performed two-tailed t-test. With regards to strain to failure, no neat nylon-6 samples were brought to failure, so values of strain to failure are not reported. For the MXene containing nylon-6, the average strain to failure was 7.42 mm/mm.

Table 2: Moduli of elasticity, UTS and strain to failure for neat and composite (5 wt. %) tensile specimens, mixed for 20 min.

Sample No.	E (MPa)	UTS (MPa)	$\epsilon_{fail}$ (mm/mm)
<b>Neat Nylon-6</b>			
1	1225	56	-
2	1173	-	-
3	1007	50	-
4	1358	50	-
5	1517	57	-
<b>5 wt. % <math>Ti_3C_2T_z</math></b>			
1	1621	51	6.6
2	1801	62	7.8
3	1333	42	4.0
4	1958	79	8.3
5	1511	59	10.3

The engineering stress-strain plots shown in Fig. 6 show an interesting difference in behavior between the neat the MXene containing nylon-6, namely that the former can be characterized by a plateau, while the latter show a local maximum or hump, before strain hardening. This hump is generally seen in neat nylon-6 when the specimen is in a fully dried state. **This is an important result because it implies that the MXene content somehow induces the nylon-6 to behave as if it were dry.**

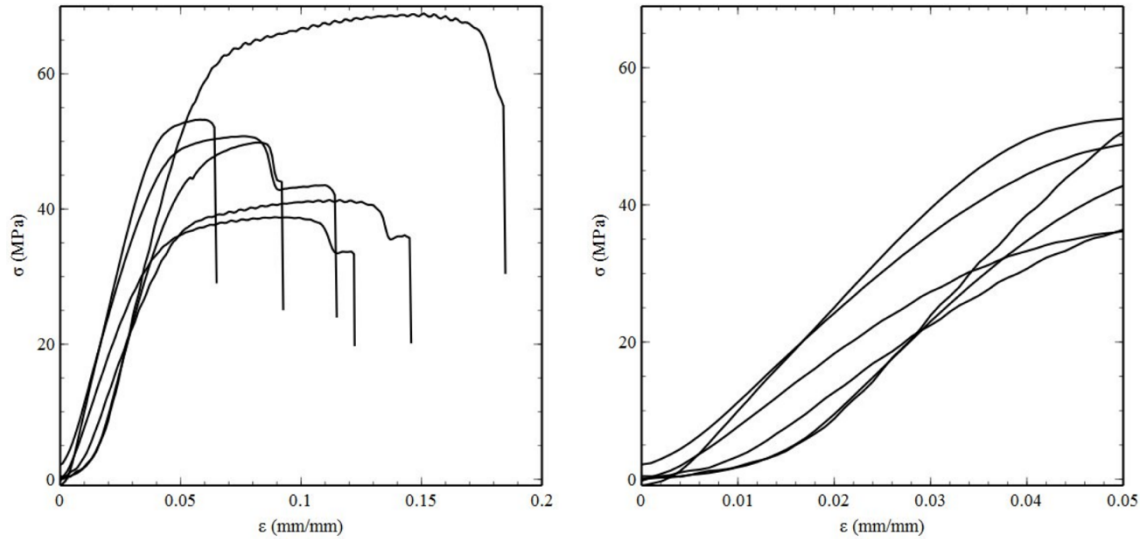


Figure 7: Full and low strain engineering stress-strain plots for MxPA6-5 filaments, dried overnight at 160 °C in vacuum.

To further explore this somewhat surprising aspect of MXene,  $Ti_3C_2T_z$  containing nylon-6 tensile samples, MxPA6-5 fibers (20 min. extrude) were dried in a vacuum oven at 160 °C overnight and transported in a desiccant containing chamber to the Instron. Six dried samples of the same geometry were tested as before. The dried MXene containing filaments predictably retained the characteristic dry stress strain behavior (Fig. 7), however the samples were now more brittle, with an average strain to failure of just 0.08 mm/mm. The Young's modulus drops to 1330 MPa.

Table 3: Moduli of elasticity, UTS and strain to failure for dried MxPA6-5 filaments, mixed for 20 minutes.

Sample No.	E (MPa)	UTS (MPa)	$\epsilon_{fail}$ (mm/mm)
<b>5 wt. % <math>Ti_3C_2T_z</math>, Dried at 160 °C in vacuum (20 min. extrude)</b>			
1	1463	52	0.054
2	1309	51	0.11
3	1033	41	0.15
4	1533	69	0.18
5	1066	39	0.12
6	1351	50	0.082

The dried composite material exhibited an average elastic modulus of 1108 MPa, an average ultimate tensile strength of 43 MPa, and an average strain to failure of 0.08 mm/mm.

Finally, tensile tests on non-dried composites continuously mixed for 5 h were conducted. The results are shown in Fig. 8 and Table 4. The average elastic modulus was determined to be  $\approx$  568 MPa, with an average UTS of  $\approx$  32 MPa and an average elongation to failure of 6.04 mm/mm. The cause for the loss of strength and ductility is not immediately apparent at this time, however it should be noted that these specimens were the most crystalline of all composite specimens at 68%.

Table 4: Modulus of elasticity, UTS and strain to failure for MxPA6-5 filaments, mixed for 5 h before extruding.

Sample No.	E (MPa)	UTS (MPa)	$\epsilon_{fail}$ (mm/mm)
<b>5 wt. % <math>Ti_3C_2T_z</math>, (5 h extrude)</b>			
1	697.00	40.12	6.12
2	577.93	32.18	6.51
3	567.66	38.54	6.32
4	564.64	24.48	4.59
5	433.79	24.33	6.64

Note the extrusion process occurs at an elevated temperature, approximately 220 °C in ambient air. It has been shown that in an oxygen atmosphere, at 200 °C, parts of  $Ti_3C_2T_z$  MXene with F/OH terminations are oxidized to obtain anatase nano-crystals evenly distributed on 2D

$Ti_3C_2$  layers [74], suggesting that some oxidation of MXene may have occurred when held at this elevated temperature for such a long period of time, thereby causing a reduction in the mechanical properties.

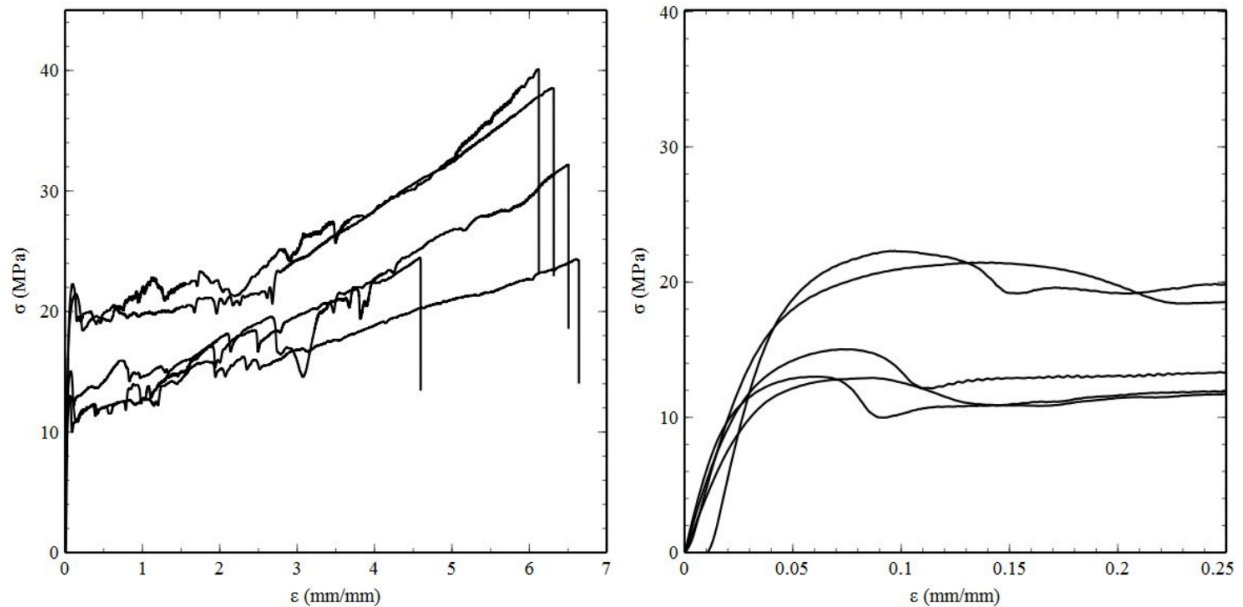


Figure 8: Full and enhanced engineering stress-strain plots for MxPA6-5 filaments which were allowed to continuously mix for 5 h.

Despite the reduction in elastic modulus and ultimate tensile strength, the composite filament when allowed to mix for 5 h still retained the behavior which mirrors that of dry, non-reinforced nylon-6.

### 3 Summary and Conclusions

The successful production of nylon-6 based composites, containing relatively small loadings of  $Ti_3C_2T_z$  MXene has been demonstrated by three methods, each with a distinct set of advantages and disadvantages. The solvent cast approach is attractive for small scale applications and proofs of concept, as the amount of material required to prepare test specimens is kept to a minimum. However, this method requires the use of strong acids and/or organic solvents which limit the scalability of this technique and is difficult to reproduce. Furthermore, the use of delaminated, colloidal MXene suspensions is not practical for synthesis on any scale larger than a few grams. Production on a larger scale is feasible by melt-processing wherein ML powders of  $Ti_3C_2T_z$  and nylon-6 pellets extruded and allowed to compound in the melt state. While this is arguably the simplest method, however, more work is needed to fully disperse the  $Ti_3C_2T_z$  flakes using this method. Despite the fact that full dispersion was not achieved, tensile testing of extruded filaments showed a 31% increase in elastic modulus and a 10% increase in UTS compared to neat nylon.

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