On the Synthesis & Characterization of Ti$_3$C$_2$T$_x$ MXene Polymer Composites

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Dedications

This work is dedicated to the many people I am gratefully indebted to for their unconditional support. To my parents, Jeffrey and Kathleen, my wonderful girlfriend, Emma and the many friends I’ve made in the course of my work.
Acknowledgments

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An investigation into the synthesis and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene polymer composites has been made, where an improvement in material properties at low filler weight percents has been achieved. Poly(acrylic acid) based composite material showed improved mechanical performance, namely a 144.8% increase in tensile strain to failure with no reduction in elastic modulus and only slight reduction in ultimate tensile strength. FTIR analysis of these films show evidence for hydrogen bonding between the functional groups of poly(acrylic acid) and the surface functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$. Nylon-6 based composites loaded at 5 and 10 wt% MXene were successfully produced by both a solvent cast and extrusion method, with MXene content verified by thermogravimetric analysis (TGA). Samples loaded at 5 wt% exhibited a 30.96% increase in modulus of elasticity, with a 10.9% increase in ultimate tensile strength. A water barrier phenomena was observed in the case of these MXene containing composites, as evidenced by the characteristic shape of the stress-strain plot. Differential scanning calorimetry results reveal a 15 °C increase in the crystallization temperature ($T_c$) with a enthalpy of crystallization 18% lower than neat nylon-6 and a degree of crystallinity of 60-70%, suggesting that MXene acts as a site for heterogeneous nucleation. X-ray diffraction results indicate that full delamination of multilayer MXene was not achieved through mechanical shearing alone, however improved mechanical properties were achieved despite this, suggesting that further improvements could be made if full exfoliation is achieved.
Chapter 1: Introduction

Making composites of two or more materials in order to obtain a product which is greater than its lone constituents has long been a technique to create high performance materials with low cost methods. Clay/polymer nanocomposites are of particular interest, in that they offer improvement in a wide range of properties at low weight fractions of low cost filler material.

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 Al(OH)$_3$ or Mg(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 its notorious manufacturing challenges 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, the marriage of polymeric materials with low weight percentages of MXene is theorized to lead to increased mechanical properties, as well as improved thermal stability, in accordance with the polymer clay literature.
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 homogenously 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 aramide fiber with a diameter of 30 nm [2]. This concept 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 [3], namely smectite type clays particularly montmorillonite (MMT), the structure of which is shown below in Figure 1.1. 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 nm², 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 [4].

![Figure 1.1 Structure of montmorillonite. Adapted from [3].](image-url)
Polymerizations in the presence of MMT has 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 [5–7]. 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 is 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%) [8]. 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 [9].

The cation exchanged clay was then mixed with ε-caprolactam in a mortar, ranging from 2 - 70 wt % of the clay. The mixture was then heated at 250-270 °C for 48 h in order to polymerize. It is supposed that in this system the clay can act as a catalyst. In order to expedite the ring-opening of ε-caprolactam, a small amount of 6-aminocaproic acid was added, which then 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 1.2.

The amount of clay in synthesized NCHs was estimated from weight-loss by an unspecified technique that is assumed to be thermogravimetric analysis (TGA). Additionally, the nylon-6 end groups, amino ($NH_2$) and carboxyl ($COOH$) 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 1.3 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 1.3 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 [9].

These nanocomposites can offer excellent improvements in a variety of material properties, namely mechanical strength, thermal stability and gas permittivity. 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 [10–13] and aromatic nylon [14], polyimides [15–17], polyolefins (such as poly(propylene) [18–21], polyethylene [22], polystyrene [23, 24], and ethylene-propylene-elastomers [25]), rubber [26–31] and thermosetting resins such as epoxy [32, 33] and phenol resins [31], along with nanocomposite hydrogels [34–38], liquid crystal-clay composites [39, 40] and block co-polymers [41].
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 $n = 1, 2, \text{ or } 3$ [42–44]. There are approximately 60 different pure MAX phases [45]. Currently the MXene family includes $Ti_3C_2$, $Ti_2C$, $Nb_2C$, $V_2C$, $(Ti_{0.5},Nb_{0.5})_2C$, $(V_{0.5},Cr_{0.5})_3C_2$, $Ti_3CN$, and $Ta_4C_3$ [43, 44]. 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 1.4 depicts this structural trend and its relation to MXene [46].

As the elemental composition and/or surface terminations of MXene can be changed, the properties may be changed readily [44]. This makes MXenes much more attractive than graphene, which has a simple composition and therefore a limited range of properties and by extension, applications. Add to this the notorious challenges in large scale production of defect free graphene [47], it is clear that MXenes are much more promising.

Figure 1.4 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 [46].

MXenes that are synthesized via wet etching, more specifically by acidic solutions containing fluoride (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 $M_{n+1}X_nT_x$.
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 [50–66].

Post processing treatments to obtain specific surface terminations has only scarcely been reported to date, but it is possible [67]. Surface terminations and flake stacking of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{V}_2\text{C}_\text{T}_x$ were recently studied by electron energy-loss spectroscopy in transmission electron microscopy (TEM) [68, 69], neutron scattering [70], and nuclear magnetic resonance (NMR) spectroscopy [71, 72] It has been shown that the true surface of the MXenes is a random distribution of the aforementioned terminations.
2.1 Production of MXene via Etching of MAX Phase

The production of $Ti_3C_2T_x$ was achieved through the etching of $Ti_3AlC_2$ MAX phase which was first reported by [42], but done through the use of hydrochloric acid and lithium fluoride, in a method reported by [73]. In this method, 0.6 g of lithium fluoride is dissolved in 10 mL of 12M hydrochloric acid in a plastic container. As this reaction is rather exothermic, hydrochloric acid is added slowly and the reaction is allowed to proceed and then cool to room temperature. While this reaction is cooling, 1.0 gram of $Ti_3AlC_2$ is weighed out. After reaching room temperature, the MAX phases is added very slowly to the lithium fluoride hydrochloric acid solution. A magnetic stir bar is added, and the reaction vessel (with a previously made venting apparatus) is added to an oil bath that is heated to 35 °C and allowed to mix for 48 h.

After this time has passed, the container is removed, the oil is wiped carefully off the outside and the contents of the container are transferred to two 50 mL centrifuge tubes so that the etched MAX phase is broken up into portions which allow for effective washing. The centrifuge tubes are then filled with water up to the 40 mL mark. Before placing into a centrifuge, the two tubes are balanced to within ± 0.2 g in order to avoid imbalances in the centrifuge which could damage the equipment. The centrifuge is run at 3500 RPM for 2 minutes, after which the tubes are removed, decanted and refilled with water. This process is continued until a pH of 6-7 is achieved after which a stable colloidal suspension is attained.

Dependent upon the final state of the MXene that is required or sought after, the next step is either direct to vacuum filtration in order to obtain a multilayer MXene or to sonication and subsequent washing to achieved a delaminated suspension of MXene in water. If the latter is desired, the centrifuge is run once more for 20 minutes at 5000 RPM, after which the contents are transferred to a mason jar and placed in the sonicator with an icebath and a continuous flow of argon for one hour. After sonication, the suspension is centrifuged for one hour at 5000 RPM and the final suspension is
collected. A small volume of this suspension is precisely measured and vacuum filtered overnight. The product of this filtration is then dried in a vacuum oven and then weighed after becoming sufficiently dry. This provides an accurate measure of the concentration of the suspension which is necessary for future use of the delaminated suspension. Concentrations are generally very low, on the order of 2.5 mg/mL with volumes of about 50 mL.

2.2 Solvent Casting of Composite Films

Cast films were obtained by dissolving a polymer into an appropriate solvent, then introducing a measured volume of the aforementioned suspension of delaminated MXene. This solution was then sonicated and/or mixed using a magnetic stir bar. After a homogeneous solution is obtained, the solution is poured into a petri dish or other similar container, and allowed to dry at either room temperature in ambient conditions, or dried at an elevated temperature under vacuum. This results in a thin film of composite material that can then be processed into specimens used to conduct tensile tests.

2.3 Extrusion of Composite Filament

2.4 X-Ray Diffraction (XRD)

The X-Ray diffractometer used was a Rigaku SmartLab with a the In-Plane Diffraction Attachment and Bragg-Bretano Optics utilizing Cross Beam Shaping Optics (CBO) and a Parabolic Mirror. A copper anode (3 kW, Long-Fine Focus, X-ray tube focal spot 0.4 mm x 12.0 mm) was used with an X-ray wavelength of $Cu_{K\alpha} = 1.54 \ \text{Å}$. Voltage was 40 kV with a current of 44 mA. Scans were done from $2\theta = 3^\circ$ to $2\theta = 65^\circ$ with a step size of 0.04 $^\circ$/sec.

2.5 Scanning Electron Microscopy (SEM)

For Scanning Electron Microscopy (SEM), a Zeiss Supra 50VP with EDS was used, although the EDS feature was not utilized. This instrument has the following features:

- Schottky Field Emission Electron Gun
- Everhart-Thornley, In-Lens Secondary, and Solid State Backscatter Imaging Detectors
• High Vacuum, Variable Pressure, and High Current Modes

• Simultaneous acquisition of EDS, SE, BSD, and specimen current signals

• Oxford Energy-Dispersive X-ray Microanalysis

• IR Chamber View

As samples were not conductive, they were plated with a 80/20 blend of platinum/palladium. Accelerating voltage was generally about 3.5 kV.

2.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to verify the weight fraction of the MXene in the composite. The temperature was ramped from 0 °C at a rate of 10 °C/min and then held at 800° C for 30 minutes under argon.

2.7 Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter 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 a solvent cast or extrusion method (see Section 2.2 & 2.3, respectively.) The temperature equilibrates down to -50 °C, then ramps to 300 °C at 10 °C/min, holds isothermally and then ramps down to 22 °C. Enthalpic values are obtained by the integration of the crystallization and melting peaks using the software packages provided by the manufacturer of the DSC.

2.8 Fourier Transform Infrared Spectroscopy (FTIR)

Poly(acrylic acid) based composite films were analyzed by FTIR from 3500 cm$^{-1}$ to 500 cm$^{-1}$ and the percent transmission was collected.

2.9 Tensile Characterization

A primary characterization method of particular interest in this work is the investigation of the mechanical properties of these composites, specifically the elastic modulus and the tensile strength.
Due to variations in processing methods and sample geometries, an array of methods to experimentally determine these properties has been employed according to the appropriate ASTM standards whenever possible. Specifically, tensile properties were investigated using a 3300 series Instron Electromechanical Universal Testing System under two different ASTM standards, namely ASTM D638-14 for strips of thin films and ASTM D3882/D3822-14 for fibers.

2.9.1 Instron

Cast Films

Composites which were produced via a solvent cast method (see section 2.2), were tested mechanically on a 3300 series Instron Universal Testing System according to the specifications of ASTM D638-14 Standard Test Method for Tensile Properties of Plastics. Cast films were cut into four strips of 12.7 mm (1/2 in) width using a razor blade. A gauge length of 12.7 mm (1/2 in) was used. Film thickness was approximately 1 mm.

Extruded Filament

Samples produced by extrusion (see section 2.3) were tested on a 3300 series Instron Universal Testing System, according to the specifications of ASTM D3822/D3822M-14 Standard Test Method For Tensile Properties of Single Textile Fibers at a strain rate of 7.62 mm/min.
Chapter 3: Discussion of Experimental Results

3.1 FTIR of PAA:MXene Composite Films

In order to gain a better understanding of the nature of bonding between $Ti_3C_2T_x$ and the poly(acrylic acid), infrared spectroscopy was employed. By measuring the transmittance as a function of wavelength in the infrared, coupled with well understood response by functional groups, the change or disappearance in specific functional groups can indicate that bonding is occurring.

![FTIR Spectra of MxPAA-5v Composite Film](image)

Figure 3.1 FTIR Spectra of MxPAA-5v Composite Film.

In Figure 3.1, the FTIR spectra of a thin (~1mm) composite film of poly(acrylic acid) and $Ti_3C_2T_x$ loaded at 5 (wt/v)% is shown along with the repeat unit of poly(acrylic acid), the functional group of which is carboxylic acid (COOH). In a spectra of poly(acrylic acid) one would expect to see a strong and broad alcohol (−OH) stretching peak centered around 3000-2500 cm$^{-1}$ along with a narrow, intense carbonyl (C=O) peak around 1780-1710 cm$^{-1}$ [74].
Table 3.1 Peak Analysis of FTIR Spectra of MxPAA Film.

<table>
<thead>
<tr>
<th>FTIR Peak Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional Group</td>
</tr>
<tr>
<td>--------------------</td>
</tr>
<tr>
<td><strong>Alkane</strong></td>
</tr>
<tr>
<td>C-H</td>
</tr>
<tr>
<td>C-H</td>
</tr>
<tr>
<td><strong>Carboxylic Acid</strong></td>
</tr>
<tr>
<td>C=O</td>
</tr>
<tr>
<td>O-H</td>
</tr>
<tr>
<td>C-O-H</td>
</tr>
<tr>
<td>C-O</td>
</tr>
</tbody>
</table>

While the location of these peaks are slightly shifted, they are much less intense in the composite material. This is a strong indication that the vibration state of the atoms in these bonds has changed, particularly in the case of the alcohol (-OH) peak. The reduction in intensities of these peaks leads to the belief that the surface functionalization of the MXene, that is \( T_x \) in \( Ti_3C_2T_x \), is hydrogen bonding with the alcohol in the poly acrylic acid. The close proximity to the carbonyl in the carboxylic acid is likely causing the reduced intensity observed in that peak as well, however not as well pronounced due to the electrophillic nature of the carbonyl bond and the partially negative dipole.

A similar phenomena was noted by Manna et al. upon loading selectively reduced graphite oxide (SRGO) into poly(vinyl alcohol). Figure 3.2, a reprint from the author’s original article, shows that as the amount of of selectively reduced graphite oxide (SRGO) is increased (from 0 to 2 phr), the intensity of the alcohol peak in poly(vinyl alcohol) is reduced, and a red shift from \( \sim 3365 \text{ cm}^{-1} \) to \( \sim 3306 \text{ cm}^{-1} \) is observed. This lower frequency shift is attributed to the presence of intermolecular hydrogen bonding between the -OH groups of PVA and SRGO. The author’s continue by proposing that the inclusion of SRGO in a PVA matrix weakens the hydrogen bonding of the -OH groups of PVA leading to a “hydrogen bond barrier” effect, with new hydrogen bond formation taking place between the -OH functional group of PVA and surplus -OH functionality in SRGO observed in
deconvoluted FTIR [75].

![FTIR spectra](image)

Figure 3.2 FTIR spectra of (a) neat PVA, (b) PVA/SRGO-0.2, (c) PVA/SRGO-0.5, (d) PVA/SRGO-1, (e) PVA/SRGO-1.5, and (f) PVA/SRGO-2, reprinted from [75]

### 3.2 Scanning Electron Microscopy Analysis

Scanning electron microscopy was used to image the edge of an MxPAA composite film which was using a laser cutter. This was done in order to verify that no perpendicular cracks or other features which would lead to premature failure were present. It can be seen in Figure 3.3 that the edge of the laser cut film is smooth.
Figure 3.3 Scanning electron micrograph of the edge of a poly (acrylic acid) based composite with 5% (w/v) $Ti_3C_2T_x$ which was laser cut. Images are at 1.00 K X, 3.5 K X and 8.00 K X magnification.

SEM was also used to image the morphology of the multilayer $Ti_3C_2T_x$. It can clearly be seen in Figure 3.4 that the MAX phase $Ti_3AlC_2$ has been etched to form a layered MXene with flake widths on the order of 1 $\mu$m and sheet thickness of several nanometers.
3.3 Analysis of Thermogravimetric Analysis Results

By loading a small amount (about 50 mg) of a sample into the TGA and ramping the temperature at a constant rate (10 °C/min) in an inert atmosphere (argon at a flow rate of 50 mL/min) and recording the mass of the specimen as a function of temperature, the weight fraction of the MXene in the composite material can be determined. This is due to the thermal degradation of the polymer, which involves the scission of backbone polymer chains, which then react together to form gaseous products like carbon monoxide, water vapor and carbon dioxide, decreasing sample mass in the process. MXene content by weight percent, obtained from thermogravimetric analysis are presented below in Table 3.2, along with plots of weight percent as a function of time (Figure 3.5) and derivative weight percent as a function of time (Figure 3.6) for each experimental run.
Figure 3.5 Thermogravimetric curves of neat nylon (red), solvent cast composite (green), extruded composite that was mixed continuously for twenty minutes (purple), and extruded composite that was mixed continuously for five hours.

Figure 3.6 Derivative weight percent thermogravimetric curves of neat nylon (red), solvent cast composite (green), extruded composite that was mixed continuously for twenty minutes (purple), and extruded composite that was mixed continuously for five hours.
Table 3.2 TGA Determined $Ti_3C_2T_x$ Content.

<table>
<thead>
<tr>
<th>Run ID</th>
<th>$Ti_3C_2T_x$ Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PA6</td>
<td>0</td>
</tr>
<tr>
<td>Solvent Cast MxPA6</td>
<td>9.7</td>
</tr>
<tr>
<td>Extruded MxPA6 (20 min)</td>
<td>4.9</td>
</tr>
<tr>
<td>Extruded MxPA6 (5 h)</td>
<td>4.8</td>
</tr>
</tbody>
</table>

3.4 Analysis of Differential Scanning Calorimetry (DSC) Results

Differential Scanning Calorimetry was frequently employed throughout the course of this project due to the versatility and simplicity of the technique. Before any extrusion was done, as received Nylon-6 pellets from Sigma Aldrich were tested on the DSC. This not only provides a baseline for future reference, but also is useful for determining appropriate zone temperatures in the extrusion process by providing the melting temperature ($T_m$) and crystallization temperature ($T_c$) for the nylon-6 pellets. Additionally, enthalpies of melting and crystallization can be extracted by integrating the respective peaks, which can then be used to determine the degree of crystallinity from the following equation

$$\chi_c = \frac{\Delta H_m}{\Delta H^0_m} \times 100,$$

(3.1)

where $\Delta H_m$ is the experimentally determined enthalpy of melting and $\Delta H^0_m$ is the latent heat of fusion for a 100% crystalline material. For nylon-6, the latent heat of fusion is 230.1 J/g [76].

For a composite material with a weight fraction of filler material $w$, the fraction of polymer matrix is simply $(1 - w)$. For these composites, degree of crystallinity can be determined using Eq. 3.2, but with the required modification of accounting for these weight fractions. For composites, the degree of crystallinity can be calculated by

$$\chi_c = \frac{\Delta H_m}{(1 - w) \Delta H^0_m} \times 100.$$

(3.2)

The weight fraction $w$ can be estimated upon synthesis of the composites, but is also verified
by thermogravimetric analysis (see Section 2.6 and Section 3.3). Using the MXene weight fractions determined from TGA (Table 3.2), the enthalpies of melting and crystallization, along with the degree of crystallinity for each experimental run can be determined. Additionally, the melting temperature \( T_m \) and crystallization temperature \( T_c \) are included. Below are differential scanning calorimetry curves for each experimental run, shown in Figure 3.7 along with enhanced plots of both the crystallization peaks (Figure 3.8) and the melting peaks (Figure 3.9). Results obtained from these plots are presented in Table 3.3.

![Differential scanning calorimetry curves of neat nylon (red), solvent cast composite (green), and extruded composite (purple) material.](image)

**Figure 3.7** Differential scanning calorimetry curves of neat nylon (red), solvent cast composite (green), and extruded composite (purple) material.
Figure 3.8 Differential scanning calorimetry crystallization curves of neat nylon (red), solvent cast composite (green), and extruded composite (purple) material.

Figure 3.9 Differential scanning calorimetry melting curves of neat nylon (red), solvent cast composite (green), and extruded composite (purple) material.
Table 3.3 Thermal Data for Neat Nylon-6 and Nylon-6 MXene Composites

<table>
<thead>
<tr>
<th>Run ID</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PA6</td>
<td>223.75</td>
<td>-129.2</td>
<td>175.55</td>
<td>78.66</td>
<td>90.33</td>
</tr>
<tr>
<td>Solvent Cast MxPA6-9.7</td>
<td>221.87</td>
<td>-55.42</td>
<td>191.49</td>
<td>70.17</td>
<td>60.44</td>
</tr>
<tr>
<td>Extruded MxPA6-4.9 (20 min)</td>
<td>221.92</td>
<td>-73.57</td>
<td>186.06</td>
<td>74.89</td>
<td>67.84</td>
</tr>
<tr>
<td>Extruded MxPA6-4.8 (5 h)</td>
<td>220.48</td>
<td>-84.69</td>
<td>191.08</td>
<td>64.44</td>
<td>68.08</td>
</tr>
</tbody>
</table>

3.5 Analysis of X-Ray Diffraction Results

Figure 3.10 XRD spectra of neat nylon-6 (red), MxPA6 composites with a mixing time of 20 minutes (black) and 5 hours (green) along with multilayer $Ti_3C_2T_x$ MXene (blue).

Figure 3.10 shows the x-ray diffraction spectra of multilayer $Ti_3C_2T_x$ MXene prior to use in composite synthesis. The peak of greatest interest is the (002) peak, which usually occurs at approximately $2\theta = 6^\circ$. For this multilayer MXene, this peak is located at $2\theta = 6.04^\circ$. Bragg’s Law
can be used to determine the c-lattice parameter.

\[ 2d_{hkl} \sin \theta = n \lambda. \] (3.3)

With an (002) peak at \(2\theta = 6.04^\circ\), a corresponding \(d_{002}\)-spacing of 29.2 Å is found. By monitoring this \(d\)-spacing, insight into the intercalation of nylon-6 can be gained. If full delamination were achieved, this (002) peak would no longer be apparent. Upon scanning both neat nylon filament and composite filament that was extruded with a continuous mixing time of twenty minutes, this (002) peak is still present at \(2\theta = 6.05^\circ\), corresponding to a spacing of \(d_{002} = 29.2\) Å. Nylon-6 loaded with 4.8\% \(Ti_3C_2Tx\) and continuously mixed for five hours before extruding showed an 002 peak at \(2\theta = 6.03^\circ\), corresponding to a spacing of \(d_{002} = 29.3\) Å.

It is known that the (200) and (202, 002) reflections of the \(\alpha\) form of nylon-6 occur at \(2\theta = 20.0^\circ\) and \(2\theta = 24.0^\circ\), respectively [77]. In the neat nylon-6 sample, a pronounced (202, 002) at \(2\theta = 23.3^\circ\) is observed, with a subdued peak at \(2\theta \approx 21^\circ\) corresponding to (200). However, in the case of nylon-6 containing 5 wt\% \(Ti_3C_2Tx\) that was continuously mixed for 20 minutes, only a (200) peak at \(2\theta = 21.3^\circ\) is observed. In the case of the same composition of composite material allowed to continuously mix for 5 hours, both peaks are observed but are much greater in intensity. This suggests that the presence of MXene orients the crystallization of the \(\alpha\) form of nylon-6, particularly in the case of longer shearing times.

These results would suggest that mechanical shearing alone is not sufficient for delamination, as the MXene (002) peak is still present with no significant change in lattice spacing. The noted lack of the MXene (010) peak around \(2\theta = 60^\circ\) could suggest that while full delamination is not occurring, shearing is causing some alignment, and work by members of the MAX/MXene group is beginning to suggest that shearing can lead to a higher intensity in this non-basal peak, however transmission electron microscopy (TEM) may be required in order to fully investigate delamination by shear. It appears from these XRD results that the full delamination that was identified by Okada et al. (1987) to be the key to achieving the best performance in composite materials has not been achieved.
3.6 Analysis of Tensile Data

This section will provide an analysis of all tensile tests, specifically the elastic modulus, ultimate tensile strength and strain to failure. The elastic modulus was calculated using Hooke’s Law:

\[ E = \frac{\sigma}{\epsilon}, \quad (3.4) \]

where \(\sigma\) is the engineering stress, defined as the measured force per unit area, where the area is the initial cross-sectional area. Expressed mathematically,

\[ \sigma = \frac{F}{A_0}. \quad (3.5) \]

In the case of a film with a rectangular cross-section, \(A = w \cdot t\) where \(w\) is the width and \(t\) is the thickness of the film. In the case of fibers, the cross sectional area is \(A = \pi r^2\) where \(r\) is the fiber radius.

The engineering strain, \(\epsilon\) is defined as the change in length over the initial length of the sample, expressed as

\[ \epsilon = \frac{\Delta l}{l_0}. \quad (3.6) \]

where \(\Delta l\) is the change in length, often referred to as extension, and \(l_0\) is the initial length of the specimen, which happens to be the gauge length for all samples considered in this section. The modulus of elasticity is calculated by taking the slope \(\left(\frac{\Delta \sigma}{\Delta \epsilon}\right)\) of the linear region, termed the elastic regime. The ultimate tensile strength, often abbreviated as UTS is simply the maximum of the stress strain plot, and the strain to failure is strain on the specimen when failure occurs.

First, the mechanical properties of poly(acrylic acid)/MXene samples prepared according to Section 2.2 and tested according to ASTM D638-14 Standard Test Method for Tensile Properties of Plastics, as described in Section 2.9.1 are presented.
3.6.1 Poly(acrylic acid) and $Ti_3C_2T_x$ MXene Composites

Figure 3.11 Full engineering stress-strain plots of neat poly(acrylic acid) and composite thin films.

Table 3.4 indicates that the average elastic modulus for the neat and composite materials are 849.95 MPa and 850.35 MPa, respectively. Additionally, the average ultimate tensile strength for the neat material was a bit higher at 20.14 MPa, with the composite material being 18.13 MPa. The average strain to failure for the composite material was 0.89, which is significantly higher than the neat material at 0.36.

Table 3.4 Modulus of Elasticity, Ultimate Tensile Strength & Strain to Failure for PAA and MxPAA Films.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>E (MPa)</th>
<th>UTS (MPa)</th>
<th>$\epsilon_{fail}$ (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat poly(acrylic acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>782.35</td>
<td>20.74</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>773.96</td>
<td>14.64</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>1007.59</td>
<td>17.76</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>835.89</td>
<td>27.40</td>
<td>0.37</td>
</tr>
<tr>
<td>poly(acrylic acid), 5 (wt/v)% MXene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>526.66</td>
<td>15.12</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>785.57</td>
<td>15.94</td>
<td>0.35</td>
</tr>
<tr>
<td>3</td>
<td>1229.84</td>
<td>17.24</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>859.31</td>
<td>24.21</td>
<td>1.07</td>
</tr>
</tbody>
</table>
From these results, it appears that the presence of \(Ti_3C_2T_x\) MXene in poly(acrylic acid) loaded at 5 (wt./v)% has little impact on the elastic modulus, with a slight reduction in the ultimate tensile strength but a drastic improvement in the strain to failure.

### 3.6.2 Nylon-6 and \(Ti_3C_2T_x\) MXene Composites

In this section, three different runs will be considered. First, a run which includes both neat nylon-6 along with composite material loaded at 4.9 wt%, extruded according to Section 2.9.1, which was allowed to continuously mix for twenty minutes. Next, composite material from the same extrusion batch was dried in a vacuum oven at 160 °C overnight, transported in a sealed container with dessicant, and tested mechanically. Finally, results of nylon-6 loaded at 4.8 wt% that was extruded according to Section 2.9.1 but allowed to continuously mix for five hours.

![Figure 3.12 Plots of engineering stress-strain of neat nylon 6 and composite filaments.](image)
Table 3.5 Modulus of Elasticity, Ultimate Tensile Strength & Strain to Failure for PA6 and MxPA6-5 Fibers, Mixed for 20 Minutes.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>E (MPa)</th>
<th>UTS (MPa)</th>
<th>(\epsilon_{\text{fail}}) (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neat Nylon-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1224.93 ± 0.11</td>
<td>55.84</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1172.59 ± 0.22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1006.84 ± 0.10</td>
<td>49.98</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1357.94 ± 0.13</td>
<td>49.61</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1517.22 ± 0.10</td>
<td>57.07</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nylon-6, 5 wt% MXene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1620.71 ± 0.16</td>
<td>51.4</td>
<td>6.63</td>
</tr>
<tr>
<td>2</td>
<td>1801.33 ± 0.24</td>
<td>62.12</td>
<td>7.79</td>
</tr>
<tr>
<td>3</td>
<td>1332.78 ± 0.19</td>
<td>41.18</td>
<td>4.04</td>
</tr>
<tr>
<td>4</td>
<td>1957.87 ± 0.28</td>
<td>78.99</td>
<td>8.30</td>
</tr>
<tr>
<td>5</td>
<td>1511.30 ± 0.21</td>
<td>58.94</td>
<td>10.33</td>
</tr>
</tbody>
</table>

The average modulus of elasticity for the neat nylon-6 was 1255.9 ± 0.13 MPa, while the average for the composite material was 1644.8 ± 0.21 MPa. This corresponds to a percent increase of 30.96%. 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 ultimate tensile strength of 58.94 MPa, while the nylon-6 had an average ultimate tensile strength of 53.13 MPa, which corresponds to be a 10.17% 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 \(\epsilon_{\text{fail}}\) are not reported. For the MXene containing nylon-6, the average strain to failure was 7.42 mm/mm.

The engineering stress-strain plots shown in Figure 3.12 show a very interesting difference in behavior between the neat nylon-6 and the MXene containing nylon-6, namely that the the neat nylon-6 samples show a plateau while the MXene containing samples show a local maximum in a hump, before strain hardening. This hump is generally seen in neat nylon-6 when the specimen is in a dried state. The hygroscopic nature of nylon-6 leads to an equilibrium water saturation of a
few percent. Nylon-6 in this state will show plateau like behavior as exhibited by the neat nylon samples in these tests. The lack of this behavior in the MXene containing samples indicates that the presence of MXene allows the composite material to behave similar to dry nylon-6, while also increasing the elastic modulus by 31%. This resistance to water permeation has been noted in nylon clay hybrids (NCHs) by Kojima et al. (1993) which is attributed to a decrease in the diffusion coefficient of water which decreased with increasing length and content of the silicate layers. The author’s report a relationship between the diffusion coefficient and the fraction of the constrained regions as follows:

\[ D = D_A (1 - C)^{1/n}, \] (3.7)

where \( D \) is the diffusion coefficient, \( D_A \) is the diffusion coefficient in the amorphous region, \( n \) is a morphology parameter that ranges from \(-1\) to 1, \( C \) is the fraction of the constrained region, with \( 1 - C \) begin the fraction of the amorphous region. This constrained region fraction is calculated by

\[ C = \frac{W}{W_0} (1 - C_0), \] (3.8)

where \( W \) and \( W_0 \) are the energy loss fraction at the glass transition temperature for the composite and neat nylon-6, respectively. This energy loss fraction increases with decreasing crystallinity [78] and when used in conjunction with the storage modulus \( E' \) and the loss modulus \( E'' \), the constrained region fraction can be obtained according to the linear viscoelastic relationship

\[ W = \frac{\pi E''}{\pi E'' + E'}. \] (3.9)

The relationship between the constrained fraction \( C \) and the clay content, along with the sorption curves of water for both NCH and nylon-6 are shown in Figures 3.13 and 3.14
Figure 3.13 Fraction of constrained region $C$ vs. clay content and sorption curves, adapted from [79].

Figure 3.14 Sorption curves for NCH and nylon-6, adapted from [79].
While these researcher’s did not observed a statistically significant change in crystallinity as a function of clay content [79], it is well known that the diffusion of water in nylon-6 occurs primarily in the amorphous region [80]

This behavior prompted the next experiment, where composite material from the same run was dried in a vacuum oven at 160 °C overnight and then retested.

Figure 3.15 Engineering stress-strain plot for MxPA6-5 fibers, dried in vacuum overnight at 160 °C.

Table 3.6 Modulus of Elasticity, Ultimate Tensile Strength & Strain to Failure for Dried MxPA6-5 Fibers Mixed for 20 Minutes.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>E (MPa)</th>
<th>UTS (MPa)</th>
<th>$\epsilon_{fail}$ (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-6, 5 wt% MXene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1463.51</td>
<td>53.23</td>
<td>0.064</td>
</tr>
<tr>
<td>2</td>
<td>1308.77</td>
<td>50.78</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>1032.86</td>
<td>41.24</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>1533.21</td>
<td>68.95</td>
<td>0.18</td>
</tr>
<tr>
<td>5</td>
<td>1066.05</td>
<td>38.76</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>1350.54</td>
<td>49.85</td>
<td>0.082</td>
</tr>
</tbody>
</table>

The dried composite material exhibited an average elastic modulus of 1107.85 MPa, an average ultimate tensile strength of 43.26 MPa, and an average strain to failure of 0.08 mm/mm. The stress-strain plot, Figure 3.15 depicts the stress-strain behavior of these dried filaments. Of particular
interest is the lack of local maximum “hump” as seen in 3.12. At 160 °C, water that is in the nylon-6 should have been extracted, along with any water that is between the layers of MXene, however the stress-strain behavior of this dried composite is more similar to hydrated nylon than to dried nylon.

![Engineering stress-strain plots for MxPA6-5 fibers, continuously mixed for five hours.](image)

Figure 3.16 Engineering stress-strain plots for MxPA6-5 fibers, continuously mixed for five hours.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>E (MPa)</th>
<th>UTS (MPa)</th>
<th>(\epsilon_{\text{fail}}) (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>697.00</td>
<td>40.12</td>
<td>6.12</td>
</tr>
<tr>
<td>2</td>
<td>577.93</td>
<td>32.18</td>
<td>6.51</td>
</tr>
<tr>
<td>3</td>
<td>567.66</td>
<td>38.54</td>
<td>6.32</td>
</tr>
<tr>
<td>4</td>
<td>564.64</td>
<td>24.48</td>
<td>4.59</td>
</tr>
<tr>
<td>5</td>
<td>433.79</td>
<td>24.33</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Table 3.7 Modulus of Elasticity, Ultimate Tensile Strength & Strain to Failure for MxPA6-5 Fibers, Mixed for 5 Hours.

Finally, tensile tests on non-dried composite material continuously mixed for five hours were conducted. The average elastic modulus was determined to be 568.20 MPa, with an average ultimate tensile strength of 31.93 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 68.08%. Additionally, the extrusion process occurs at an elevated temperature, that is approximately 220 °C in an atmosphere with a oxygen partial pressure of $P_{O_2} = 0.21\ atm$. It has been shown that in an oxygen atmosphere, at 200 °C, parts of $Ti_3C_2$ MXene with F/OH terminations were oxidized to obtain anatase nano-crystals evenly distributed on 2D $Ti_3C_2$ layers [81], suggesting that some oxidation of MXene might have occurred, reducing the mechanical properties as a result. Additionally, holding the polymer at this elevated temperature for a long period of time could also result in some degradation of the nylon-6. At this point the mechanism that lead to this reduction in properties is not known and requires further investigation.
Chapter 4: Conclusions

In conclusion, it is apparent that $Ti_3C_2T_x$ MXene can be incorporated into a polymer matrix at low weight percents to form a composite material in both the case of poly(acrylic acid) and nylon-6. Additionally, FTIR results indicate that there is a degree of hydrogen bonding occurring between the functional groups of the polymer and the surface of the MXene.

Analysis of differential scanning calorimetry results show that the degree of crystallinity ranges from about 60-70\% for nylon-6 based composites. While the melting temperature of the composite material was reduced a few degrees, the temperature at which crystallization occurs increased dramatically in the presence of MXene, along with a reduction in the enthalpy of crystallization. In this composite material, it is posited that MXene acts as a site for the promotion of heterogeneous nucleation, allowing for crystallization to occur at higher temperatures. The temperature of crystallization ($T_c$) increases by 10.51 °C in the case of extruded filament continuously mixed for twenty minutes and loaded at 4.9 wt\%. In the case of extending this mixing time to five hours, the $T_c$ increases by 15.53 °C with 4.8 % MXene by weight. In the material which was solvent cast at a load of 9.7 wt\%, $T_c$ increases by 15.94 °C.

Tensile tests of the MXene/poly(acrylic acid) composites loaded at 5 (wt/v)\% indicated a significant increase in the strain to failure, with no appreciable loss in elastic modulus and only slight reduction in the ultimate tensile strength. Analysis of mechanical properties of nylon based composites indicates that a peculiar phenomena is occurring with regards to the presence of MXene and the specimen’s hygroscopic behavior. Non-dried tensile specimens containing 4.9 wt\% MXene show stress-strain behavior of dried nylon-6, specifically a hump in the stress-strain plot with subsequent strain hardening. It is well known that MXene’s are hydrophilic [46] and that the diffusion of water in nylon-6 occurs primarily through amorphous polymer [80] and in an attempt to decouple this phenomena and determine whether this effect is due to a higher degree of crystallinity in MXene containing samples or due to the presence of water in both the amorphous nylon and between the
layers of MXene, specimens from the same production run were dried at 160 °C in a vacuum oven overnight and tested in tension. The resulting stress-strain behavior shows some degree of the aforementioned “hump” but fracture occurs shortly thereafter. Quantification of the interaction between MXene and water in these systems requires further study.

In non-dried composites which were continuously mixed for twenty minutes before extruding, a 30.96% increase in elastic modulus from $1255.9 \pm 0.13$ MPa to $1644.8 \pm 0.21$ MPa was noted, with a slight increase in ultimate tensile strength from 53.13 MPa to 58.94 MPa at 4.9 wt% MXene loading. In nylon based composites that were loaded at 4.8 wt% MXene and continuously mixed for five hours, the elastic modulus was 568.20 MPa, with an ultimate tensile strength of 31.93 MPa and strain to failure of 6.04 (mm/mm). The cause of this reduced performance of the specimens produced from this run is unknown.

Investigation of the crystallographic nature of these composites by x-ray diffraction leads to the conclusion that complete delamination, that is, loss of order in the non-basal directions was not achieved through mechanical shearing in the extruder alone. This is evidenced by the continued presence of a 002 peak at $2\theta \approx 6^\circ$, corresponding to a $d_{002}$ spacing of approximately 29.2 Å. A dramatic increase in intensity was noted in the case of the extruded composite that was mixed continuously for five hours, suggesting that some alignment but not full delamination occurred.

Despite this lack of full delamination, the mechanical properties of nylon-6 MXene composites were improved, suggesting that if full exfoliation of the MXene sheets were achieved, a further increase in properties could be expected.
Chapter 5: Future Work & Outlook

This chapter will briefly discuss the future outlook of this project including other methods of characterization and synthesis of these composites. Electronic properties of these composites should be investigated, although it is unlikely that at such low MXene loading percentages that electronic conductivity would be achieved. Additionally, thermal conductivity and gas permeability results would be of interest. The future characterization techniques of the current nylon-6 based composites should include a thorough investigation into the role of MXene in the composite and the sensitivity to water of the material. This may be done by conducting a number of additional tensile tests, including testing neat nylon-6 in a dried state in order to make a meaningful comparison between the obtained results for the composite material and the neat nylon-6. Additionally, spectroscopic techniques like attenuated total reflection (ATR) may be useful for gaining insight into chemical structure of the composite in both a hydrated and dried state, however the thickness and opacity of the composites may make obtaining results from ATR difficult as the penetration depth is on the same order as the thickness of fibers which can currently be extruded. This can be partially addressed by moving towards injection molding as a processing technique rather than relying on extrusion to make uniform fibers that are wound around a torque motor.

Injection molding would allow for samples of precise geometries to be produced on a reliable basis, along with thicker specimens. The difficulty in achieving this is the current lack of a pelletizer - a device that will allow for homogeneous material to be mixed, extruded and then cut into small pellets at the die that are uniform in shape to allow for efficient use in an injection molder. Additionally the design of molds for a specific geometry can become quite complex as the geometry and runner design could lead to residual stresses or voids in the final product or thermal gradients in the injection process. While this can be overcome with a combination of good design and optimization of the injection parameters, doing so was beyond the scope of this project from both an equipment and temporal perspective.
A route of synthesis which may be of particular interest would be the combinatorial use of organic solvents and an injection/molding process. It has been shown that MXene’s will disperse in a stable manner in the presence of polar, aprotic solvents such as dimethyl formamide (DMF), n-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), acetone, and acetonitrile [82]. The pairing of a solvent which is both a good solvent for the dispersion of MXene and the dissolution of the chosen polymer can result in the ability to dissolve a polymer and introduce the MXene to the solution. This is how MXene/PAA samples were produced in this work, with the solvent simply being water. There was also some work done which is not reported here with the used of hexafluoro-2-propanol (HFIP) and formic acid (both good solvents for the nylon-6) in order to dissolve the nylon and then introduce multilayer \( Ti_3C_2T_x \). These solutions would then be mixed, sonicated and cast into films.

While this proved to be an effective method of producing a solution, films that were cast from these solutions were not suitable for cutting and testing as they were in the case of poly(acrylic acid). This is likely due to the volatility of these solvents. It should be noted that both HFIP and formic acid are polar, protic solvents, which were also shown to be effective but to a lesser extent than polar aprotic solvents. Since long term stability of the MXene in these solutions is not of utmost importance, this is not an issue [82].

A proposed method of synthesis that is of great personal interest is the use of this solvent dispersion technique in which the polymer and MXene are precipitated out of solution after shearing the mixture using a shear emulsifying mixer capable of very high levels of shear. If successful, small “pellet-like” composite will be obtained after washing. If uniform in size these could be used directly in an injection molder. If precipitation of the composite out of the solution is not possible, or results in non-uniform precipitates, the solution could be cast, cut into small pieces and then extruded and pelletized before use in an injection molder. This combination of a solvent based method and the mechanical shearing induced by both the shear emulsifying mixer and the extruder/injection molder should result in the best chance at delamination.

With regards to the choice of polymers used as a host matrix, nylon-6 was chosen due to it being the first polymer chosen at the beginning of the polymer clay work by Okada et al. However, the
thermal sensitivity of polyamides in production along with the hygroscopic nature of nylon-6 makes studying the effect of the MXene rather difficult. Polymers without this sensitivity to temperature and moisture like polyethylene and other polyolefins are of interest both for the aforementioned lack of these issues along with their industrial relevance. Additionally, polymers that are commonly used in the lithium-ion battery field are of specific interest. These include poly(ethylene oxide) (PEO) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). Some work has been done on composites of $Ti_3C_2T_x$ and poly(vinylidene fluoride) (PVDF) which showed enhanced thermal properties and increased storage modulus [83], but this composial material was not the PVDF-HFP copolymer which is of industrial relevance in this field.

Of course, composites that involve other members of the MXene family are of great interest, but since $Ti_3C_2T_x$ is by far the most studied MXene to date, and work on MXene polymer composites is still in infancy, it may be a few years before enough is known about composites containing $Ti_3C_2T_x$ in order to move to other MXenes.
Bibliography


Monolayer Ti2CO. A promising candidate for nh3 sensor or capturer with high sensitivity and selectivity yu.


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